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POLLUTION PREVENTION DESIGN

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CHEMICAL PROCESS DESIGN FOR ENVIRONMENTAL CONSIDERATIONS

In view of growing environmental concern and stringent legislation, there is a critical need for environmental considerations in the developing large-scale chemical processes. The increasingly tighter environmental constraints imposed by regulators have led to the identification and development of alternate processes to eliminate, or at least minimize, effluents in a chemical process. Nowadays, industries are practicing the art of *pollution prevention*, which involves fundamental changes in processes to minimize the formation of pollutants, as opposed to *pollution control*, involving end-of-pipe treatment of process emissions. This philosophy of pollution prevention adopted by the chemical process industries (CPIs) uses suitable pathways and operations to make products without generating hazardous materials, or as in some cases, recover in full or in part the materials referred to as "waste." Techniques for pollution prevention often lead to structural process alternatives and parametric alternatives related to process and operating conditions, or both, resulting in significant reduction in pollutant formation with minimal increase in capital and operating costs. Currently, environmentally friendly or "green" processes are designed on the basis of new concepts in process engineering, such as process integration, which embodies a number of closely related methodologies for designing new processes and retrofitting existing ones by considering the performance of the entire process. The main advantage of process integration techniques is that they are inherently "conservation-oriented" and enhance the process performance by minimizing the use and/or maximizing the recovery of energy and materials, consistent with the goals of pollution prevention, source reduction, and waste minimization (1). Incorporating pollution prevention concepts into design and development at the initial stages leads to processes that are less cost-intensive, thereby reducing the technical and economic risk from environmental issues. In addition to pollution prevention, integrated environmental control (IEC) strategies introduced in the early design stages of a process, rather than an end-of-pipe control option introduced in the later stages, improve the technical and economic performance of a process. For example, studies by the Electric Power Research Institute (EPRI) show that as

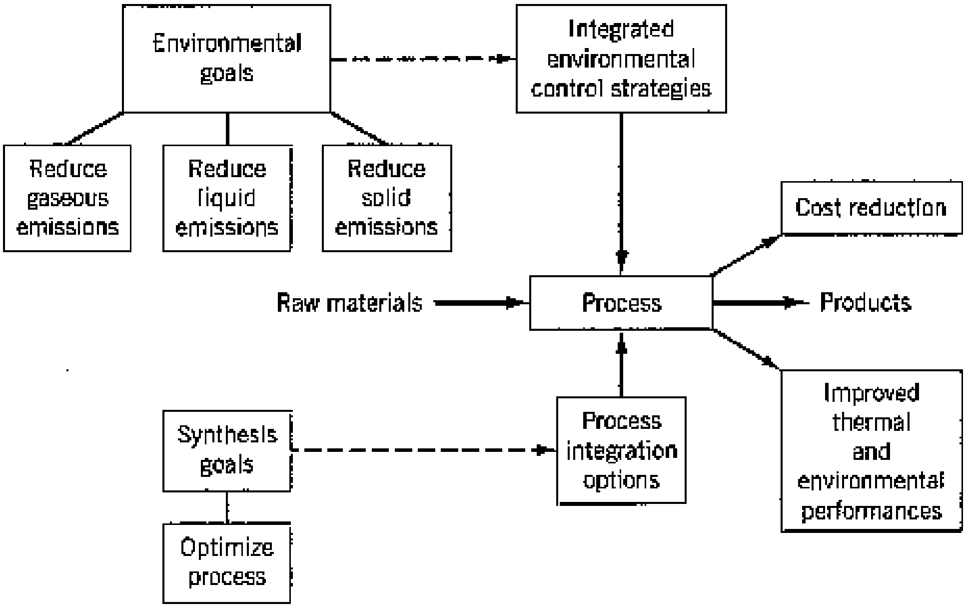

Figure 1. An integrated approach to pollution prevention.

much as 50% reduction in total environmental control system costs for coal-fired power plants is achieved by processes using integrated environmental control design compared to plants using end-of pipe control devices (2). Figure 1 shows how the concepts of integrated environmental control strategies and process integration, working together, result in developing "clean" process technologies.

A consensus for future directions in the area of environmental considerations in process design and simulation was defined in December 1992, when professionals from the industry, academia, and the government met to address several issues related to the environmental objectives for designing new processes and retrofitting existing ones. The outcome was a recommendation for a focused *process synthesis* approach from an environmental perspective. This task consists of making decisions regarding which units should integrate a process, how they should be interconnected, and determines their sizes and the operating conditions so that the desired objectives (economic, environmental, etc) are attainable. The conclusion of the participants in the workshop, which was jointly sponsored by the American Institute of Chemical Engineering (AIChE), Environmental Protection Agency (EPA) and the Department of Energy (DOE), was to rank research to develop new and improved methods for synthesizing chemical processes that meet environmental objectives by incorporating pollution prevention concepts in the early stages of a design. This would enable developing alternate process flowsheets (diagrammatic representations of the process operations with their interconnections) and has applications extending far beyond the capability of existing commercial process simulators. Some of the identified needs are as follows (3):

- Integrate process synthesis and process simulation.
- Adopt a sophisticated optimization approach to synthesize processes.
- Develop knowledge-based expert systems for synthesis.
- Explore better modeling capabilities to treat the probabilistic nature of environmental data in chemical processes.
- Develop nonconventional technological alternatives for pollution control.
- Identify alternate reaction pathways and catalysts.
- Identify barriers in process models or heuristics.
- Implement rate-based modeling capabilities (as opposed to equilibrium modeling which is performed by most commercial simulators).
- Develop data acquisition and enhanced modeling capabilities for separating dilute components of streams to identify process designs for a range of environmental, cost, and operating needs.
- Develop techniques for defining ultimately limiting process efficiencies.
- Identify better techniques to assess environmental costs and impacts.

A key component in the design of clean process technologies inherent in almost all the identified needs is related to developing sophisticated tools for process simulation and synthesis. Commercial process simulators, developed in the late 70s and used extensively by the chemical process industries to track component flows in the process, are equipped with detailed process and cost models and elaborate physical property data banks, but they lack any capability for process synthesis incorporating environmental control processes. Further, it is now understood that nearly all analyses of environmental control technologies in the early phase of research and development involve uncertainties. Commercial simulators possess no capabilities for uncertainty analysis and probabilistic (stochastic) modeling, which is considered an important tool for assessing the economic risk associated with a particular design. Further, the necessity to synthesize processes in the presence of uncertainties is greater in the context of emerging innovative technologies, such as environmental control systems, because the available performance data for these process technologies are scant due to little or no commercial experience, and the technical and economic parameters are not well established. Because the conceptual design of any "clean" chemical process involves identifying possible flowsheet configurations given any inherent uncertainties, synthesis methods for pollution prevention must also address critical issues in process synthesis under uncertainty (stochastic synthesis), as it has important implications for process viability and other quality measures, such as controllability, safety, and environmental compliance. This article presents an overview of the state-of-the-art in process simulation, mathematical modeling, and optimization for the synthesis of processes incorporating pollution prevention options, and addresses some of the issues related to the needs for environmental considerations in process design and development. Recommended activities that could lead to substantial improvement in process simulation and modeling and offer some scope in building efficient tools for process synthesis, keeping the environmental objectives in view, are also described.

PROCESS SIMULATION: AN ENVIRONMENTAL PERSPECTIVE

Process simulation is the utilization of computer software resources to develop mathematical models for constructing an accurate, representative model of a chemical process to understand its actual behavior during regular plant operations. In the past, process simulation was mainly concerned with the development of sophisticated unit operation blocks to predict accurate mass flows of principal components in a process. In recent years, environmental consciousness and considerations in process design and simulation demand an effort extending far beyond the capability of existing process simulators to model processes with environmental control options. Nowadays, environmental goals necessitate tracking even trace components (eg, resulting from fugitive emissions) that affect environmental compliance or even the society's view of an environmental concern, besides providing an inventory of the major components through complete material balances. Complying with this demand for models with higher degrees of detail for every operation to meet requirements in process engineering creates the need for sophisticated computer-aided process modeling tools to evaluate and screen processes in the presence of uncertainties in identifying low cost, environmentally friendly solutions. Any industry involved in transforming raw material to useful products and byproducts (that may be environmentally unacceptable) uses such process simulation tools to model their processes. Chemical industries involved in processing organic and inorganic material, electric power industry involved in the transforming fossil fuel to produce energy for lighting our homes, biological treatment plants for waste water are some examples, which depend on accurate process simulation for assessing the material and energy flows through the process, so that the thermal, environmental, and economic performance can be estimated. For any chemical industry, addressing the environmental objectives through better simulation, design, and synthesis is the key to successful plant operation in which emissions are reduced to a minimum.

Process Simulation Tools

The key components of process simulation software are presented to illustrate how they are used effectively and efficiently to model complex processes with environmental controls. The essential building blocks of a process simulator or flowsheeting package are as follows:

- *Data bank:* this consists of data related to the component physical properties and cost.
- *Thermodynamic models:* these are models developed to predict the different physical properties of the components under process conditions.
- *Unit module models:* these are routines that simulate the different unit operations (distillation, mixing, splitting, heat exchange etc.) and processes (reactions).

In addition to these, there are mathematical routines for numerical computations, and cost routines for performing an economic analysis of the process.

General process simulation software is generally sequential modular, equation-oriented, or simultaneous modular in its approach. In a sequential modular simulator, the unit operations and processes are modules and the output stream values are computed given the input stream values and the equipment parameters. Each unit module in a flowsheet is therefore solved sequentially. The overall flowsheet calculations in a sequential modular simulator follow a hierarchical approach. Thermodynamic models and routines are at the bottom of this hierarchy, followed by the unit operation modules performing the necessary material and energy balances based on the thermodynamic property routines. The next in the level of hierarchy are the design specifications that involve iterative calculations around the units, superseded by the recycle iterations for stream convergence. The utilities like optimization occupy the highest level in the calculation hierarchy in the sequential modular framework. This particular nature of the hierarchy and the presence of recycle streams and design specification operations results in inefficiencies due to the iterative calculations that need to be performed. Consequently, sequential modular simulators lack the flexibility to perform design and optimization tasks because of the way the calculation flow is structured in the simulator. Nevertheless, the sequential modular approach is reliable, easy to assemble, and since each unit is solved individually along with its thermodynamic models rather than simultaneously with other units, it is more robust, particularly if the models are nonlinear. On the other hand, because the efficiency in convergence and optimization depends on the amount of information available from the flowsheet (and lacking in sequential modular simulators), other types of simulators (eg, equation-oriented) came into existence. A equation-oriented process simulator uses a set of nonlinear equations representing the process modules, mass and energy balances in the process, and solves them simultaneously. Although, the equation-oriented simulators are more flexible in terms of information flow, they lack robustness. The simultaneous modular approach adopts the sequential modular approach (ie, the output stream values are computed from the input stream values and equipment parameters), but also require solving a set of linear equations relating the output values approximately to a linear combination of input values for each module. This relationship of the output stream values to the linear combination of the input stream values results in finding linear coefficients that model the units for any changes in the inputs through successive iterations (4). The main advantage of this approach is that if some of the input values are unknowns, they are computed from the specified output stream values, if the input and output variables constitute a set that lead to a solution. A comparison of the different types of simulators shows that the executive program that controls the user input, collects the problem description, and performs the execution is easier to write for sequential modular simulators than for equation-oriented simulators. In contrast, equation-oriented simulators are more flexible, allowing users to write their own process model equations, although the solution procedure can be extremely complicated. The fact that equation-oriented simulators are more tedious in their usage probably explains why most commercial simulators are sequential modular in nature. Process simulators are also classified on the basis of the nature of the processes, ie, whether the processes being considered are steady-state or dynamic. Accordingly, steady-state vs. dynamic simulators arise for modeling continuous type processes. A list of common process simulators and their associated references is presented in Table 1. Although this list is by no means exhaustive, it shows some of the simulation software used in the past and to a greater or lesser extent at present to model complex chemical processes. A brief discussion of some of the recent trends in computer-aided simulation is in (13).

Introducing environmental considerations in process design and development leads to a synthesis approach for evaluating and screening the various alternatives for environmental control. Before process simulation is performed to evaluate the potential of candidate technologies, it is necessary to outline the synthesis task, the first step in the design and development of large scale environmentally friendly processes.

SYNTHESIS APPROACH TO POLLUTION PREVENTION

The synthesis approach to pollution prevention is classified in three categories, namely (*1*) knowledge-based approach (*2*) thermodynamic approach and (*3*) optimization approach. Advances in knowledge-based approaches applied to process synthesis involve methods, in which particular pollution prevention ideas are transferred from one process to another (14,15), and artificial intelligence for simulating human thought processes for developing environmentally friendly chemical processes (16). Perhaps, the most systematic knowledge-based approach is the hierarchical decision procedure that involves a logical sequence of process flowsheet evolutions (17). In this procedure, the essential decisions for developing a flowsheet at each level are identified, and if these decisions are altered, then process alternatives are generated. This is usually followed by an economic study of the different alternatives, so that only the viable process options are considered for the next evolutionary stage. The hierarchical approach has also been represented by the "onion model" (18), which characterizes the synthesis task as a set of nested decisions pertaining to different operations, as depicted in Figure 2. Because the reaction system is the key component in transforming the raw materials into valuable products, it forms the core of the synthesis exercise. The reaction system defines the nature of the separation and recycling system, which in turn, influences the design of the heat exchanger network. Any excess requirement or deficit related to the heat content of process streams must be handled by the hot and the cold utilities, affecting the design of the utility system. Quite recently, a similar procedure was outlined by for the synthesis of processes, keeping in view the environmental objective of minimizing waste in process industries (19). The procedure related to process synthesis for waste minimization follows a hierarchical approach, similar to the "onion model", and is summarized in the following paragraphs:

Table 1. Process Simulation Tools

Simulation Package	Type	References
FLOWTRAN	Sequential modular	5
FLOWPACK II	Sequential modular	6
PRO II (previously PROCESS^{SM})	Sequential modular	7
ASPEN	Sequential modular	8
SPEEDUP	Equation-oriented	9
ASCEND	Equation-oriented	10
gPROMS	Equation-oriented	11
MODEL.LA	Equation-oriented	12

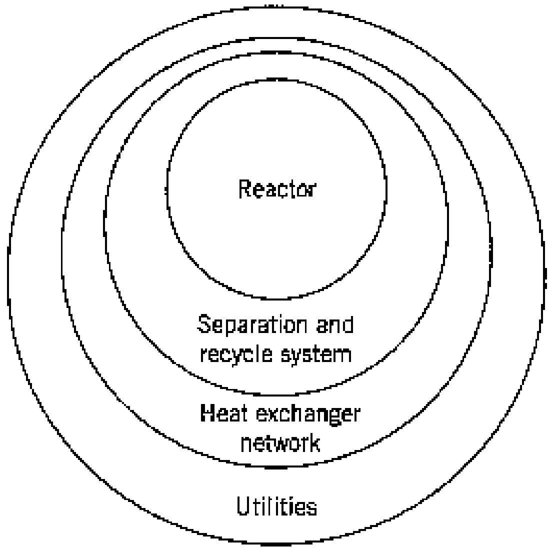

Figure 2. The "onion" model. Adapted from Ref. 18.

- Level *1:* List input information. In this level, information regarding the production rate, product value and purity, reaction rates and conditions, raw material costs and streams, product distribution, catalyst properties, processing constraints, plant site and physical property data, data concerning safety, toxicity and environmental impact, and cost data for the by-products generated (including the "wastes", which have negative economic value) are obtained.
- Level *2:* Define input–output structure of the flow sheet. The decisions that must be considered at this level pertain to the need to purify the feed streams, whether to recover and recycle some of the reactants, and the necessity of recovering and recycling by-products formed by secondary reversible reactions. In cases where waste minimization problems are caused by the reaction chemistry, it is recommended that alternate pathways for transforming the raw materials be investigated.
- Level *3:* Specify the recycle structure of flow sheet. The recycling decisions depend on the excess reactant at the

reactor inlet, the addition of a diluent such as steam to shift the equilibrium or act as a heat carrier, and the need for adding an external solvent to the process. Problems caused by adding diluents and solvents must be eliminated by changing them in favor of a suitable solvent, given the environmental objectives of the process.

- Level *4:* Identify the separation systems. It is desired that the first attempt in the synthesis of a separation system involve phase splits. If phase split is not possible, other types of separation systems are also used. For example, vapor recovery systems are used to prevent valuable components from leaving the process with gaseous streams. Liquid recovery systems are used to separate components between phases or to separate liquid mixtures. In this context of separation systems, distillation is the most preferred from a pollution prevention viewpoint, because other means, such as the use of extractive agents like water in liquid-liquid extraction, often result in pollution problems. Other liquid separation procedures, such as adsorption in removing colored materials from liquid streams, result in the disposal of spent adsorbents in landfills. Solid recovery systems, such as filtration involve cake washing (using water, for example), resulting in additional water treatment facilities.
- Level *5:* Evaluate the alternatives. This is guided mostly by economic considerations influenced by environmental objectives. The main drawback is that the evaluation and screening task becomes tedious in the presence of several alternatives.
- Level *6:* Flexibility, control and safety. This level involves decisions related to the operability, controllability, and safe operation of the plant.

The hierarchical approach, based primarily on heuristic methods, relies on intuition and engineering judgment for quick selection of alternate process configurations. Although, this is an advantage in the generation of alternatives, the solutions that some heuristic rules predict are poor. Further, heuristic rules may contradict one another and may require assigning arbitrary weights to resolve conflicts.

Thermodynamic approaches to process synthesis for waste minimization are related to pinch technology. Pinch technology started receiving attention in the early 1970s when the energy crisis affected the chemical process industries. At that time, pinch technology utilized information about heat flows through the process and identified opportunities for energy savings by allowing heat transfer between process streams, thereby reducing external requirements for hot and cold utilities (20). The inclusion of pinch technology for process integration leads to an interesting outcome. Process integration through pinch technology results in energy savings (which was the main goal in the early 1970s), and it also leads to waste minimization and emission reduction. Commercial software in the area of pinch technology has been developed (ADVENT from Aspen Technology, Inc., SuperTarget from Linnhoff March, etc), which assesses the trade-off between energy consumption and capital cost for a system of heat exchanger networks. In recent years, the concept of pinch analysis has also been extended to mass transfer applications, where mass concentration gradients (as opposed to temperature gradients for heat transfer) are used to transfer undesirable species from a number of waste (rich) streams into a number of lean streams that are regenerated and reused (21).

The complexities of chemical processes involving environmental implications and the vast majority of promising candidate technologies are inhibiting in the screening and selection procedure for "optimum" process technologies. This, coupled with the fact that numeric computations are less expensive because of the state-of-the-art in computer hardware, has resulted in the acceptance of optimization approaches for evaluating and screening the candidate technologies to identify the best option based on any given criterion.

Optimization Approach to Process Synthesis

A methodology to pollution prevention through process synthesis consistent with almost any simulation environment is based on an algorithmic approach. The main idea in this approach is to formulate the synthesis task as an optimization problem. This approach involves integrating sophisticated optimization techniques into process simulation models, and requires an explicit or implicit representation of a specified set of process alternatives from which the optimal solution is derived. The main advantage of this approach is that cost equations are incorporated as part of the model-optimization structure, providing a more systematic framework for handling a variety of synthesis problems and indicating how design decision variables affect process economics. Early approaches, based on optimization, which were applied to a number of waste minimization problems, depended on mathematical models to develop cost vs emission limit curves (1). These enabled engineers to understand the effect of fundamental process changes on the cost and emission levels, which were then used to define the least cost-intensive means of achieving any given emissions target. The algorithmic approach has the important property of generating alternate process configurations automatically and has been gaining much interest in recent years. Although, this approach poses some difficulties (all the alternatives must be determined *a priori* by heuristic and knowledge-based approaches, the computations are time consuming for a problem not well formulated, and the optimality is quaranteed only for the alternatives considered in the overall problem representation etc.), an algorithmic approach based on optimization strategies identifies subtle differences between the alternate process technologies and thereby selects the optimum process option.

A Mathematical Programming Approach to Process Synthesis. A much more automated synthesis approach to pollution prevention is based on mathematical programming techniques, which, by virtue of the advances in the field of computer hardware and software, have gained much prominence and have led to the development of rigorous modeling and optimization capabilities. The mathematical programming approach to process synthesis is simply stated as follows: Given a set of structural alternatives or options in a process (a set of environmental control options to remove emission(s), a set of heat-exchange network configurations, a set of separating system configurations for removing trace amounts of a pollutant for reuse or regeneration), an objective (process cost), and a set of constraint(s) (maximum allowable effluent generated by a process), the goal is to find the optimum configuration for the process flowsheet. This is also referred to as

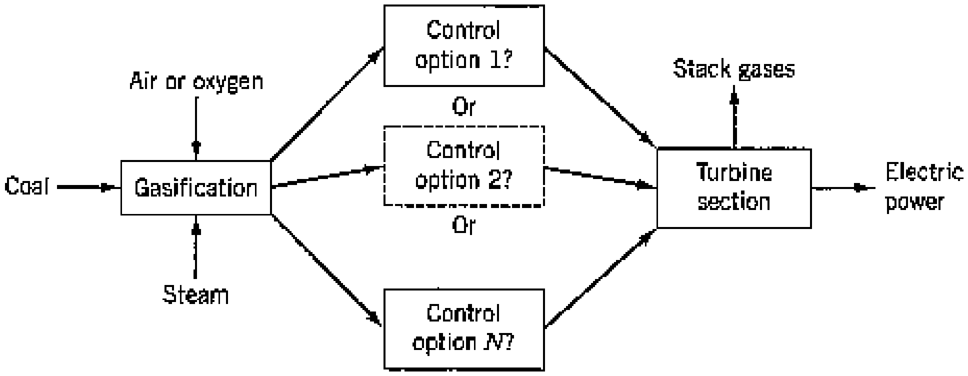

Figure 3. Synthesis task applied to electric utility system.

structural optimization. The synthesis problem, however, goes beyond selecting a suitable structural configuration for the process. It also optimizes certain parametric conditions associated with the various process operations, thereby improving the process to attain the desired objective. This stage is referred to as *parametric optimization* and must be performed along with structural optimization to complete the synthesis task. To cite an example, consider Figure 3, which shows the key steps in a typical electric utility system generating energy from a fossil fuel. After gasification, the fuel gas must be treated to remove sulfurous compounds before it enters the gas and steam turbine sections of the process. In principle, this is achieved by the different sulfur-removal strategies in industrial practice resulting in alternate process configurations. Further, because each of these structural alternatives involves several process operations, to optimize the entire process, the operating conditions (ie, pressure, temperature, etc) in the alternatives themselves must be optimized. The performance index, in this case, may very well be the overall cost of the process, whereas the environmental constraint may be such that the total amount of sulfur emitted by the process must be less than a threshold number set by legislative actions.

The mathematical formulation of such a synthesis problem for pollution prevention is expressed as follows:

$$\underset{x,y}{\text{Optimize}}\ Z = z(x,y)$$

$$\text{Subject to } h(x,y) = a$$

$$g(x,y) \leq b$$

where Z is the objective function of interest (eg, process cost), x is the set of design (decision) variables for the continuous parameters (pressure, temperature, etc) associated with a selected alternative, and y is the set of discrete parameters (the various options that constitute the structural alternatives). The set of constraints $h(x,y)$ refers to the process equations that govern the unit operations and processes, whereas the constraint set $g(x,y)$ may imply environmental constraints (eg, the total waste generated in the process must be less than a maximum allowable value) associated with the given process. Although, the mathematical formulation appears simple, the solution procedure for solving this discrete-continuous problem is complicated by the inherent nonlinear behavior of most physical systems. Consequently, this field has been the focus of research in recent years. A detailed treatise of the methodology is presented elsewhere (22), and only the salient features are presented here to illustrate how the methodologies are applied to design processes with environmental control objectives.

The discrete-continuous optimization problems defined by the formulation above are commonly solved by mixed-integer nonlinear programming (MINLP) algorithms. A class of MINLP algorithms addressing such problems in chemical process industries is designed so that the objective function and the constraints, obtained after solving the process model, are linear with respect to the discrete decisions and nonlinear with respect to the continuous decision variables (23). Figure 4 shows a framework for solving a large class of discrete-continuous problems using a mixed-integer, nonlinear (MINLP) programming technique, where the objective function is linear with respect to the discrete variables and nonlinear with respect to the continuous variables. The MINLP solver belonging to this class involves solving an alter-

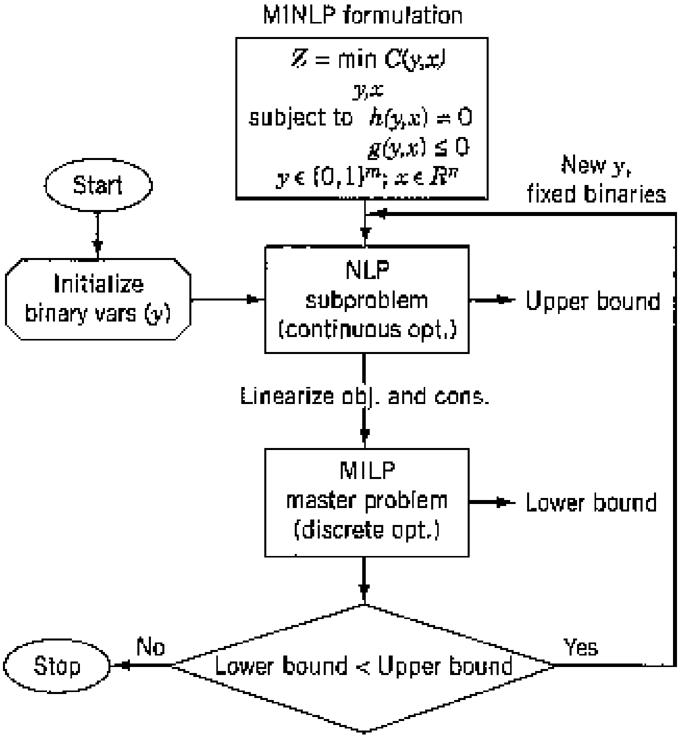

Figure 4. A MINLP framework for solving discrete-continuous optimization problems.

nate sequence of mixed-integer, linear program (MILP) master problems and nonlinear (NLP) subproblems. The MILP master problem (outer loop) predicts the integer or binary decision variables which select a process configuration from the several candidate alternate configurations. The NLP subproblem (inner loop) optimizes the continuous variables associated with the flowsheet configuration selected by the MILP master problem. The NLP subproblem analyzes the objective function and constraints after the process model is executed and predicts the new continuous variables. Once a NLP solution is obtained, the objective function and constraints are linearized, and this linearization information is transferred to the MILP master problem, which then predicts another process configuration. A solution to the complete MINLP problem is obtained when the upper (lower) bound from the NLP subproblem is lower than the lower (upper) for a minimization (maximization) problem. Although, MINLP algorithms are particularly well suited for equation-oriented simulators, recently they have also been extended to sequential modular simulators (24). Nevertheless, the complexities related to the inherent nontransparency or "black-box" nature of sequential modular simulators (25), suggest that a combination of combinatorial optimization techniques, such as simulated annealing and nonlinear programming, are a promising tool for addressing discrete-continuous optimization problems within a sequential modular environment.

In most cases, the alternatives considered for the final MINLP synthesis stage are developed primarily by a hierarchical design procedure, followed by process integration ng pinch technology. This strategy, based on a combination nowledge-based, thermodynamic (pinch technology) and ithmic approaches is more appropriate for large-scale problems involving pollution prevention and integrated environmental control options. Recently, a methodology combining hierarchical design procedure, thermal integration, and an MINLP-based synthesis approach was used for an economic evaluation of a process retrofit through waste minimization and process integration (26). The following paragraphs present an illustrative example of the synthesis of an integrated gasification and combined cycle (IGCC) system for power generation incorporating integrated environmental control options based on the MINLP procedure outlined previously.

Example A: Synthesis of Integrated Gasification and Combined Cycle Systems for Power Generation. There is significant interest today in the ability of integrated coal gasification combined-cycle (IGCC) systems to provide electricity reliably and at lower cost relative to conventional fossil fuel. The ability of IGCC systems to meet stringent environmental emission standards is another attractive feature of this technology. Environmental control systems, however, account for a significant part of the cost and complexity of IGCC systems. Current systems require cooling the gas stream prior to cleanup, thus generating a significant waste water stream which must be treated in addition to the air pollutant and solid waste streams normally associated with coal-based electric power generation. Hot-gas cleanup systems offer the potential for significantly simplifying and reducing the cost of environmental control for many IGCC systems. In addition to the technical aspects of IGCC technology, there is also a strong need for "systems" research to identify the best ways of configuring IGCC systems and of incorporating advanced cleanup and other technology to produce electricity at minimum cost. For example, the most common design for sulfur removal using hot-gas cleanup is through the use of solid sorbents. Sulfur capture occurs either through the addition of a solid reactant in the gasifier (ie, in-bed desulfurization), by external desulfurization of the flue gas (eg, zinc ferrite process), or by a combination of these two methods.

The first step in solving the process synthesis problem is developing the superstructure containing all alternative designs to be considered for the optimal solution (27). The superstructure for the three alternative desulfurization configurations for the advanced IGCC system is shown in Figure 5. There is a total of three additional splitters, one additional mixer, and six binary decision variables, ie, two decision variables (branches) per node. Each binary (0–1) variable represents the presence ($y = 1$) or absence ($y = 0$) of the branch associated with that variable. At the first node, the two decisions involved are in-bed desulfurization ($y_1 = 1$) or only external desulfurization by the zinc ferrite process ($y_2 = 1$). Because these two decisions are mutually exclusive, the following constraint is added to the optimization problem:

$$y_1 + y_2 = 1 \tag{1}$$

If in-bed desulfurization is selected, then, at the second node, there is a choice of the zinc ferrite process after in-bed desulfurization ($y_3 = 1$) or the cyclone separator marking the end of the desulfurization section ($y_4 = 1$). These two decisions are also mutually exclusive and apply only in the presence of in-bed desulfurization ($y_1 = 1$). This leads to

$$y_3 + y_4 = y_1 \tag{2}$$

The last node in the desulfurization process exists on the zinc ferrite branch. If the zinc ferrite process is selected, the decision about whether the SO_2 should be recycled ($y_5 = 1$) or passed to the sulfuric acid plant ($y_6 = 1$) is decided at this node. Again, these events are mutually exclusive and are considered only when the zinc ferrite process is selected ($y_4 = 0$). The recycle alternative is applicable only for combined in-bed and gas stream desulfurization ($y_1 = 1$, $y_5 = 1$). Coupled with the zinc ferrite-only option is the presence of the sulfuric acid plant ($y_6 = 1$). These conditions are represented by the following logical constraints

$$y_5 + y_6 = 1 - y_4 \tag{3}$$

$$y_6 = y_2 \tag{4}$$

The six binary decision variables along with the above four constraints (eqs. 1–4) result in three feasible alternative technologies:

1. In-bed desulfurization plus external "polishing" by zinc ferrite desulfurization:
$$Y_1 = (1, 0, 1, 0, 1, 0)$$
2. Gas stream desulfurization only via zinc ferrite with byproduct recovery:
$$Y_2 = (0, 1, 0, 0, 0, 1)$$
3. In-bed desulfurization only, via limestone or dolomite injection:
$$Y_3 = (1, 0, 0, 1, 0, 0)$$

As an example of implementing the binary variables, consider the binary variable y_1. This variable is introduced into

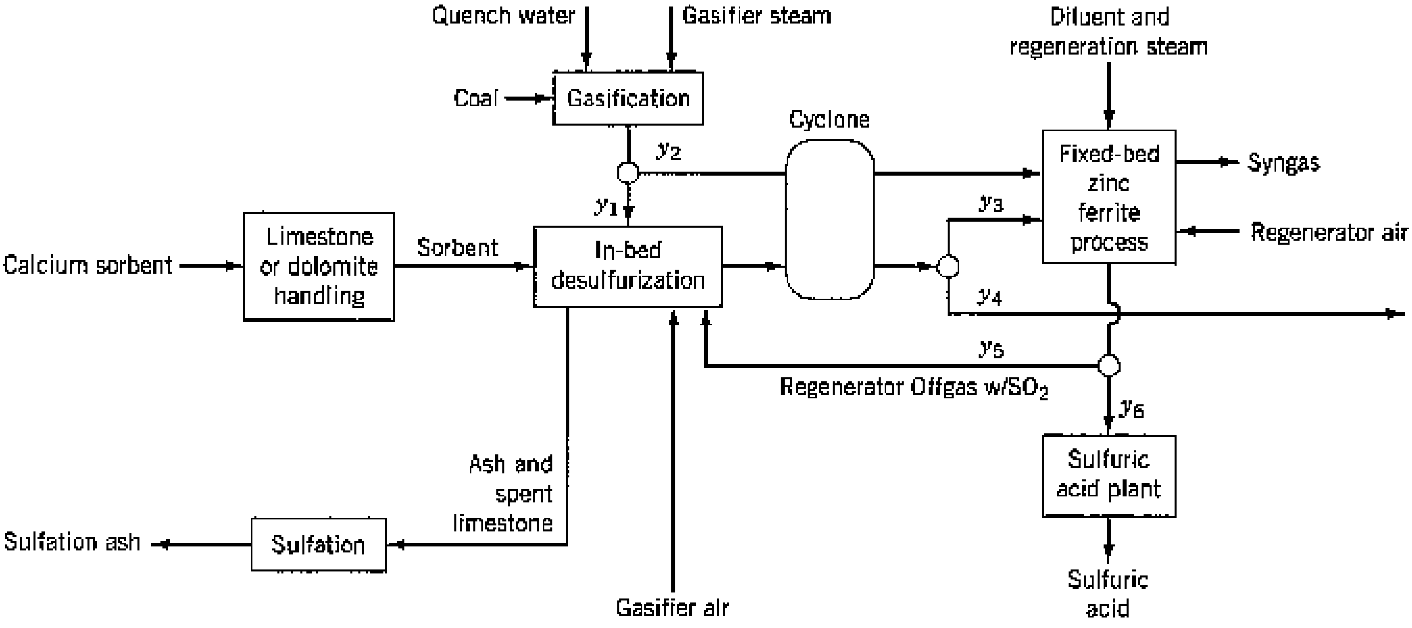

Figure 5. A superstructure incorporating all of the possible alternative configurations for the IGCC example problem.

the appropriate performance and cost model equations to represent the presence of unit operations associated with sorbent handling. Thus, assuming that the direct capital cost of the limestone handling section, for example, is given by

$$DC_L = (1160 + 0.026\, m_L) \qquad (5)$$

where m_L is the mass flow rate of limestone used, the use of binary variables results in

$$DC_L = y_1(1160 + 0.026\, m_L) \qquad (6)$$

This implies that, if in-bed desulfurization (using limestone) is selected, then $y_1 = 1$, and the capital cost of the in-bed desulfurization section is calculated from equation 6. Otherwise, if the in-bed desulfurization section is not selected, then $y_1 = 0$, and the capital cost of the limestone handling section is 0. The other binary variables are applied similarly to the equations used to estimate annual costs and performances (thermal and environmental) for the affected process areas.

The purpose of this exercise is to obtain a flowsheet configuration and design variables which minimize the levelized cost of electricity, given an environmental constraint on total sulfur emissions:

$$E_{SO_2} \le \frac{0.015 \text{ lb } SO_2}{10^6 \text{ Btu}} \qquad (7)$$

The continuous decision variables selected for this preliminary study are the in-bed desulfurization efficiency (η_s), the zinc ferrite absorption cycle time (t_a), and the maximum vessel height to diameter ratio (L/D) for the zinc ferrite absorbers. The in-bed desulfurization efficiency determines the limestone sorbent requirement and removal of residual sulfur evolved in the zinc ferrite process area. This variable is allowed to vary up to 90% per pass of gasifier sulfur removal. In the absence of sorbent about 15% of the sulfur is removed in the gasifier bottom ash. This gives the lower limit for the efficiency. The zinc ferrite absorption cycle time is allowed to vary from 30 to 172 h and the zinc ferrite vessel height to diameter ratio ranges from 2 to 4.

The MINLP problem at this stage consists of three continuous and six binary decision variables, the above four equality constraints for the binary logical variables (eqs. 1–4), the environmental constraint on total sulfur emissions (equation 7), and three inequality constraints (eqs. 8–10) for the three continuous decision variables, which are related to the binary variables via upper and lower bounds:

$$0.15 \le \eta_s \le (0.75y_1 + 0.15) \qquad (8)$$

$$30(y_2 + y_3) \le t_a \le 172(y_2 + y_3) \qquad (9)$$

$$2(y_2 + y_3) \le L/D \le 4(y_2 + y_3) \qquad (10)$$

The optimal flow sheet obtained with the MINLP algorithm is shown in Figure 6. Given the environmental constraint that total SO$_2$ emissions must be less than or equal to 0.015 lb per 10^6 Btu of coal throughput, the in-bed desulfurization scheme is infeasible. The results for the different structural and parametric alternatives are shown in Table 2. It is worth mentioning here that independent evaluation by Southern Company Services shows that the hybrid system involving both in-bed and external desulfurization is required to achieve the desired environmental/performance goals. The fact that mathematical programming methods also predicted a similar result indicates the potential of using an optimization-based synthesis approach for designing and developing processes involving environmental control strategies.

Recent studies with discontinuous objective functions reveal that probabilistic techniques for solving large-scale, combinatorial problems, such as simulated annealing are well-suited for synthesis applications in a sequential modular simulation environment (28). A methodology combining simulated annealing and nonlinear programming (SA-NLP) is complementary to MINLP approaches and presents a robust technique for the synthesis of large-scale process flow sheets.

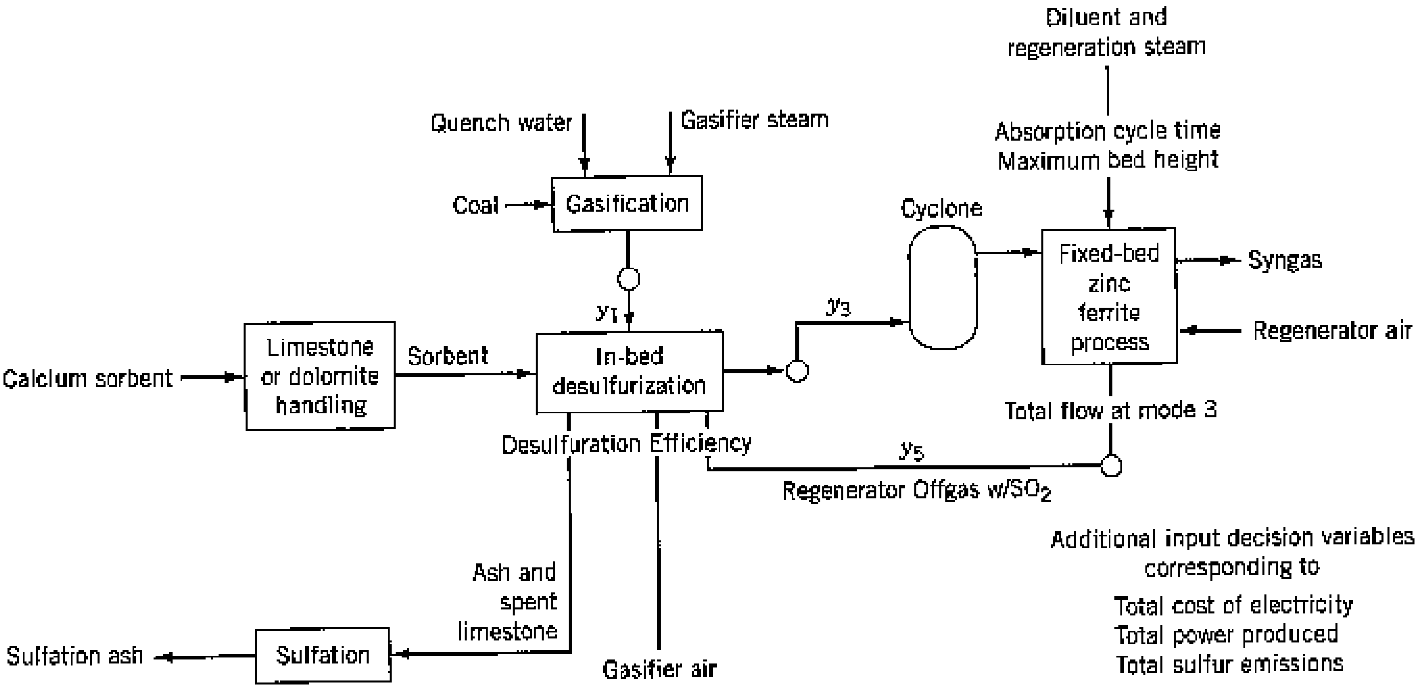

Figure 6. Optimal design configuration for the IGCC flow sheet example.

Table 2. Alternative Scenarios in IGCC Design Example Problem

Technological Alternative	Desulfurization Efficiency	Absorption Cycle Time, h	Maximum Length/Dia.	Cost of Electricity, mills/kWh[a]
In-bed + ext. desulf.	0.89	150.5	2.29	53.76
Ext. desulf.	0.15	30	2.0	62.30
In-bed desulf.	Infeasible	Not applicable	Not applicable	Infeasible

[a] One mill is equivalent to 1/1000 U.S. dollar.

In this case, the simulated annealing algorithm predicts discrete configurations, which is predicted by the MILP master problem in a MINLP algorithm. Nevertheless, although the results produced by the SA-NLP and the MINLP approaches are similar, an MINLP approach for a well-formulated problem is less time-consuming than the SA-NLP approach. The SA-NLP approach, however, is more amenable as a synthesis tool in a sequential modular simulation environment.

A Simulated Annealing Approach to Process Synthesis. Simulated annealing is a heuristic approach for solving combinatorial optimization problems, complementary to techniques for solving MILP problems, such as branch and bound and cutting plane methods. It is a probabilistic method based on statistical mechanics, a branch of physics that deals with the behavior of physical systems with many degrees of freedom. Physical systems, such as liquid metals, freeze and crystallize or "anneal" as the temperature is lowered. At high temperatures, the molecules of liquid metals are more thermally mobile. If such a system is cooled slowly (ie, annealed), the atoms orient themselves to form pure crystals, thus attaining the lowest energy state of the system. On the contrary, if the liquid metal is cooled (ie, quenched), it does not reach this minimum energy state, but rather attains a polycrystalline or amorphous state with high energy.

In the context of an optimization problem where the decision variables are integers, the objective function is analogous to the energy of a physical system. The aim of such a problem is to minimize the objective function (energy), $E(\mathbf{x})$, where $\mathbf{x} = (x_1, x_2, x_N)$, represents a particular configuration of the system. In a typical synthesis application, a particular set $\mathbf{x}$ represents an unique process alternative. To observe the behavior of the system, the system is perturbed from its present configuration to another configuration by changing any element $\mathbf{x}_i$ in the vector set $\mathbf{x}$. This is referred to as a *neighborhood move*. The behavior of such a system subject to a neighborhood move is determined from observation of the objective function. For a minimization problem, if the configuration results in a lower energy state (or objective), the move is always accepted. On the contrary, if the move results in a higher energy state, the move is *still* accepted according to a certain probability given by the Metropolis algorithm (29). A pseudocode of the simulated annealing algorithm is outlined as follows.

Initialize variables: T_{initial} (initial temperature or initial energy level/objective function), accept and reject limits or N (number of allowable moves at a temperature), initial configuration set $\mathbf{x}_i$, and objective function Obj($\mathbf{x}_i$), while T (current temperature) $> T_{\text{frozen}}$ *do*, while $i < N$ *do*, generate a random move $\mathbf{x}'$ by perturbing $\mathbf{x}$

$$\Delta\text{Obj} = \text{Obj}(\mathbf{x}') - \text{Obj}(\mathbf{x})$$

If $\Delta\text{Obj} \leq 0$ or random(0,1) $< \exp(-\Delta\text{Obj}/T)$ then accept $\mathbf{x}$, $\mathbf{x} = \mathbf{x}'$, update number of accepts and rejects until equilibrium is reached at T (ie, when $i = N$) update $T_{\text{new}} = \alpha T (0.8 \leq \alpha \leq 0.98)$ until $T \leq T_{\text{frozen}}$.

At each temperature (energy level) of the system being optimized, a large number of moves, decided a priori, are allowed. The temperature is then lowered and the process continues until no further improvement in the objective function, within a given tolerance, is attained. As the temperature is lowered, the probability of making uphill moves defined by the Metropolis algorithm decreases. Simulated annealing utilizes these random uphill jumps at initial high-temperature stages to ensure that the system is not confined to a local minimum. In other words, moves which are highly probable are rejected, and very improbable moves are accepted occasionally. By successfully lowering the temperature, it is possible to simulate the system attaining equilibrium at each newly reduced temperature, and thus mimic the physical annealing process. The advantage of simulated annealing over MINLP-based techniques is that it can be applied to nonconvex functions, does not require gradient information (which may be unobtainable or difficult to compute), and offers the possibility of a random jump out of a local minimum so as to attain global minima. A pictorial description of the annealing procedure is shown in Figure 7.

The techniques outlined in this section meet some of the needs for chemical process design for the environment and provide the tools for process synthesis and optimization to prevent pollution. The following example illustrates how a combined simulated annealing and nonlinear programming approach is applied to synthesizing optimal waste blends for hazardous site remediation.

Example II: Environmental Restoration of a Hazardous Waste Site. Radioactive waste produced by nuclear processes is classified into *low level* and *high level* fractions based on the content to be immobilized for future disposal. It is desired that the high level waste is converted to borosilicate glass for storage in a geologic repository, because radioactivity does not easily leak through glass. This process, termed "vitrification", requires satisfying certain conditions related to "processibility" and "durability," so that the conversion is achievable. The conditions of processibility ensure that, during the processing stage, the glass melt has properties such as viscosity, electrical conductivity, and liquidus temperature within ranges acceptable for the vitrification process. The considerations of durability ensure that the resultant glass meets the quantitative criteria for storage in a repository.

The site has 177 tanks with capacities ranging from 50,000 to 1 million gallons. During the vitrification process it is required that the wastes in the tanks and appropriate glass forms (frit) are mixed and heated in a melter to form glass that satisfies the constraints. The main objective is to add the minimum amount of frit and still achieve reclamation of the wastes. This has major implications. First, this keeps the frit costs to a minimum and second, the amount of waste per glass log formed is maximized, thus keeping waste disposal costs to a minimum. The minimum amount of frit is used if the high-level wastes are combined to form a single waste for the feed to the vitrification process. Unfortunately, the large volume of waste and the time period over which the waste needs to be processed, makes this a humongous task. The essential problem then is to choose the proper set of wastes in the tanks to form blends and add the right amount of each of the frit components to the blends, so that the total quantity of frit required is minimum.

Figure 8 is a pictorial description of this vitrification problem. N different waste sources or tanks must be blended together to form a discrete number of blends B. It is required that *all* the waste from any given tank must combine with other wastes to form a single blend, each blend containing wastes from N/B sources. Further, if $w^{(i)}$ is the mass of the ith component in the waste, $f^{(i)}$ the mass of the ith component in the frit, and $g^{(i)}$ the mass of the ith component in the glass, the following equality constraints result:

$$g^{(i)} = w^{(i)} + f^{(i)} \tag{11}$$

$$G = \sum_{i=1}^{n} g^{(i)} \tag{12}$$

$$fg^{(i)} = \frac{g^{(i)}}{G} \tag{13}$$

where G is the total mass of the glass formed, n is the total number of components, and $fg^{(i)}$ denotes the fraction of the ith component in the glass. The formation of glass from the blend is governed by several constraints, such as component bounds, crystallinity constraints, solubility constraints, and glass property constraints. For a small subset (21) of the total number of

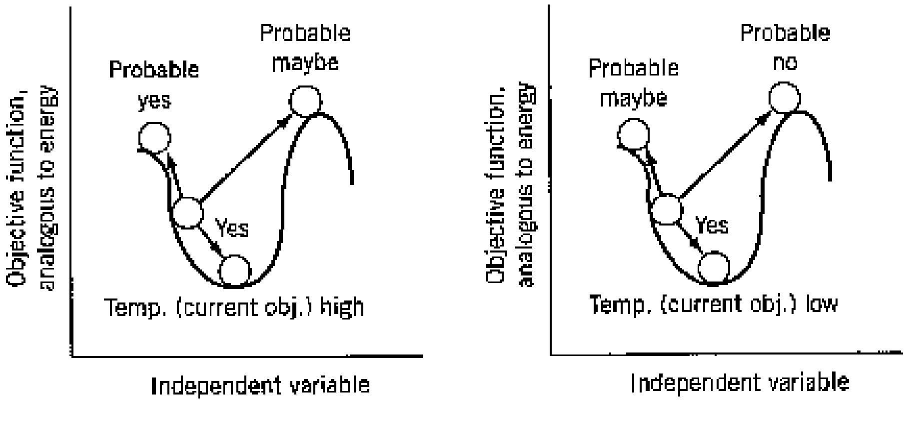

Figure 7. Simulated annealing procedure.

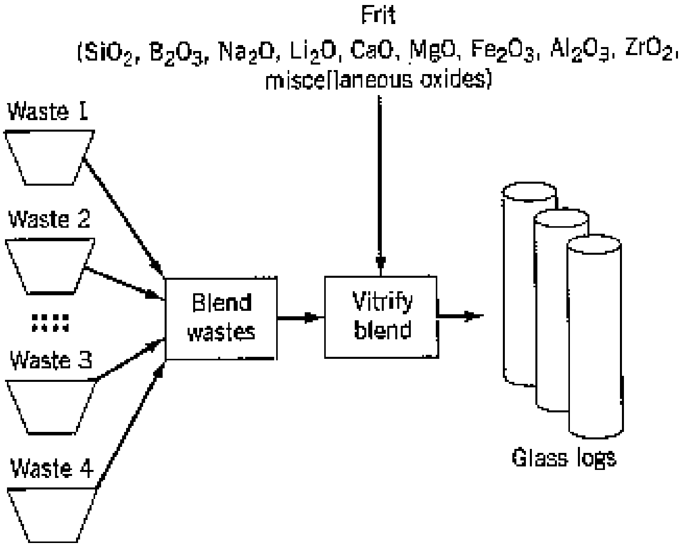

Figure 8. Schematic diagram of the vitrification problem.

tanks to be partitioned into three blends, there are 66,512,160 possible ways to form the three blends. This number poses an overwhelming problem for common search algorithms to determine the optimal blend configuration.

A two-stage approach based on SA-NLP was proposed to determine the optimal blend configuration (30). A schematic diagram of the solution procedure is shown in Figure 9. For the 21-tank problem, the discrete decisions involved the distribution of the tanks among the three blends. This decision is generated by the outer loop of the SA-NLP algorithmic procedure and is formulated as a minimization problem:

$$Min \sum_{j=1}^{3} \sum_{i=1}^{n} f_j^{(i)} \text{ (SA formulation)}$$

This formulation is interpreted as minimization of the total amount of frit over a given combination of blends, where $f_j^{(i)}$ is the mass of the ith component in the frit for the jth waste blend, and n denotes the number of components. Once the blend is fixed, the resultant NLP problem is formulated as follows:

$$Min \sum_{i=1}^{n} f^{(i)} \text{ (} j \text{ fixed) (NLP formulation)}$$

subject to equality constraints (eqs. 11–13), individual component bounds, crystallinity constraints, solubility constraints, and glass property constraints.

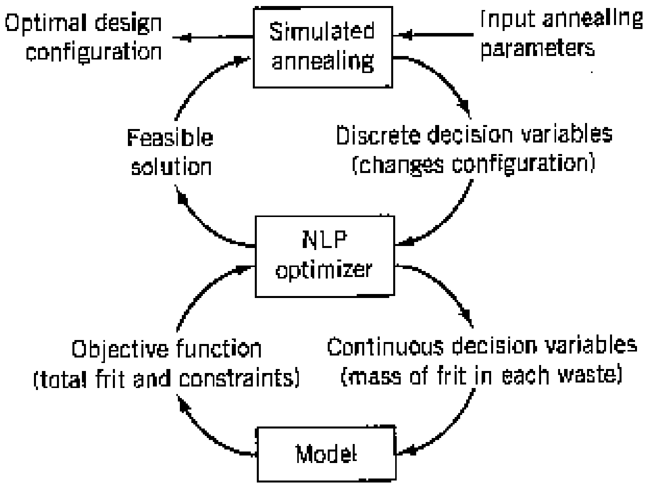

Figure 9. Coupled simulated annealing–nonlinear programming (SA-NLP) procedure for solving discrete-continuous optimization problems.

The combined SA-NLP approach identifies an optimal solution (11,028 kgs) which is lower than the solution predicted by heuristic (knowledge-based) approaches and GAMS-based MINLP methods. This optimal solution was further verified by a branch and bound strategy to confirm the global optimum, showing the potential of the SA-NLP for the synthesis of large-scale processes involving environmental implications.

The problem formulation above represents a simplified view of the actual problem, because it assumes that all the data pertaining to the input quantities are constant or known with certainty. The very nature of environmental problems demands an uncertainty analysis due to the inherent uncertainties of many environmental processes. This, in turn, leads to the synthesis of processes with uncertainties. The following section addresses key issues in modeling processes with uncertainties and presents an integrated framework for stochastic (probabilistic) modeling. This framework illustrates how deterministic simulators are used effectively to model processes with inherent uncertainties.

STOCHASTIC MODELING OF PROCESSES

Conventional simulators typically employ a Fortran code which produces deterministic (point estimate) results for a particular set of input assumptions. Such an approach is simplistic and unrealistic, leading to the incorporation of large safety or "fudge" factors to accommodate the uncertainties in equipment design and resulting in over-estimated thermal, environmental, and economic performance indicies. Chemical plants are usually faced with uncertain conditions during their operation. These uncertainties arise from variations in external parameters, such as the quality of feed streams, or from internal process parameters such as transfer coefficients, reaction constants, and physical properties. If the technology is new, there are additional uncertainties due to limited performance data. The ability to analyze uncertainty is especially important for ongoing research and development, where technical and economic parameters for individual processes and system designs are not well established. Uncertainty analysis is also important in comparing advanced system designs equipped with integrated environmental control strategies with "baseline" systems reflecting currently commercial technology (31).

To analyze uncertainty, the capability of performing sensitivity analysis through a series of multiple runs is usually available. Typically, however, only one or two parameters at a time are varied in a simulation framework which contains a large number of independent variables. Thus, important interactions or cases may be overlooked. Although, larger number of cases may be run as part of a sensitivity study, the volume of output generated makes results cumbersome or difficult to interpret and/or display. Even where many cases are analyzed, sensitivity analysis still provides no information as to the likelihood of different outcomes. In short, because the process analysis of real systems requires an uncertainty analysis, enhanced probabilistic modeling capabilities must be developed in commercial process simulators. The following paragraphs present a brief overview of the methodology used to analyze the uncertainties in processes systematically in a general probabilistic modeling framework. Key issues to bear in mind during stochastic modeling of processes are also described.

Statistical Terms and Heuristics

The uncertainty or variability in engineering models can be expressed in terms of probabilistic distributions. The probability distributions show the range of values a variable could take and the likelihood that each value occurs within the range. Thus, the distributions define the rule for describing the probability measures associated with the values of a random (uncertain) variable. Probability distributions are described in their entirety as cumulative distribution functions or by selected parameters, such as fractiles or moments (eg, mean and variance). A more complete review of these methods is in the literature (32). The following sections present key concepts utilized in the probabilistic modeling of advanced control technologies.

Specifying Uncertainty Using Probability Distributions. To accommodate the diverse nature of uncertainty, different distributions are used to represent the uncertain parameters in a process, as shown in Figure 10. The type of distribution chosen for an uncertain variable reflects the amount of information available. For example, the uniform and loguniform distributions represent an equal likelihood that a value lies anywhere within a specified range, on either a linear or logarithmic scale. On the other hand, the modified forms of these distributions, uniform and loguniform, allow distinguishing several intervals of the range. Further, a normal (Gaussian) distribution reflects a symmetric but varying probability that a parameter value is above or below the mean value. In contrast, lognormal and triangular distributions are skewed so that there is a higher probability that values lie on one side of the median than on the other. A beta distribution provides a wide range of shapes and is a very flexible means of representing variability over a fixed range. Finally, in some special cases, user-specified distributions are used to represent any arbitrary characterization of uncertainty, including chance constraints (ie, fixed probabilities of discrete values).

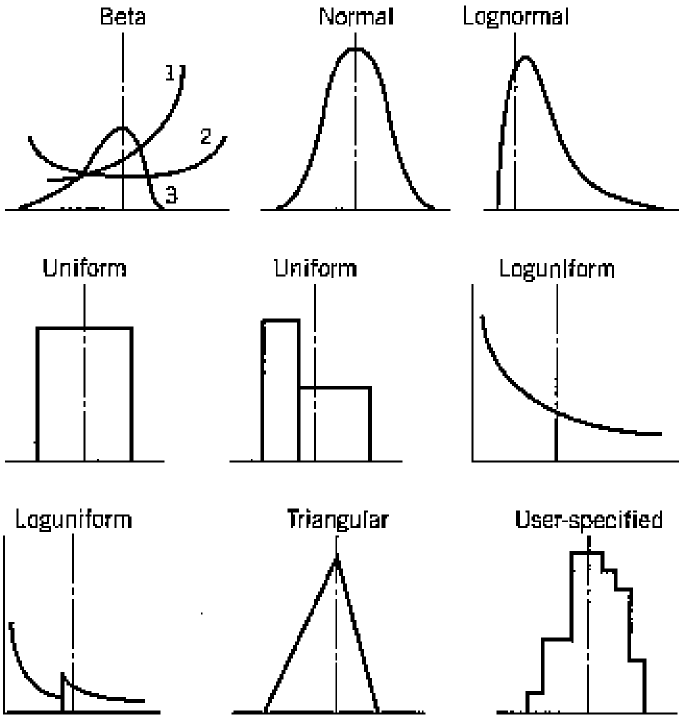

Figure 10. Typical probability distributions used in stochastic (probabilistic) modeling of processes. Note: The beta-distribution can have different forms depending on the parameters chosen, as shown in the shapes 1, 2, and 3 of the beta-distribution.

Sampling Techniques in Stochastic Modeling. Once probability distributions are assigned to the uncertain parameters, the next step is to perform a sampling operation from the domain of multivariable uncertain parameters. One of the most widely used techniques for sampling from a probability distribution is the Monte Carlo sampling, which is based on a pseudorandom generator to approximate a uniform distribution (ie, having equal probability in the range from 0 to 1). The specific values for each input variable are selected by inverse transformation over the cumulative probability distribution. Monte Carlo sampling also has the important property that the successive points in the sample are independent. The main advantage of the Monte Carlo methods lies in the fact that the results from any Monte Carlo simulation can be treated by classical statistical methods. Thus, results can be presented in the form of histograms, and methods of statistical estimation and inference are applicable. Nevertheless, in most applications, the actual relationship between successive points in a sample has no physical significance. Hence the randomness/independence for approximating a uniform distribution is not critical. In such cases, uniformity properties plays a central role in sampling. As a result, constrained or stratified sampling techniques are more appealing. Latin hypercube sampling is one form of stratified sampling which yields more precise estimates of the distribution function. In Latin hypercube sampling, the range of each uncertain parameter X_j is subdivided into nonoverlapping intervals of equal probability. One value from each interval is selected at random with respect to the probability distribution in the interval. The n values thus obtained for X_1 are paired randomly (ie, in equally likely combinations) with n values of X_2. These n values are then combined with n values of X_3 to form n-triplets, and so on, until n k-tuplets are formed. The main drawback of this stratification scheme is that it is uniform in one dimension and does not provide uniformity properties in k-dimensions. Further, for Latin hypercube sampling (and its variant, median-Latin hypercube sampling), sample scenarios are random, but not completely independent. Recently, an efficient sampling technique (Hammersley sequence sampling) based on Hammersley points has been developed, which uses an optimal design scheme for placing the n points on a k-dimensional hypercube. This scheme ensures that the sample set is more representative of the population, showing uniformity properties in multidimensions, unlike Monte Carlo, Latin hypercube, and its variant, the median-Latin hypercube sampling techniques. The uniformity properties of different sampling techniques are illustrated in Figure 11 for a sample size of 100.

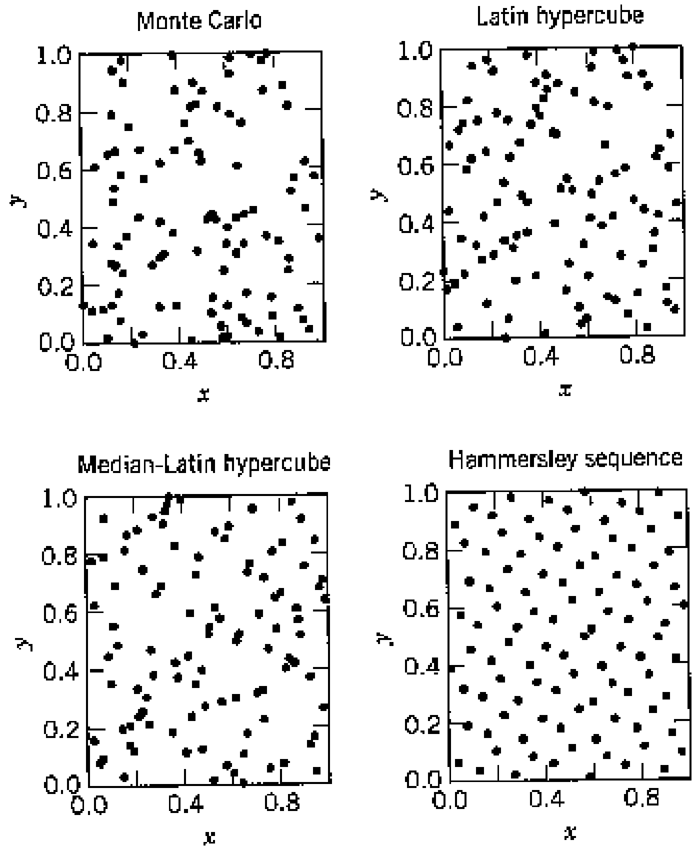

Figure 11. Uniformity of different sampling techniques.

Sample Size Selection in Stochastic Modeling. The sample size on which the sampling is performed is critical, as it defines the accuracy or precision of the probability space in multidimensional problems. It is possible, however, to measure the precision of an estimate of the cumulative distribution function in terms of the confidence interval. The confidence interval for Y_p, the pth fractile, is given by (y_i, y_k), where y_i is the lower end point and y_k is the upper end point of the interval. The intervals i and k are estimated by

$$i = np - c\sqrt{np(1-p)} \tag{14}$$

and

$$k = np + c\sqrt{np(1-p)} \tag{15}$$

where n is the sample size and c is the deviation enclosing probability α of the unit normal distribution. The sufficiency of the number of samples n can be judged from the values of the confidence interval precision.

The implication of choosing a suitable sample size is crucial in stochastic experiments. Although, some applications demand a large sample size, the number is usually based on practical considerations, such as the computational cost of the run and the objective of the run. Because stochastic simulation involves a recursive loop, a compromise is usually desired between the cost of the simulation runs and the precision in estimating the output probability functions in certain cases.

Classical statistical methods predict the sample size requirement for a given confidence interval for only Monte Carlo sampling and overpredict the sample size requirement for other sampling techniques (33). Recently, a methodology based on fractal dimensions has been proposed to predict the sample size requirement for non-Monte Carlo methods by characterizing the interval width for a given confidence level (accuracy) (34). This has major implications in stochastic modeling experiments, because it can be used to predict the sample size requirements for innovative, uniform sampling methods, such as Hammersley sequence sampling.

Sensitivity Analysis. Once the input sample sets have passed through the flowsheet and all the sample runs are completed, the stochastic block is used to quantify the sensitivity of an output to each input parameter. Two closely related but different measures are presented. These are the partial correlation coefficients and standardized regression coefficients. From the sampling data, it is possible to construct an approximate regression model which relates an output parameter y_i to the input parameters x_i:

$$y_i = b_0 + \sum_j b_j x_j \tag{16}$$

The constants b_j are ordinary regression coefficients which are easily influenced by units of measurement. This problem is circumvented if the regression model is written using the transformed variables x^* and y^* given by

$$x^* = \frac{(x - \mu_x)}{\sigma_x} \tag{17}$$

and

$$y^* = \frac{(y - \mu_y)}{\sigma_y} \tag{18}$$

and a regression model in the standardized form:

$$y^* = \sum_j b_j^* x_j^* \tag{19}$$

where the μ and the σ refer to the mean and the standard deviation, respectively.

The coefficients in this model are called standardized regression coefficients, and they provide a direct measure of the relative importance of the input variables. The accuracy of this model is judged by the value of R^2_y, the coefficient of determination, given by

$$R_y^2 = \frac{\sum_i (\hat{y}_i - \mu_y)^2}{\sum_i (y_i - \mu_y)^2} \tag{20}$$

where $\hat{y}_i$ is the calculated value of y_i using the regression model.

The partial correlative coefficients provides a measure of the linear relationship between the output and input variables. When nonlinear relationships are involved, the standardized correlation coefficients and partial regression coefficients are calculated on the basis of ranks rather than the absolute value.

The importance of probabilistic modeling for chemical processes is illustrated by revisiting the example of integrated gasification and combined cycle (IGCC) systems for power generation. The objective of this example is to show the role of uncertainties in predicting the thermal, economic, and environmental performance of a process.

Example C: Modeling Uncertainties in Advanced Power Generation Technologies. IGCC systems essentially consists of the following steps: conversion of coal to a fuel gas by reaction with steam and oxygen in a pressurized reducing atmosphere; cleanup of the fuel gas to remove particulates, sulfur compounds, and other contaminants; combustion of the fuel gas

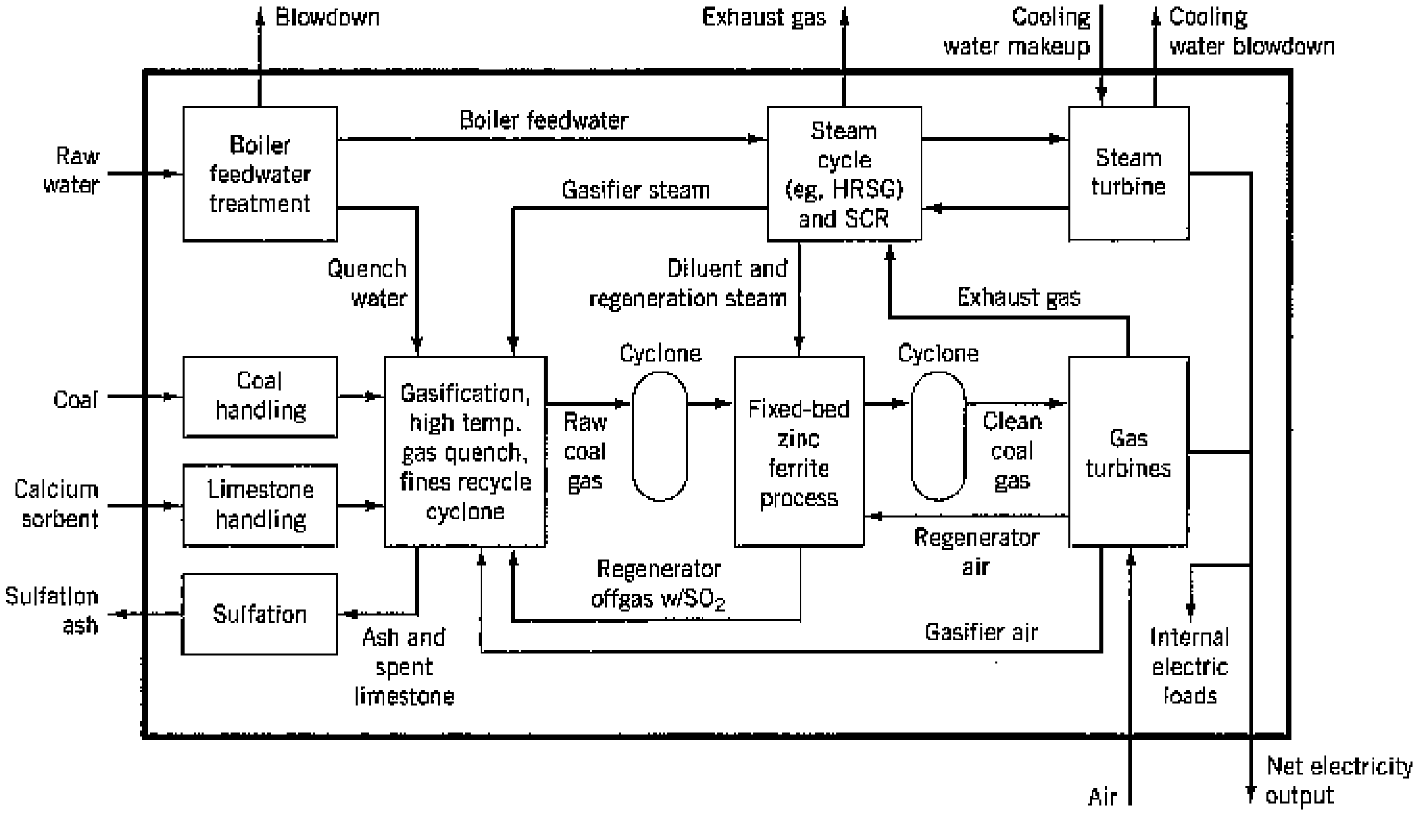

Figure 12. The Kellogg–Rust–Westinghouse (KRW) IGCC system.

in a gas turbine combined-cycle system. IGCC systems are capable of higher thermal efficiency and have lower gaseous, liquid, and solid discharges than conventional pulverized coal-fired power plants. However, only a few IGCC system concepts have been commercially demonstrated. For many other IGCC concepts that are in early stages of development, there are uncertainties regarding process performance, emissions, and cost, that may not be resolved until a commercial-scale demonstration plant is built. Uncertainties are particularly important for many advanced concepts featuring high temperature, "hot" (eg, 540°C) dry fuel, gas-cleanup technology. Hot-gas cleanup offers the potentially key advantages of higher plant thermal efficiencies and lower costs.

A promising hot-gas cleanup configuration is an air-blown Kellogg-Rust-Westinghouse (KRW) IGCC system. A schematic of this technology is shown in Figure 12. The hot-gas cleanup system features in-bed desulfurization in the fluidized bed gasifier with limestone or dolomite, subsequent sulfur removal from the fuel gas with a zinc ferrite sorbent, and high efficiency cyclones and ceramic filters for particulate removal. The off-gas from the zinc ferrite reactor, containing sulfur compounds, is recycled to the gasifier. The characterization of performance uncertainties focused on five major process areas: gasification, sulfation, zinc ferrite desulfurization, gas turbine, and selective catalytic reduction (SCR) section for NO_x removal. Uncertainties in additional cost model parameters are characterized, including direct and indirect capital costs, operating and maintenance costs, financial assumptions, and unit costs of consumables, byproducts, and wastes. A detailed description of the extensive list of uncertainties is in (31), and is not elaborated here, for brevity. For the purpose of illustration, however, the uncertainties in the gasification section are presented in Table 3. The results for this probabilistic analysis based on a 730 MW plant using Illinois No. 6 coal are presented in Table 4. A few of these results are discussed in more detail in the following section.

Uncertainty in Performance and Cost. The uncertainty in the plant thermal efficiency covers a 90% probability range of less than 2 percentage points, and the mean, median, and the deterministic values coincide approximately. As far as environmental performance is concerned, this system, which is equipped with SCR for NO_x control, has lower NO_x emissions than a typical coal-fired power plant. From Table 4, the median NO_x emission rate is lower than the deterministic estimate. This is explained by the negative skewness of the uncertainties in both the formation rate of ammonia in the gasifier and in the conversion rate of fuel-bound nitrogen (ammonia) to NO_x in the gas turbine combustor. In Figure 13, the uncertainty in total capital cost is compared to the deterministic estimate. There is approximately a 50% chance of a cost overrun associated with the deterministic estimate of \$1535/kW. The 90% probability range for capital cost is \$240/kW, or approximately ± \$120/kW from the nominal estimate, which is a relatively narrow range of capital cost uncertainty compared to other technology options. In spite of the agreement between the deterministic and probabilistic results for capital cost, the two analyses do not agree on the cost of electricity, as seen in Figure 14. There is more than a 75% probability that the cost will be higher than the deterministic estimate. This example depicts the primary advantage of

Table 3. Uncertain Parameters and Distributions in Gasification Section of IGCC Process Example

Description and Units	Det. Value[a]	Distribution and Parameters: Type	Lower Bound	Upper Bound	Additional Parameter[b]
Gasifier pressure, bar	31.24				
Gasifier temperature, K	1311	Triang.	1900	1950	(1900)
Overall carbon conversion, wt %	0.95	Triang.	0.90	0.97	(95)
O_2/C molar ratio	0.46	Triang.	0.45	0.47	(0.46)
H_2O/O_2 molar ratio	0.45				
Sulfur capture, mole of inlet sulfur	90	Triang.	85	95	(90)
Ca/S molar ratio	2.6	Triang.	2.0	2.8	(2.6)
Ammonia yield, fraction of coal nitrogen	0.10	Triang.	0.005	0.10	(0.10)

[a] Det. value = deterministic or nominal (best guess) value.

[b] Additional parameters are required for some distributions. In the case of the triangular distribution, the additional parameter is the mode or the peak value.

Table 4. Results for Probabilistic Simulation of KRW-IGCC System[a]

Parameter[b]	Units[c]	Deter. Value[d]	Median, $f_{0.50}$	Mean, μ	Std Dev, σ	Range $f_{0.05}-f_{0.95}$
Plant performance						
Thermal Efficiency	%, HHV	40.9	41.0	40.9	0.5	39.9–41.7
Coal consumption	kg/kWh	0.337	0.336	0.337	0.0041	0.330–0.345
Process water cons.	kg/kWh	0.349	0.349	0.349	0.0068	0.337–0.360
Plant discharges						
SO_2 emissions	kg/10^6 kcal	0.023	0.025	0.025	0.0018	0.023–0.028
NO_x emissions	kg/10^6 kcal	0.267	0.187	0.187	0.050	0.104–0.265
CO emissions	kg/kWh	0.0023	0.0023	0.0028	0.0014	0.0023–0.0041
CO_2 emissions	kg/kWh	0.781	0.776	0.781	0.0095	0.77–0.80
Solid waste	kg/kWh	0.104	0.104	0.104	0.0054	0.093–0.112
Plant Costs						
Total capital cost	$/kW	1,535	1,530	1,527	79	1,408–1,653
Fixed operating costs	$/kW·yr	51.4	54.3	54.6	4.6	46.7–63.0
Variable oper. costs	mills/kWh	19.9	20.8	20.9	0.6	19.9–22.0
Coal	mills/kWh	15.3	15.2	15.3	0.2	15.0–15.6
Other	mills/kWh	4.7	5.5	5.6	0.6	4.7–6.6
Cost of electricity	mills/kWh	56.8	58.2	58.2	2.1	54.6–61.5

[a] Notation titles in heading are defined as follows: f_n = nth fractile ($f_{0.50}$ = median), μ = mean; and σ = standard deviation of the probability distribution. The range enclosed by $f_{0.05}$ to $f_{0.95}$ is the 90% probability range. All costs are Jan. 1980 dollars.

[b] Coal consumption is on an as-received basis. Water consumption is for process requirements including makeup for steam cycle blowdown, gasifier steam, zinc ferrite steam, and SCR. Solid waste includes gasifier bottom ash and nonrecycled fines from fuel gas cyclones.

[c] HHV = higher heating value.

[d] Deterministic value based on a deterministic simulation in which median or modal values of uncertain variables are assumed as "best guess" inputs to the model.

probabilistic simulation, allowing the *simultaneous* incorporation of uncertainties in multiple model inputs, over traditional sensitivity analysis. The resulting interactions among uncertainvariables result in uncertainties in the measures of process viability. Research can provide additional information about the uncertain input variables, leading to changes in their uncertainty distributions (such as the mean or standard deviation), and therefore, in the overall uncertainties of the technology. Thus, it is possible to reduce the uncertainties of key variables that contribute most to the risk of technology failure. The methods based on probabilistic analysis are therefore necessary for chemical design involving environmental control options, so that any uncertainties associated with the control technologies are resolved through research and development in the earlier stages of the project.

SYNTHESIS UNDER UNCERTAINTY

The concept of design under uncertainty has received considerable attention in the past decade. Now its relevance to environmental considerations for process design and development, however, is truly significant, because of the large number of emerging control strategies that are promising technologically, but lack commercial performance data. Most of the earlier approaches were based on mathematical programming techniques well suited for an equation-oriented environment. The development of the first probabilistic modeling capability around the public version of the ASPEN process simulator resulted in a foundation to model a process probabilistically using deterministic, sequential modular simulators (32). Because process synthesis in the

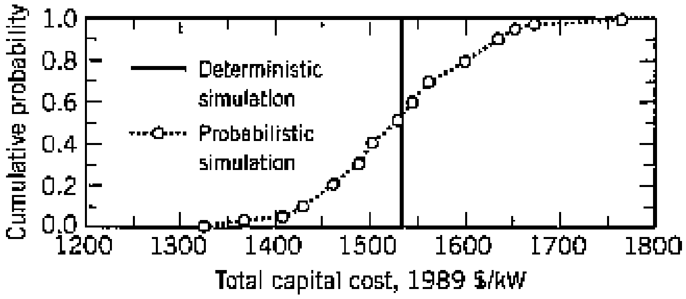

Figure 13. Uncertainty in the total capital cost for the KRW-IGCC system.

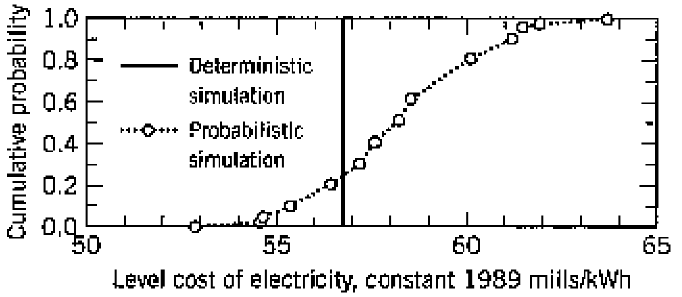

Figure 14. Uncertainty in the level cost of electricity for the KRW-IGCC system.

presence of uncertainties in the process, technical, or economic parameters must incorporate a probabilistic modeling capability, it is now possible to synthesize chemical processes using uncertain estimates of process, economic, and environmental factors.

The problems related to design under uncertainty essentially fall into two categories: (*1*) stochastic optimization, and (*2*) stochastic programming. A detailed treatise is beyond the scope of this article and can be obtained elsewhere (35). From a conceptual design standpoint, synthesis under uncertainty is a stochastic optimization problem, where decisions made now guide and influence project planning and developments in the future.

Mathematical Formulation of Stochastic Optimization

To understand the essential concepts involved in stochastic optimization, it is necessary to consider the differences between the deterministic and stochastic optimization scenarios. The goal of a deterministic optimization problem is to determine the set of discrete decision variables (y) and continuous decision variables (x) that optimize some aspect of the deterministic model represented by the objective function (Z), subject to the equality constraints (h) and the inequality constraints (g) (Fig. 15**a**). Mathematically, this is represented as

$$\underset{x,y}{\text{Optimize}}\ Z = z(x,y)$$

$$\text{subject to } h(x,y) = a$$

$$g(x,y) \le b$$

A generalized form of the stochastic optimization problem, where the decision variables and uncertain parameters are

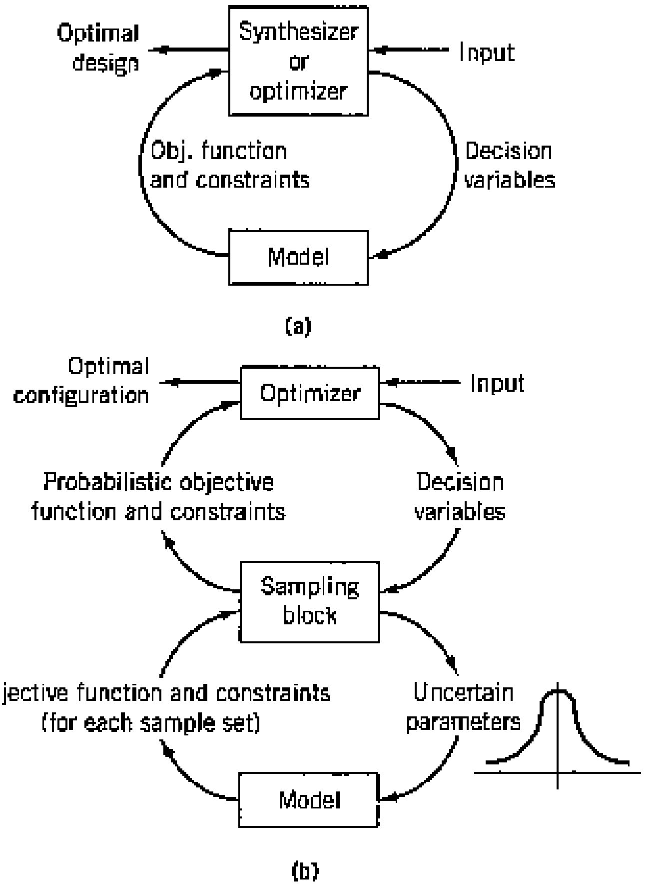

Figure 15. (**a**) Deterministic optimization scheme; (**b**) stochastic optimization scheme.

separable is as follows:

$$\underset{x,y}{\text{Optimize}}\ Z = P_1(z(x,y,u))$$

$$\text{subject to } P_2((h(x,y,u)) = a) \le \beta_1$$

$$P_3((g(x,y,u)) \le b) \le \beta_2$$

where u is the vector of uncertain parameters and P_1, P_2 and P_3 represent any probabilistic function such as the mean, variance or a fractile. If P_1 represents the expected value or mean of any function, then it is possible to estimate the probability function P_1 based on results in classical statistics. For an expected value minimization of a function Z, with a cumulative probability distribution p, formulation **C** can be restated as:

$$\text{Optimize} \int_0^1 Z\,dp$$

$$\text{subject to } P_2((h(x,y,u)) = a) \le \beta_1$$

$$P_3((g(x,y,u)) \le b) \le \beta_2$$

For a random sample size N_{samp} obtained by sampling from the distribution, the sample mean is an unbiased estimator for the actual mean and is given by

$$E(Z) = \frac{\sum_{i=1}^{N_{samp}} Z_i}{N_{samp}} \qquad (21)$$

It is apparent from the above formulations that, unlike a deterministic optimization problem, the stochastic optimization problem must operate on some probabilistic function of the objective function and the constraints (Fig. 15b). In stochastic optimization, therefore, the stochastic modeler performs the sampling operation (ie, assigns values to the uncertain parameters based on their probability distribution by selecting samples based on the sampling schemes mentioned in the previous section), combines them together to form a sample set, and finally passes the sample values of each of the uncertain parameters to the model. The model is run with the assigned values of the uncertain parameters for each sample set to determine the objective function and the constraints. This recursive operation is performed for each set of samples until all the N_{samp} samples sets are analyzed by the model. Finally, when all the sample sets are through the cycle, the stochastic modeler analyzes all the output objective function and constraints and determines the probabilistic function for the objective function and constraints, which is passed on to the optimizer. The optimizer, in turn, predicts new decision variables. Because, at each optimizational iterative stage, one needs to run the stochastic model with a large number of samples to calculate the probabilistic functions, the computational intensity in stochastic optimization is large.

Recently, an algorithm has been developed for judiciously choosing the sample size so that the computational intensity is minimized (36). This algorithm, called stochastic annealing, is a variant of simulated annealing where the sample size selected for each optimizational iteration is predicted by the optimization routine, in addition to the set of decision variables (Fig. 16). Stochastic annealing achieves computational efficiency without any significant loss of solution accuracy. The framework based on stochastic annealing affords a capability for process synthesis in the presence of uncertainties in technical and economic parameters for large-scale problems. The general procedure for performing synthesis of large-scale processes with uncertainties, using a coupled stochastic annealing and nonlinear programming approach, is illustrated by revisiting the problem of the environmental restoration of the hazardous waste site, assuming that there are uncertainties in the waste composition and the glass physical property models. The presence of uncertainties coupled with the combinatorics of the problem renders the synthesis task intractable by other methods. The methodology based on the coupled stochastic annealing and nonlinear programming determines the optimal waste blend configuration in computationally affordable time.

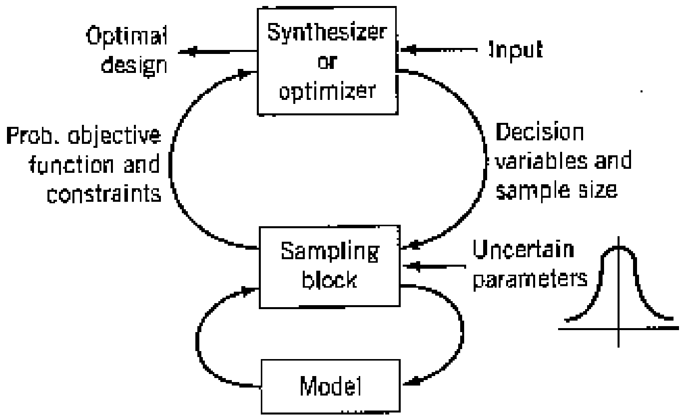

Figure 16. The stochastic annealing framework for synthesis under uncertainty that manipulates the sample size automatically.

Example D: Environmental Restoration of the Hazardous Waste Site: Effect of Uncertainties. The role of uncertainties in the synthesis of processes involving environmental considerations is illustrated by revisiting the waste blend problem described previously. Recent findings show that uncertainties exist in some of the input assumptions which may affect the optimal blend configuration. The following sections describe how the uncertainties are incorporated in the model formulation.

Characterization of Uncertainties. The sources of uncertainty in the waste blending problem are caused by (*1*) uncertainties in the waste composition and (2) uncertainties in the physical property models. The wastes in the tanks were formed as by-products in different processes used to produce radioactive materials. Consequently, a certain degree of variability is associated with each of these tanks. Any experimental sample of the waste drawn from the tank is not representative of the tank as a whole, which contributes significantly to the uncertainty associated with the waste composition. Based on the mean and the relative standard deviation for each component in the tank, normal probability distributions can be developed for the individual mass fractions. For a particular tank, the range of uncertainty in the mass fractions of the components is shown in Table 5. The normal distributions are sampled to develop N_{samp} waste composition input sets (mass fractions). The number of samples N_{samp} is predicted by the stochastic annealing algorithm, which manipulates the sample size selection process depending on whether the current process configuration is closer to or farther away from the optimum. Given the set of mass fractions corresponding to N_{samp} samples and normalized to 1.0, these component mass fractions are then used in the model runs.

On the other hand, the uncertainty in a predicted property value for a given glass composition is devised on the basis of empirical correlations. This uncertainty factor is then incorporated into the glass property constraints, so that the feasible region for the applicability of the glass property models is narrowed. This results in a value of the minimum quantity of frit required higher than when the uncertainties related to the glass property models are neglected.

The presence of uncertainties increases the computational intensity of this problem because, as mentioned previously, the mathematical formulation for this stochastic optimization problem involves a recursive sampling loop. Further, the highly nonconvex nature of the constraints and the large combinatorial size of the discrete blending problem require innovative combinatorial optimization techniques to determine the optimal blend configuration.

The problem of determining the optimal blend configuration with uncertainties in the waste composition and in the physical property models is posed as a stochastic optimization problem. The stochastic optimization problem requires that the waste composition for a particular waste source (tank) must be represented in terms of expected values. Thus, equations 11–13 are represented as

$$[g^{(i)}]_e = E[w_{ij}^{(i)}] + [f^{(i)}]_e \tag{22}$$

$$[G]_e = \sum_{i=1} [g^{(i)}]_e \tag{23}$$

Table 5. Uncertainties in Waste Composition of Tank at Hazardous Waste Site

Components	Mass Fractions	Mass, kgs	RSD[a]	Uncertainty
Al_2O_3	0.02002	25165.1	0.15	25165.1(1 ± 3 × 0.15)
B_2O_3	0.000856	1075.9	0.13	1075.0(1 ± 3 × 0.13)
CaO	0.011293	14195.3	0.07	14195.3(1 ± 3 × 0.07)
Fe_2O_3	0.229344	288285.2	0.04	288285.2(1 ± 3 × 0.04)
Li_2O				
MgO	0.0002687	3377.6	0.04	3377.6(1 ± 3 × 0.04)
Na_2O	0.080439	101111.7	0.04	101111.7(1 ± 3 × 0.04)
SiO_2	0.175263	220305.4	0.04	220305.4(1 ± 3 × 0.04)
ZrO_2	0.000041	51.4	0.12	51.4(1 ± 3 × 0.12)
Other oxides[b]	0.480056	603429.9	0.056	603429.9(1 ± 3 × 0.056)
Cr_2O_3	0.014986	18837.4	0.03	18837.4(1 ± 3 × 0.03)
F				
P_2O_5	0.248923	312895.9	0.04	312895.9(1 ± 3 × 0.04)
SO_2				
Noble metals				

[a] Relative standard deviation (RSD) is defined as the ratio of the standard deviation to the mean.

[b] Collective term for trace quantities of oxides not explicitly characterized.

and

$$[fg^{(i)}]_e = \frac{[g^{(i)}]_e}{[G]_e} \tag{24}$$

where the subscript "e" signifies that the quantities are based on the expected value and $E[w^{(i)}]$ signifies the expected value of the waste mass of the ith component in the waste. Similarly, the individual component bounds, crystallinity constraints, solubility constraints, and the glass property constraints are also based on the expected values.

The solution procedure adopted for this waste blending problem is based on a coupled, stochastic annealing-nonlinear programming algorithm, illustrated in Figure 17. It incorporates a sequence of three loops nested within one another. The inner loop corresponds to the sampling loop, which generates the samples for the mass fractions of the different components of the waste, evaluates the mean of the waste mass for each tank, which is then propagated through the model that determines the property constraints. The loop above the sampling loop controls the NLP optimizational scheme. The outer loop in the sequence consists of the stochastic annealing (STA) algorithm which predicts the sample size for the recursive sampling loop and generates the blend configuration so that the total amount of frit is minimum over all the blends:

STA formulation:

$$Min \sum_{j=1}^{3} \sum_{i=1}^{n} [f_j^{(i)}]_e$$

where $[f^{(i)}]_e$ is the mass of the ith component in the frit based on the expected values for the waste composition and the uncertainties in the physical property models for the jth waste blend, and n denotes the number of components. The NLP problem is solved on the basis of the expected value of the objective function at each configuration predicted by the stochastic annealing algorithm. Hence, the NLP problem formulation is as follows:

NLP formulation:

$$Min \sum_{i=1}^{n} [f_j^{(i)}]_e$$

subject to equality constraints (eqs. 22–24), individual component bounds, crystallinity constraints, solubility constraints, and glass property constraints.

The optimal design configuration was identified by the coupled STA-NLP approach using both Latin hypercube and Hammersley sampling sequences. The minimum quantity of the frit required in both cases is 11,307 Kgs. This study clearly indicates how uncertainties affect the optimal solution and the need for incorporating them in the development of realistic models for environmentally friendly processes.

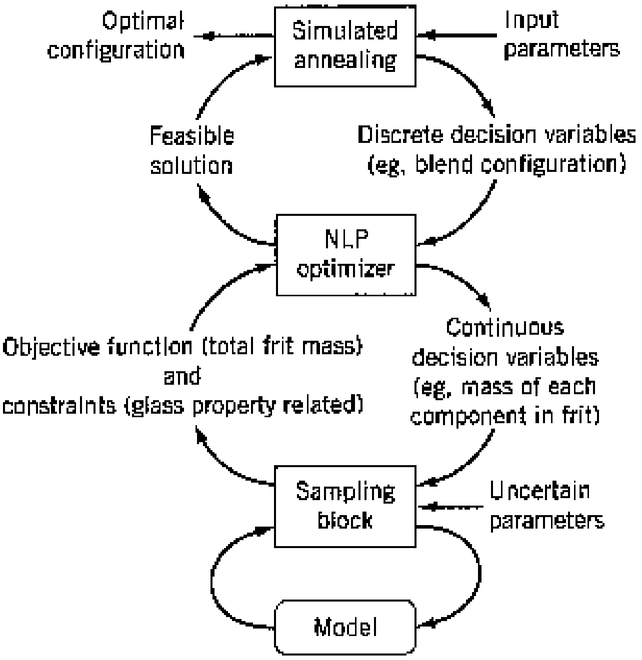

Figure 17. Coupled stochastic annealing and nonlinear programming algorithm for discrete-continuous optimization of processes with uncertainties.

FUTURE DIRECTIONS

The methods described in this article represent a consolidated effort to illustrate several facets of a design problem having environmental implications. The complex nature of the environmental control problem indicates, however, that much still remains to be done to achieve the goals set forth by regulators. Hence, the following paragraphs are pointers to new methodologies/analytical schemes related to process synthesis/design of processes involving environmental constraints. Three key issues that are gaining importance and affect the design of environmentally friendly processes are discussed.

Life-Cycle Analysis. Life-cycle analysis (LCA) is an environmental auditing tool that quantifies the environmental burdens of any process activity by considering all interrelated systems. It has the potential of identifying and quantifying the environmental performance of a process or a product from the "cradle to the grave." In the past, the methodology of life-cycle analysis was applied to process design, but its capability of accounting for mass and energy flows in a system has rendered it invaluable in process design. Recently, a life-cycle analysis framework was used to perform an environmental and economic analysis of a nitric acid plant (37). The LCA approach provided a comparison of the environmental performance of the design alternatives, relating the economic performance to the mass and energy flows in the process. A life-cycle analysis approach optimizes both the environmental and economic performance and thus is a powerful decision making tool for designing clean process technologies.

Multiobjective Optimization. The task of process design while keeping environmental objectives in view is truly a multiobjective optimizational problem. Essentially, the job of the process engineer is to maximize the economic performance by minimizing the emissions. Methods to address such types of problems (38,39) are potential tools for addressing the environmental control problem.

Environmental Impact Assessment. The reduction of the environmental impact of processes has recently drawn attention to finding the best way to reduce the impact of chemical plants. In this procedure, the waste generation problems are ranked by waste minimization criteria dealing with technology changes, process revamps, and recycling of waste materials. Quantitative guidelines have been proposed to address the environmental impact of process technologies (40,41). A methodology for environmental impact minimization combining life-cycle analysis and process optimization is a suitable approach if the various metrics (air and water pollution, solid waste, global warming and ozone depletion) are properly considered in process design and development (42).

SUMMARY

The key issues and concepts that must be considered during process development to satisfy environmental criteria have been presented. The discussion has been based primarily on a process synthesis approach, because it represents an important tool for developing cleaner, environmentally friendly processes. The capability of existing process simulation tools and their inherent deficiency in performing this task has been elucidated. The effect of recent advances related to optimizational techniques and their viability in determining environmental solutions has been described. The role of uncertainty and its importance in process design and development is also significant. From a R&D standpoint, a combined process synthesis, environmental impact or risk assessment, and life-cycle analytical tool can be truly beneficial for the general process design problem with environmental implications. As we welcome the twenty-first century, the advancement in computer architecture will enable the development of sophisticated modeling tools, and the power of the Internet will provide easy data acquisition, so that the environmental impact of processes is characterized with certainty.

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