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Greener by Design

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Process simulation models and other design tools allow engineers to design, simulate, and optimize chemical processes. However, there is a critical need to incorporate green engineering into the design of these processes. This calls for extending the breadth of the design process. This paper presents an integrated framework for greener design. The framework starts the decision-making as early as the chemical and material selection stage and also includes management and planning decisions. The design goal is not restricted to profitability, but environmental and ecological objectives are also added. However, this integration poses challenging problem of discrete and continuous decisions, nonlinear models, and uncertainties. Furthermore, there are multiple and conflicting objectives to be considered. Therefore, the core of this integrated framework is the efficient algorithmic framework for multi-objective optimization under uncertainty. Two real world case studies are presented that illustrate the promise of such a framework.

Introduction

Chemical process industries are considered to be a major source of waste in the modern world. Realizing this fact, these industries are practicing the art of pollution prevention that involves fundamental changes in the processes to minimize the formation of pollutants, as opposed to pollution control, involving end-of-pipe treatment of process emissions. However, there is still a long way to attain the goal of sustainability. Recently, Ananstas and Zimmerman (*1*) presented 12 principles of green engineering to achieve sustainability through science and technology. Table 1 presents these principles briefly. Some of these principles have been demonstrated and practiced at local levels. For example, currently, environmentally friendly or "green" processes are designed based on concepts of process integration, which embodies a number of closely related methodologies for designing new processes and retrofitting existing ones by taking into consideration the performance of the entire process as a whole (*2, 3*). Process integration addresses the Principle 10 from Table 1. The main advantage of process integration is that it is inherently "conservation oriented" and enhances the process performance by minimizing the use and/or maximizing the recovery of energy and materials. In addition to process integration, integrated environmental control strategies introduced in the early design stages of a process, rather than an end-of-pipe control option introduced in the later stages, have been shown to improve the technical and economic performance of a process. However, to attain sustainability one has to extend this framework beyond process integration and environmental control technologies. This means introducing green engineering principles as early as possible and at all levels of engineering decision-making. However, integrating all these principles at all levels is an onerous task. Process simulation technology along with newly developed systems analysis algorithms and tools can provide a viable option to implement these principle in integrated framework. This is the focus of the current endeavor. Table 1 translates the green engineering principles in systems analysis (SA) terms such as defining objectives, identifying important decisions, and defining appropriate design direction.

Figure 1 shows steps involved in traditional process design. As shown in the figure, process design starts with chemical synthesis where the chemical pathway from reactants to the product is defined at the laboratory scale. Process synthesis translates the chemical synthesis to a chemical process. It involves decisions about process units and connections. Simulation, the focus of current systems analysis approaches, is the next step in part because effective simulation programs and models are available. Unfortunately, simulation is the last step in decision-making; it predicts only the behavior of a given plant (or strategy) if it is in fact constructed (or implemented). Therefore, the current emphasis has only limited potential for maximizing performance and reducing costs. Integrating the other steps into computer-aided decision-making guided by the green engineering principles shown in Table 1 could lead to less cost-intensive, environmentally friendly plants and strategies; reduce technical, economic, and operational risks; and increase efficiency.

Figure 2 shows the integrated framework developed to include the green engineering principles at all stages. Unlike the traditional process design where engineers are looking for low-cost options, environmental considerations include various objectives such as the long-term and short-term environmental and other impacts. This new framework includes decisions at all levels starting from the chemical or material selection to the process synthesis stages to the management and planning stage, linked to the green objectives and goals shown on the top left left-hand corner of the figure.

Definition of various objectives is a key component in the design and implementation of clean process technologies and is identified to be the most difficult task. The goals in terms of profitability are relatively easy to define, and researchers in academics and industries have used simulators and modeling tools to achieve profitability where environmental considerations are considered as definable constraints. However, "complete ecological considerations" to be included as environmental impact objectives is a formidable task. Thus, multi-objective optimization methods are necessary to handle the conflicting and different objectives involved in the problem of greener by design. Multi-objective optimization approach is particularly valuable in the context of pollution prevention (*4, 5*), waste management (*6, 7*), life cycle analysis (LCA; *8*), and sustainability as there are a large number of desirable and important objectives that are not easily translated into dollars. Extending the envelope from simulation to chemical synthesis on one end and management and planning on the other end and broadening the scope to include multiple objectives other than profitability increase uncertainties. Furthermore, the decision-making then involves discrete decisions related to selection of alternatives as well as continuous decisions that define the operations and design of plant. Thus, at the crux of the framework based on this "water fall" kind of model (Figure 2) are efficient algorithms, methods, and tools for multi-objective optimization and uncertainty analysis. This algo-

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TABLE 1. 12 Principles of Green Engineering and Systems Analysis Terminology

no.	green engineering	SA terms
1	designers need to ensure that all material and energy inputs and outputs are inherently nonhazardous as possible	qualitative objectives
2	it is better to prevent waste than treat or clean up waste after it is formed	qualitative objective
3	separation and purification operations should be designed to minimize energy consumption and materials use	design directions
4	products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency through process intensification	design directions
5	products, processes, and systems should be "output pulled" rather than "input pushed" through the use of energy and materials	design directions
6	embedded entropy and complexity must be viewed as an investmentwhen making design choices on recycle, reuse, or beneficial disposition	design directions
7	targeted durability, not immortality, should be a design goal	qualitative objective
8	design for unnecessary capacity or capability (e.g. "one size fits all") solutions should be considered a design flaw	design directions
9	material diversity in multicomponent products should be minimized to promote disassembly and value retention	qualitative objective
10	design of products, processes, and systems must include integration and interconnectivity with available energy and material flows	design directions
11	products, processes, and systems should be designed for performance in a commercial "after life"	qualitative objective
12	material and energy inputs should be renewable rather than depleting	qualitative objective

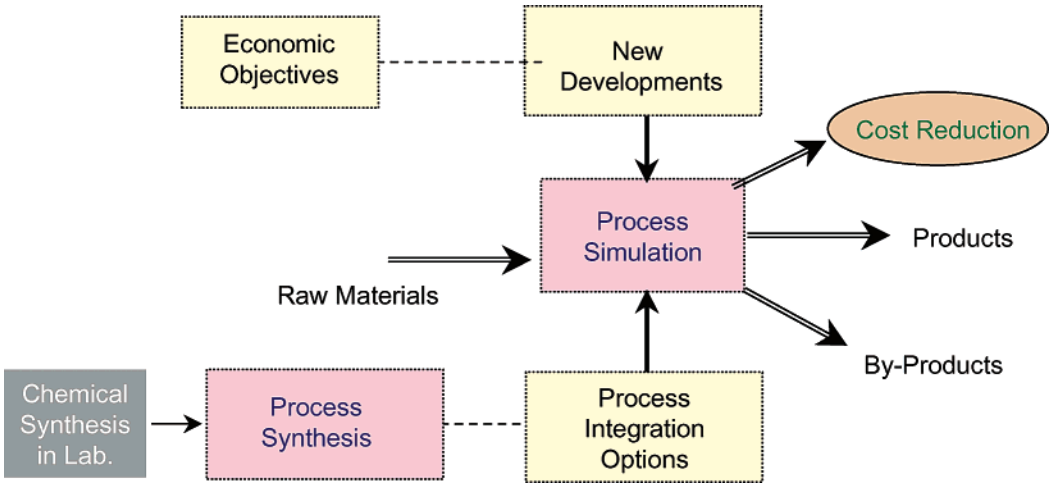

FIGURE 1. Traditional process design steps.

rithmic framework is described in the next section. There are objectives such as LCA, renewability, diversity, commercial "after-life" considerations that involve qualitative, and order of magnitude knowledge. Hence, these objectives are shown to be outside the bracket (Figure 2) of the algorithmic framework.

The next two sections are devoted to two real world case studies that illustrate how this framework with the use of green engineering principles and new algorithms can obtain greener and cost-effective designs. Energy is an important part of any manufacturing unit, but in general, power generation is fraught with environmental problems. Therefore, the first case study is devoted to synthesizing greener energy source on demand. This case study describes the design process starting from the process synthesis stage and explains how to include management and planning decisions to make the design more sustainable. The second case study extends the design framework to the chemical synthesis stage and addresses a very crucial and commonly encountered problem of waste solvents and separation systems design. The importance of this problem in the context of green engineering is also obvious from the fact that it is mentioned as a separate principle (Principle 4) in Table 1.

Algorithmic Framework

The algorithmic framework behind the integrated framework consists of five calculation levels as shown in Figure 3. The basis of this framework is numerical optimization algorithms for selecting discrete and continuous decisions in the face of multiple objectives and probabilistic uncertainty analysis to account for uncertainties and variabilities in objectives, constraints, and parameters.

Level 1: Innermost Level Corresponding to Models for Process Simulation. This level defines all possible chemical and process alternatives for a particular process. Currently, for this framework, Aspen Plus (*9*) is used for steady-state models mostly applicable for continuous processing, and for batch processing MultibatchDS (*10*, *11*) is employed.

Level 2: Sampling Loop. The diverse nature of uncertainty, such as estimation errors and process variations, can be specified in terms of probability distributions. In general, uncertainties can be characterized and quantified in terms of probabilistic distributions. Some of the representative distributions are shown in Figure 4. The type of distribution chosen for an uncertain variable reflects the amount of information that is available. For example, the uniform and log-uniform distributions represent an equal likelihood of a value lying anywhere within a specified range on either a linear or logarithmic scale, respectively. Furthermore, a normal (Gaussian) distribution reflects a symmetric but varying probability of a parameter value being above or below the mean value. In contrast, log-normal and some triangular distributions are skewed such that there is a higher probability of values lying on one side of the median than the other. A Beta-distribution provides a wide range of shapes and is a very flexible means of representing variability over a fixed

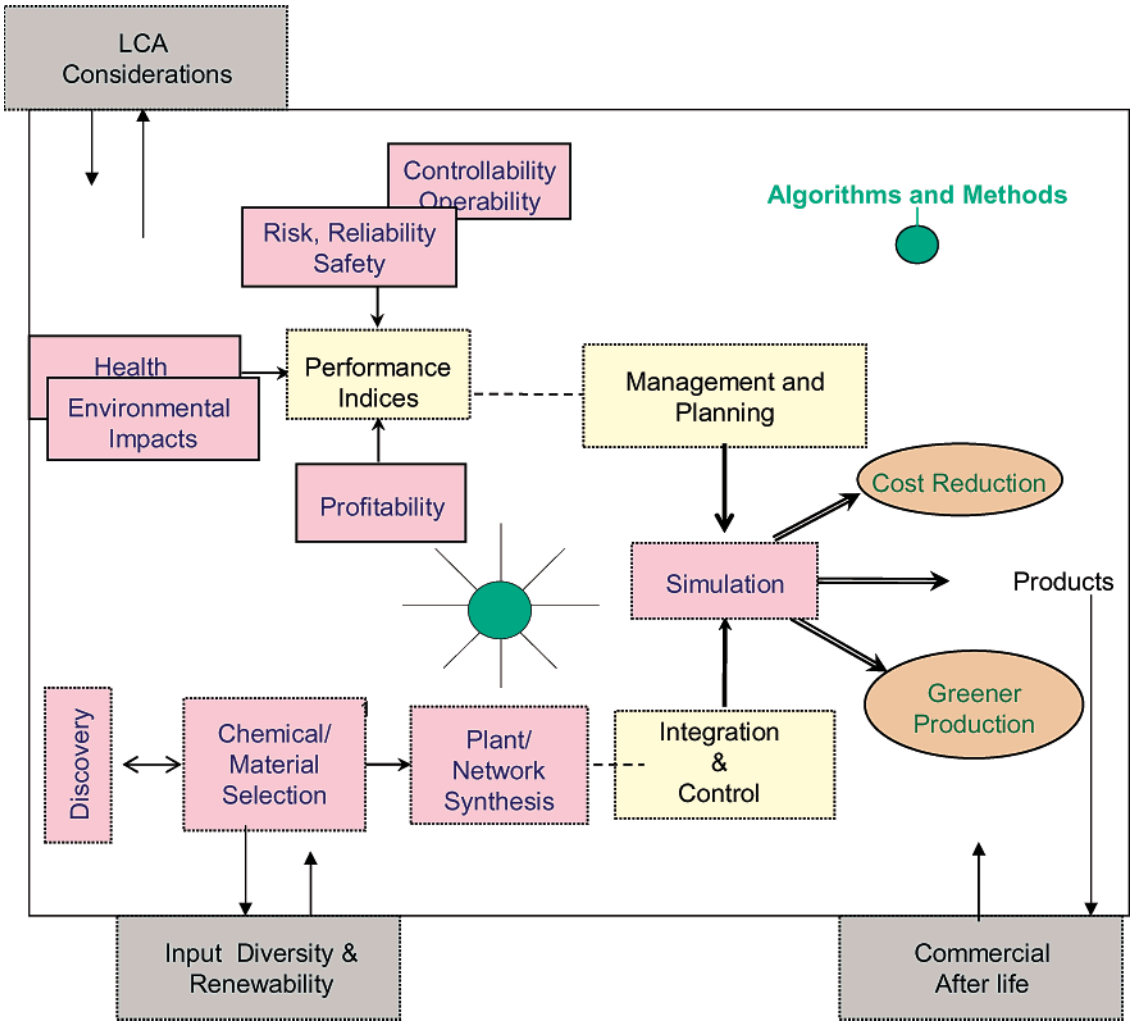

FIGURE 2. Integrated framework for green engineering.

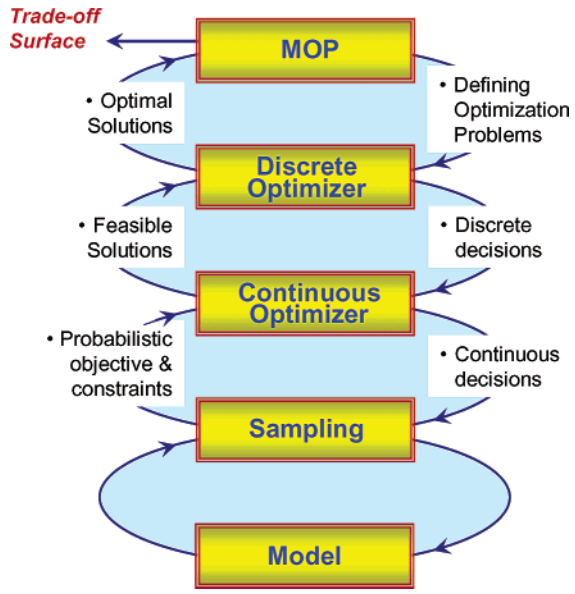

FIGURE 3. Algorithmic framework.

range. Modified forms of these distributions, uniform* and log-uniform*, allow several intervals of the range to be distinguished. Finally, in some special cases, user-specified distributions can be used to represent any arbitrary characterization of uncertainty, including chance distribution (i.e., fixed probabilities of discrete values).

It is easier to guess the upper and lower bounds of uncertain variables; hence, uniform distribution provides the first step toward uncertainty quantification. If one can identify the most likely value, then triangular distributions can be used (*12*, *13*). Recently, Kim and Diwekar (*14*) used extensive data obtained from DECHEMA (*15*, *16*) and obtained realistic quantification of uncertainties related to UNIFAC parameters for the chemical synthesis problem reported in the section on Coupling Chemical and Process Synthesis with Design.

Once probability distributions are assigned to the uncertain parameters, the next step is to perform a sampling operation from the multi-variable uncertain parameter domain. Alternatively, one can use collocation-based methods to derive a response surface of the actual uncertainty surface (*17*, *18*). Although this method requires a significantly less number of runs than a sampling method, one needs to have substantial knowledge of the model as discontinuities or non-smoothness can result in erroneous results, and the reduced order model derivation phase can be very tedious. Thus, the sampling approach provides wider applicability and is used in this work.

One of the most widely used techniques for sampling from a probability distribution is the Monte Carlo sampling (MCS) technique, which is based on a pseudo-random generator to approximate a uniform distribution (i.e., 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. A MCS tech-

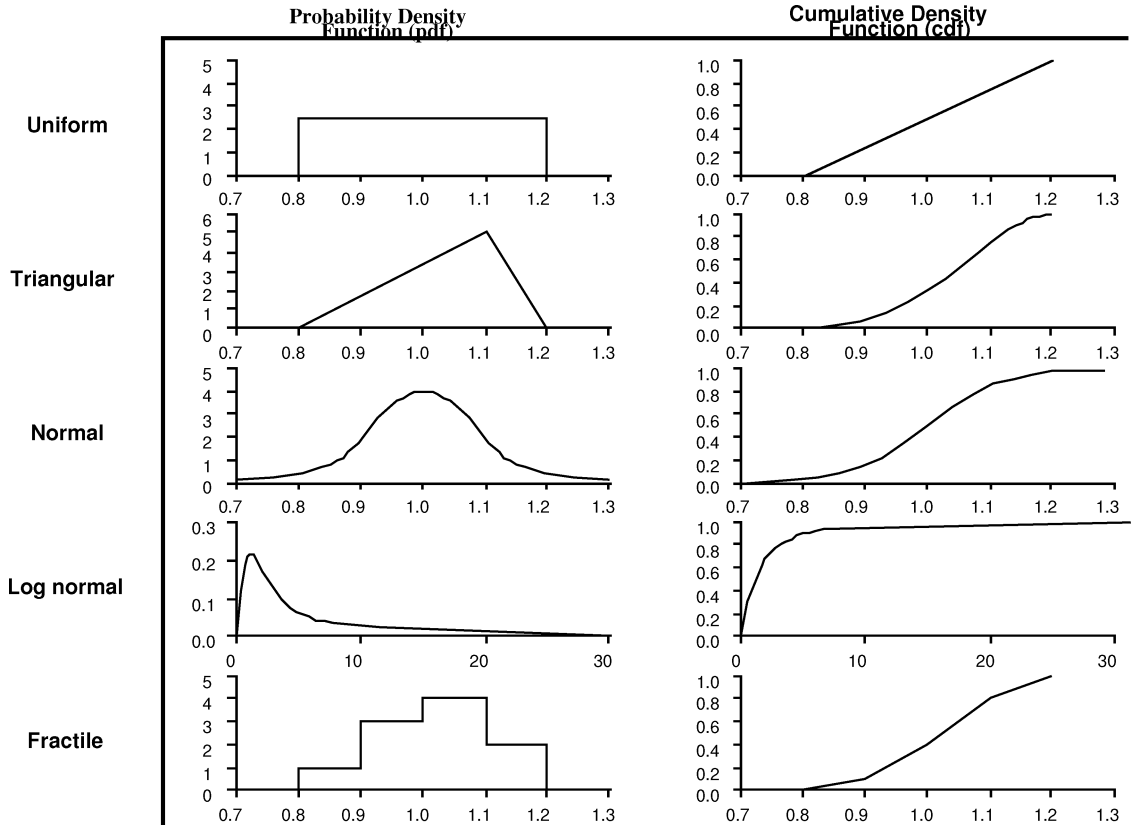

FIGURE 4. Examples of probabilistic distribution functions for stochastic modeling.

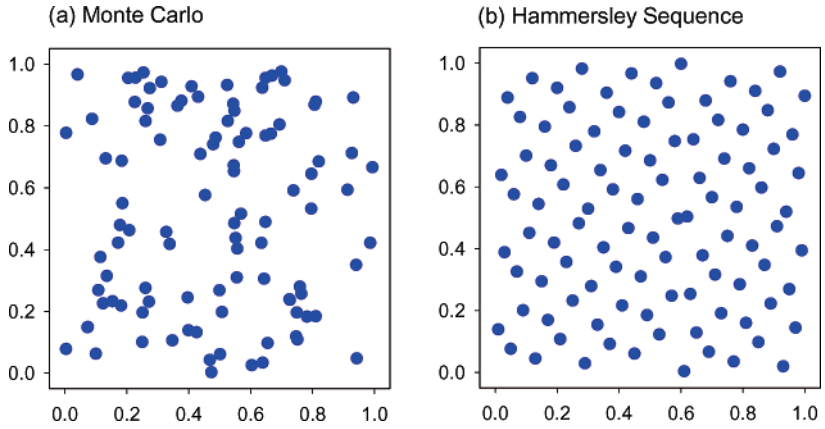

FIGURE 5. Samples of MCS and HSS for two uniformly distributed random variables.

nique also has the important property that the successive points in the sample are independent. 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 more critical role in sampling; as a result, constrained or stratified sampling techniques are more appealing. Latin hypercube sampling (LHS) (*19*) is one form of stratified sampling that can yield more precise estimates of the distribution function. The main drawback of LHS stratification scheme is that it is uniform in one dimension and does not provide uniformity properties in *k*-dimensions. Sampling based on cubature techniques (*20*) or collocation techniques (*21*) face similar drawbacks. These sampling techniques perform better for lower dimensional uncertainties. Therefore, many of these sampling techniques use correlations to transform the integral into one or two dimensions.

An efficient sampling technique (Hammersley sequence sampling, HSS) based on Hammersley points was developed by my group (*22*, *23*). HSS 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 of random variables in multidimensions, unlike Monte Carlo, LHS, and its variant the Median Latin hypercube sampling technique. Figure 5 shows samples generated for two uniform uncertain (random variables) using MCS and HSS. It has been found that the HSS technique is at least 3−100 times faster than LHS and Monte Carlo techniques and hence is a preferred technique for uncertainty analysis as well as optimization under uncertainty and is used in this framework.

Level 3: Continuous Optimizer. This step involves continuous decisions such as design and operating conditions for a process. Derivative-based quasi-Newton methods where the gradient (i.e., Jacobian) is approximated based on

differences in the x and $f(x)$ obtained from previous iterations are widely used in process optimization. Among the quasi-Newton-based methods, the successive quadratic programming (SQP) method is used for this framework because it requires far fewer function and gradient evaluations than other methods for highly nonlinear constrained optimization, and it does not need feasible points at intermediate iterations. Both of these properties make SQP one of the most promising techniques for problems dealing with nonlinear constraint optimization, like process simulations.

Level 4: Discrete Optimizer. This involves dealing with discrete decisions such as chemical and process structural alternatives. This is the most difficult optimization step. New algorithms are designed by improving efficiency in two steps: (i) improving the discrete optimization algorithm by using quasi-random numbers such as the HSS and (ii) providing efficient interaction between the discrete optimization and the sampling technique for efficient stochastic optimization. The new algorithms are found to be 99% more efficient than the traditional algorithms. For details of these algorithms, please see refs *14* and *24*.

Level 5: Multi-Objective Programming (MOP). This represents the outermost loop in Figure 3. A generalized multi-objective optimization (or multi-objective programming) problem can be formulated as follows:

$$\begin{aligned} \min \quad & Z = Z_i,\ i = 1, \ldots, p \quad p \geq 2 \\ \text{s.t.} \quad & h(x, y) = 0 \\ & g(x, y) \leq 0 \end{aligned} \tag{1}$$

where x and y are continuous and discrete decision variables, and p is the number of objective functions. The functions $h(x, y)$ and $g(x, y)$ represent equality and inequality constraints, respectively. There are a large array of analytical techniques to solve this MOP problem; however, the MOP methods are generally divided into two basic types: preference-based and generating methods. Preference-based methods such as goal programming attempt to quantify the decision-maker's preference, and with this information, the solution that best satisfies the decision-makers's preference is then identified (*24*). As is well-known, mathematics cannot isolate a unique optimum when there are multiple competing objectives. Mathematics can at most aid designers to eliminate design alternatives dominated by others, leaving a number of alternatives in what is called the Pareto set (*25*). Generating methods, such as the weighting method and the constraint method, have been developed to find the exact Pareto set or an approximation of it. For each of these designs, it is impossible to improve one objective without sacrificing the value of another relative to some other design alternative in the set. From among the dominating solutions, it is then a value judgment by the customer to select which design is the most appropriate. At issue is an effective means to find the members of the Pareto set for a design problem, especially when there are more than two or three objectives; the analysis per design requires significant computations to complete, and there are an almost uncountable number of design alternatives. A pure algorithmic approach to solving is to select one to minimize while the remaining objectives are turned into an inequality constraint with a parametric right-hand-side, L_k. The problem takes on the following form:

$$\begin{aligned} \min \quad & Z_j \\ \text{s.t.} \quad & h(x, y) = 0 \\ & g(x, y) \leq 0 \\ & Z_k \leq L_k,\ k = 1, \ldots, j-1, j+1, \ldots, p \end{aligned} \tag{2}$$

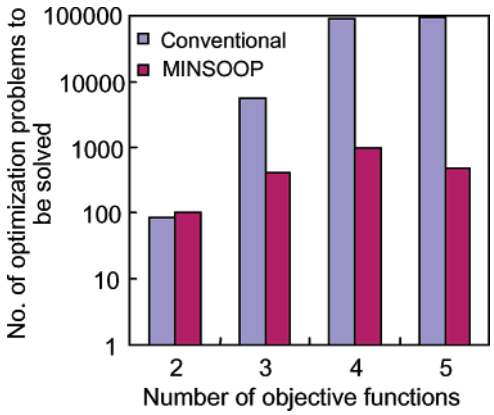

FIGURE 6. Computational speed-up through MINSOOP.

where Z_j is the chosen jth objective that is to be optimized. Solving repeatedly for different values of L_k chosen between the upper, $Z_U(j)$, and the lower, $Z_L(j)$, bounds leads to the Pareto set. The multi-objective optimization algorithm used in this work uses the HSS to generate combinations of the right-hand side. The aim is to MInimize the Number of Single Objective Optimization Problems (MINSOOP) by exploiting the n-dimensional uniformity of the HSS technique. Figure 6 shows how this MINSOOP (*26*) algorithm improves efficiency for a simple, nonlinear, convex optimization problem as the number of objectives increases.

Synthesizing Greener Energy Supply on Demand

Incorporation of pollution prevention concepts into design and development at initial stages lead to processes that are less cost-intensive and environmentally friendly. Therefore, process synthesis remains an important step in analyzing and designing environmentally benign processes. In this case study, a greener power plant is synthesized using the new framework and the guidelines provided by green engineering principles.

Fuel cells are more or less a "zero" emission technology as the emissions are much lower than other competitive technologies in the market for energy generation (*27*). Selecting a fuel cell power plant for generation of electricity follows the green engineering Principle 2. However, the extremely low emissions of this technology require higher costs, and there are a number of challenges and issues that need to be addressed to make the use of this technology widespread and economically viable. Although for this technology LCA questions need to be addressed to ensure that Principle 1 is addressed adequately, currently very few LCA studies (*28*, *29*) are available for fuel cell power plants as the technology is considered to be futuristic and data are scarce. Therefore, this work concentrates on other steps in the framework. Similar to LCA, Principles 7, 11, and 12 represent objectives that can only be defined qualitatively. Hence, they are not directly addressed here.

Hybrid Fuel Cell Power Plant. Distributed power generation is one of the most attractive applications of the fuel cell technology. A major bottleneck in the design of fuel cell power plants for this application is to package them in a system balance of plant (BOP) that allows them to function effectively. Here the principles of process intensification (Principle 4) and process integration (Principle 8) can be utilized. This is explained in following paragraphs.

Process Intensification. All fuel cells, especially those operating at high temperatures such as molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC), need spent fuel utilization or waste heat recovery subsystems to increase process efficiency. Low-temperature fuel cells (e.g., polymer electrolyte membrane (PEM)) also require fuel re-forming

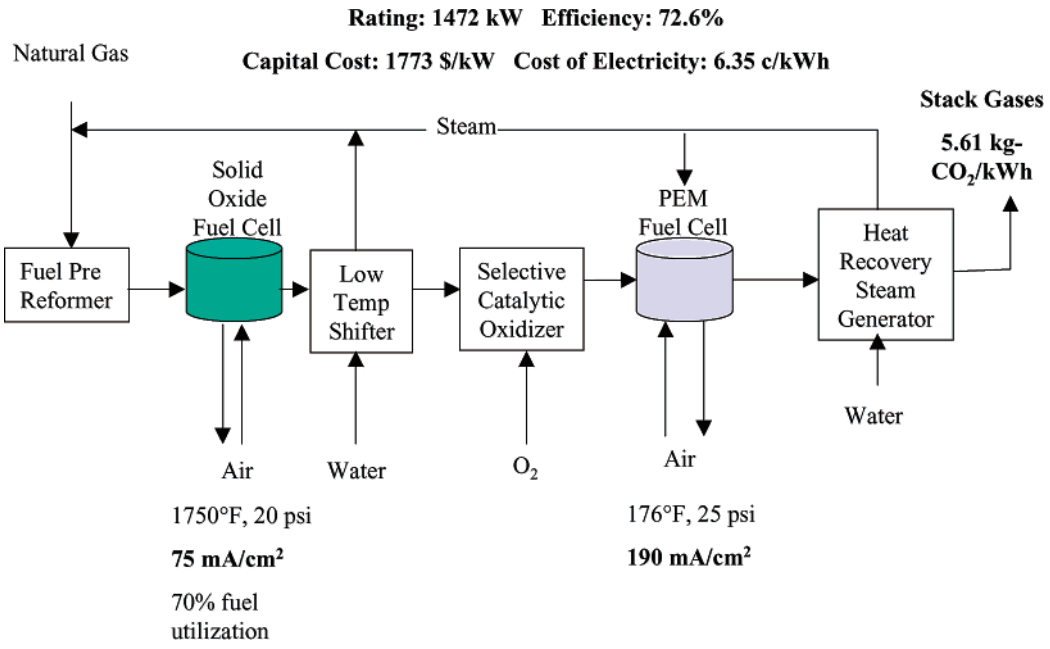

FIGURE 7. Schematic of the hybrid fuel cell power plant.

subsystems. A common approach for providing the BOP has been to integrate the fuel cell with a heat engine, which gives rise to a fuel cell/heat engine hybrid system. This is also a very effective means to utilize the waste heat of the fuel cell but compromises on several features of the fuel cell and distributed power generation. The plant is no longer a compact module, and it is now difficult to scale it up. The addition of the heat engine bottoming cycle with moving parts leads to an increase in noise and calls for more maintenance. Moreover, the dynamics and turndown characteristics of the fuel cell plant no longer remain simple. These considerations have fueled the development of fuel cell/fuel cell hybrid power plants as a very effective way to achieve the BOP. Generally, a high-temperature internally re-forming fuel cell (SOFC) needs to be combined with a low-temperature fuel cell (PEM) having a complementary electrolyte (anion-conducting vs cation-conducting electrolytes) to get such a synergistic effect. Figure 7 shows the schematic of such a hybrid power plant. This SOFC−PEM hybrid plant (*30*, *31*) uses the following process integration steps to enhance the efficiency further.

Process Integration. The plant contains two fuel cells (one each of SOFC and PEM) combined with a heat recovery steam generation cycle. The use of two fuel cells makes this cycle up to 37.8% more efficient than the case where only a SOFC is used (maximum efficiency of 52.4%). Natural gas is used as the fuel. It is processed in a fuel re-former to scrub H_2S and other sulfur compounds and fed to the SOFC. The SOFC acts both as an electricity producer and as a fuel re-former for PEM. The exhaust fuel from the SOFC is cooled and shifted in a low-temperature shifter that also functions as a low-pressure steam boiler. Shifted fuel gas is then treated with pure oxygen in a selective catalytic oxidizer to reduce CO from several hundred parts per million (ppm) to below 10 ppm. The utilization of this re-formed fuel is completed in the PEM. The exhaust from the PEM cell goes to the waste hydrogen burner and heat recovery steam generator to utilize the waste heat of the exhaust stream to make steam from water. This steam produced in the low-temperature shifter and the heat recovery steam generator is used in both SOFC and PEM. In the SOFC, steam is used as a reactant for the re-forming and downstream shift reactions and to control against the carbon. In the PEM, steam is used to humidify fuel and airstreams to maintain water balance in the electrolyte and electrodes.

Using green engineering Principle 5, the fuel utilization is chosen as the decision variable to manipulate the output. The fuel utilization in SOFC can be limited to a range necessary, only to re-form the natural gas and make the exhaust gas suitable for use by PEM after some treatment but not completely oxidize it. This way, the re-formed fuel (SOFC exhaust) can be completely oxidized in the PEM where more favorable thermodynamics apply rather than forcing a higher fuel utilization in the SOFC, which can cause a drop in current density and cell voltage. Another important SOFC design aspect is internal recuperation, whereby efficient heat management is used maximize system compactness and power density by minimizing the required air−fuel equivalence ratio. One of the important points that should be noted in applying Principle 5 is that the optimal decisions will depend on what objective (output) you are trying to manipulate in this multi-objective situation. This is generally not obvious when one is looking at a single objective as will be discussed in the context of multi-objective results below.

Multi-objective Optimization. The following is the formulation of the problem of design of SOFC−PEM hybrid power plant as a multi-objective optimization problem (*31*, *32*):

$$\begin{aligned} &\max && \text{overall efficiency (ACEFF)} \\ &\min && \text{capital cost (CAP)} \\ &\min && \text{cost of electricity (COE)} \\ &\max && \text{current density SOFC (CDSOFC)} \\ &\max && \text{current density PEM (CDPEM)} \end{aligned} \tag{3}$$

subject to:

$$\text{power rating (PWRTG)} = 1472$$

$$\text{mass \& energy balance constraints (modeled in Aspen Plus)}$$

The decision variables used are the fuel utilization (UTIL) and equivalence ratio (ERAT) in the SOFC (derived from the green engineering Principle 5) and the pressure of the PEM (PPEM) and fuel and air flows. The algorithmic framework

TABLE 2. Bounds for Different Objectives: A Payoff Table

	max ACEFF	min ACEFF	min CAP	min COE	min CO_2EM	max CO_2EM	min CDPEM	max CDPEM	min CDSOFC
design no.	1	2	3	4	5	6	7	8	9
ACEFF	0.723	0.520	0.601	0.583	0.543	0.707	0.575	0.708	0.726
CAP ($/kW)	1456	1600	995	993	1444	1282	740	1290	1665
COE (R/kW-h)	5.67	5.63	4.16	4.28	5.05	4.15	3.68	5.15	6.28
PWRTG (kW)	1475	1466	1568	1469	1634	1470	1500	1496	1472
CO_2EM (kg/kW-h)	0.273	0.379	0.328	0.339	0.364	0.279	0.343	0.279	0.272
CDSOFC (mA/cm^2)	102	672	531	616	737	158	678	149	76
CDPEM (mA/cm^2)	290	305	309	308	295	294	320	287	294
UTIL	0.700	0.551	0.436	0.403	0.411	0.700	0.400	0.700	0.700
PPEM (psi)	23	37	40	36	20	26	75	20	25
ERAT	1.37	5.69	1.25	1.25	3.01	1.80	1.89	1.70	1.25
fuel (lb-mol/h)	20.2	27.8	25.8	24.9	29.8	20.6	25.8	20.9	20.0
air (lb-mol/h)	189.3	851.9	137.3	122.4	359.8	252.4	189.8	242.9	171.1

shown in Figure 3 is used to solve this problem. Since the discrete decisions related to process synthesis are decided using the process intensification and process integration heuristics obtained from expert knowledge and since at this stage uncertainties related to this technology are not yet fully quantified and characterized, this case study only uses the Loop 3 (continuous optimizer) and Loop 5 (MOP loop) in Figure 3 to obtain the Pareto or the tradeoff surface for various objectives.

Capacity Planning. Green engineering Principle 8 states that design for unnecessary capacity solutions should be considered a design flaw. Capacity planning decisions (e.g., power rating = 1472 kW in eq 3) are the management and planning decisions decided by the demand. These decisions are also linked to the MOP problem and can be obtained by using the same algorithmic framework for solution of the following capacity planning problem as shown in refs *33* and *34*.

The mathematical formulation of the problem is given below:

$$\min \quad E[\text{cost}] \tag{4}$$

$$\text{s.t.} \quad \text{cost} = \sum_t \text{cost}_t^{\text{op}} + \text{cost}_t^{\text{cap}} + \text{cost}_t^{\text{buy}} \tag{5}$$

$$\text{cost}_t^{\text{op}} = \sum_i P_t^i \overline{\text{oc}_t^i} \tag{6}$$

$$\text{cost}_t^{\text{cap}} = \sum_i \alpha^i (AC_t^i)^{\beta^i} \tag{7}$$

$$\text{cost}_t^{\text{buy}} = \tilde{\kappa}_t (\tilde{d}_t - tp_t)^{\gamma} \tag{8}$$

$$c_t^i = c_{t-1}^i + AC_t^i \tag{9}$$

$$tp_t = \sum_i P_t^i \tag{10}$$

$$P_t^i \le c_t^i \tag{11}$$

$$i \in \text{technology}_1, \text{technology}_2, \ldots, \text{technology}_{\text{I}}$$

$$t \in \text{period}_1, \text{period}_2, \ldots, \text{period}_{\text{T}}$$

where E denotes expected value. Equation 5 sums up the respective costs for operation, capacity expansion, and the option to purchase electricity for meeting demand in case the total available capacity is below demand. The operating costs are calculated using eq 6, where oc_t^i is a cost parameter for electricity generation of technology i in time period t, and P_t^i are decision variables determining how much electricity should be produced using technology/power plant i at time t. Equation 7 determines the cost of capacity expansion. In this formula, α_i is a proportionality factor for capacity expansion, while β_i provides the exponential factor that allows capital expansion cost to follow economies of scale. The capacity (i.e., power rating) required to meet the demand for a particular technology i like the fuel cell plant presented here is obtained by solving the above optimization problem.

Payoff Table. As a first step toward obtaining the whole Pareto set, the bounds for all the objective functions are generated, this is the payoff table. A payoff table is widely used in decision analysis where it specifies the alternatives, acts, or events. Especially in MOP, a payoff table shows a potential range of values of each objective. In more detail, a payoff table contains individual objective values (Z_k^*) for single optimization problems (k) and also provides potential ranges of the objectives on the Pareto surface (i.e., Z_{L} to Z_{U}). In this way, an approximated range of the right-hand side L_k in the Pareto surface is determined. These are presented in Table 2. It has been found that the capital cost (CAP) and cost of electricity (COE) follow the same trend, so these objectives can be combined in one. Again, the SOFC current density and CO_2 emissions are seen to have the same trend and can be combined as one, while the PEM current density objective can be dropped because there is not much change. The reduced objective set is then used to obtain the complete Pareto set of a power plant of fixed capacity (i.e., 1472 kW).

Pareto Set. The algorithmic framework shown in Figure 3 is used to obtain the complete Pareto set using only 150 single optimization problem instead of 10 000 optimization problems required by other algorithms. The results are plotted in Figures 8 and 9. These plots provide great insights into the design especially in the face of such diverse objectives. The high-efficiency and low-emissions regions involve high capital costs. There are some low-cost regions at high SOFC current density but involve low efficiency and high emissions. Another major low-cost region is with SOFC current density between 350 and 500 mA/cm^2, overall efficiency between 60 and 65%, and CO_2 emissions between 0.30 and 0.32 kg/kW-h. Although CO_2 emissions for these designs are significantly less than CO_2 emissions from currently operating power plants (0.920 kg/kW-h) based on coal (*35*), these emissions need to be reduced further to achieve sustainability.

The Pareto set designs have again been normalized with respect to maximum values of the objectives from Table 2 and replotted in order to identify certain quantitatively similar design groups. These designs are shown in Figure 10, and the comparison of the various design groups is presented in Table 3. This new framework provided designs with up to

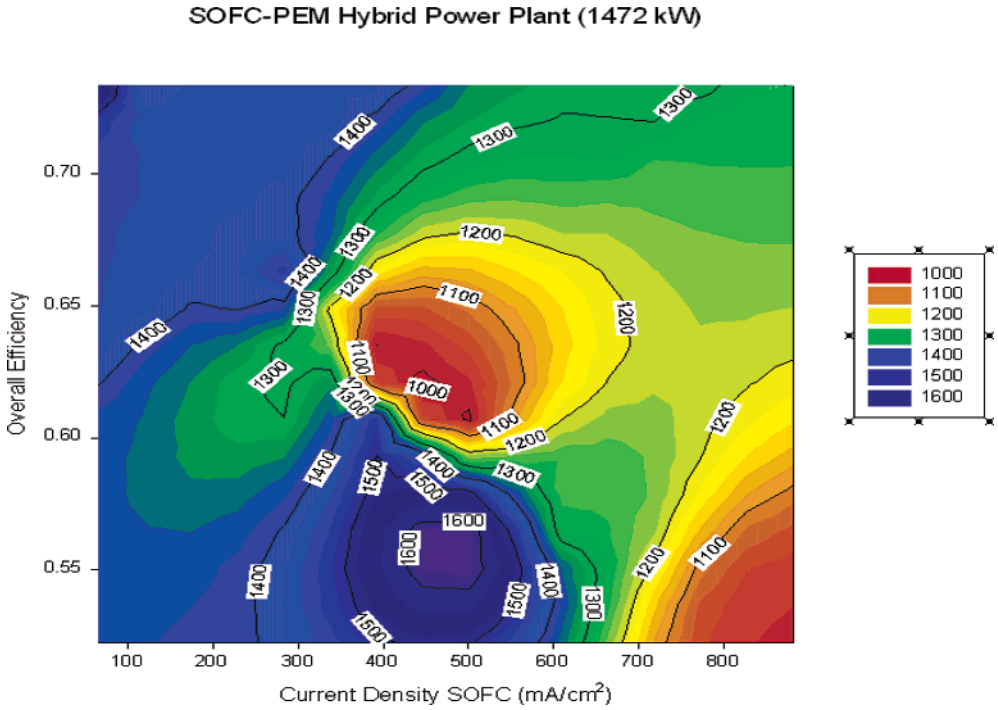

FIGURE 8. Tradeoff surface for efficiency, SOFC current density, and cost.

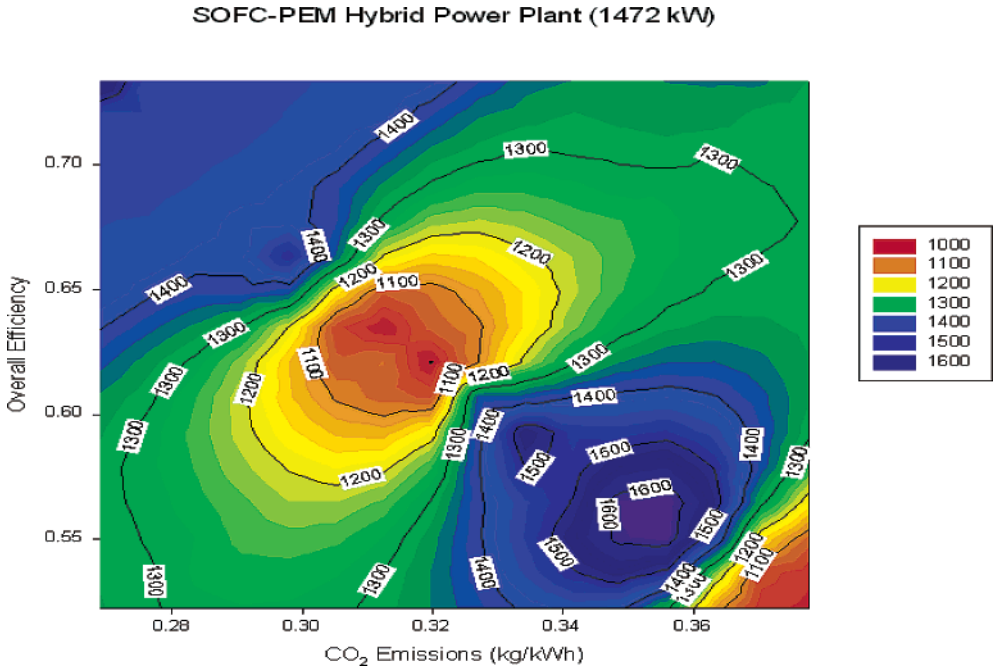

FIGURE 9. Tradeoff surface for CO_2 emissions, SOFC current density, and cost.

44% lower costs, 43% lower CO_2 emissions, and 12 times higher SOFC current density than the base case. Group 1 is the minimum capital cost group with 44 lower capital cost than the base case capital cost of 1773 $/kW. [Note that the base case cost of this plant is higher than the cost range of 1250−1600 $/kW reported for different integrated gasification combined cycle power plants, for much smaller capacity power plants (*36*).]

There are designs that have lower CO_2 emissions (up to 34%) and higher SOFC current density (up to 6.5 times) than the base case, but these are competitive in terms of overall efficiency. These types of designs are recommended when cost is the most important factor. Group 2 presents designs with maximum CDSOFC (up to 12 times that of base case) and low capital cost (1014−1022 $/kW). But again we have to compromise heavily on efficiency and CO_2 emissions (22% higher than group 1 though still 20% lower than base case). These designs are recommended when emission standards are not that stringent and high SOFC current density is desired. These also require operation of PEM at a higher pressure. Group 3 designs are the ones representing the high-cost regions right in the middle of the Pareto surface plots. These have a higher cost than groups 1 and 2 although still up to 16% lower than base case. These also have intermediate values of current density, CO_2 emissions, and overall efficiency. These regions in the Pareto surface should be avoided if one can choose designs from the other three groups. Group 4 designs efficiency on the higher side and

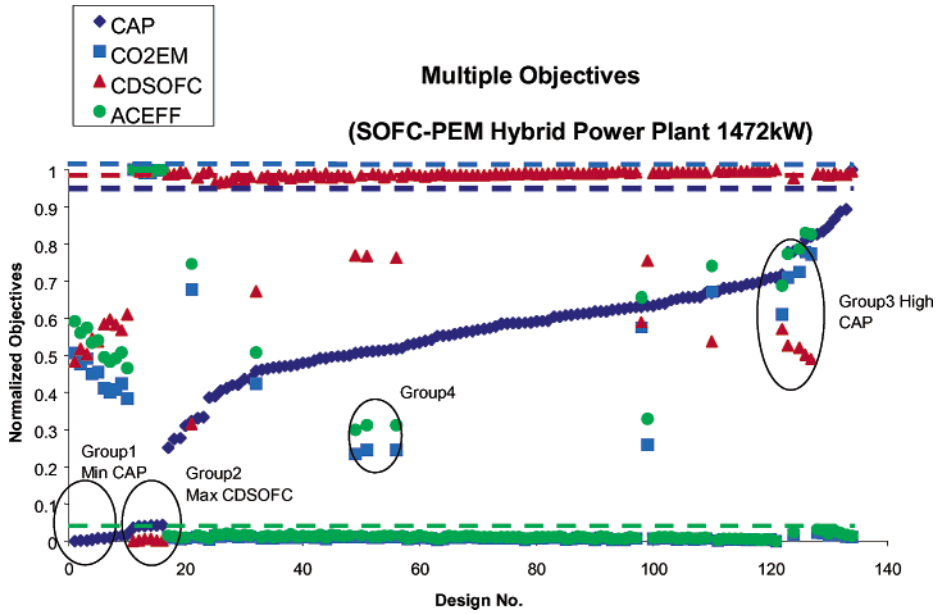

FIGURE 10. Normalized objective functions in pareto surface designs.

TABLE 3. Qualitative Regions in Pareto Surface

	base case	group 1	group 2	group 3	group 4
feature		min CAP	max CDSOFC	high CAP	
objective					
CAP ($/kW)	1773	986−1001	1014−1022	1501−1657	1399−1409
CDSOFC (mA/cm^2)	75	384−487	876−881	401−483	254−260
CDPEM (mA/cm^2)	190	305	319	291−301	307
overall efficiency	72.6%	60−64%	52.2−52.4%	55.8−59.5%	66.7−67%
cost of electricity ($/kW-h)	6.35	4.28−434	4.33−4.50	5.43−5.79	5.3−5.33
CO_2 emission (kg/kW-h)	0.468	0.31−0.324	0.376−0.378	0.332−0.354	0.294−0.296
		Decision Variables			
UTIL	0.7	0.45−0.51 0.4	0.68−0.7	0.68−0.7	
PPM (psi)	25	31−36	74−75	22−37	53−56
ERAT	1.25	1.25	6.0	4.65−5.65	2.67−2.9
fuel (lb-mol/h)	20	22−24	25−28	23−27	21
air (lb-mol/h)	200	133−143	583−630	762−1001	388−429

lower values for SOFC current density and CO_2 emissions. The capital cost is also in the intermediate range. This group shows “moderate” designs.

If one looks at the decision variables such as the fuel utilization and the equivalence ratio (Table 3) that reflect closely the green engineering Principle 5 (products and processes should be “output pulled” than “input pulled”), the values (or range) of these decision variables changes according to which "output (objective)" is more important. This illustrates that one can use the green engineering principles as a guideline in choosing decision variables and design directions. However, for the exact range of decision values of these operating variables, it is important to obtain these tradeoffs surfaces.

This case study illustrated how the new integrated framework based on efficient optimization and uncertainty analysis algorithms can be used to obtain greener and minimum cost designs. The case study extended the design envelope to include process synthesis and management and planning stages and used various green engineering principles leading to designs beyond compliance. However, in this case study separation and purification stages are not included as some of the carbon sequestration options are not considered in the design. The next case study explicitly addresses this very important problem (Principle 3).

Coupling Chemical and Process Synthesis with Design

Separation processes are not only vital for isolating and purifying valuable products but are also crucial for removing toxic and hazardous substances from waste streams emitted to the environment (Principle 3). Figure 11 shows one example of separation processes using extraction and distillation for acetic acid (HOAc) separation and recycling. HOAc, an in-process solvent (IPS), is a valuable chemical but is also a pollutant when released to the environment. HOAc can be directly separated from water in a single distillation column; however, this requires a very large number of equilibrium stages (i.e., long column, high entropy system, please refer to Principle 6, Table 1) due to close boiling temperatures of water and HOAc (100 vs 118 °C), resulting in high capital and operating costs. Instead of using a single distillation, this separation, in practice, consists of an extraction column followed by a distillation column. An aqueous stream containing acetic acid enters the extraction column in which a solvent extracts acetic acid from the water. The extract is then supplied to the azeotropic distillation column where the bottom product is pure acetic acid and the top product is a heterogeneous water−new solvent azeotrope. The pure acetic acid product is recycled to upstream processes whereas the azeotropic mixture is condensed and then decanted. The organic phase from the decanter is recycled while the aqueous phase goes to the wastewater treatment facility. It has been

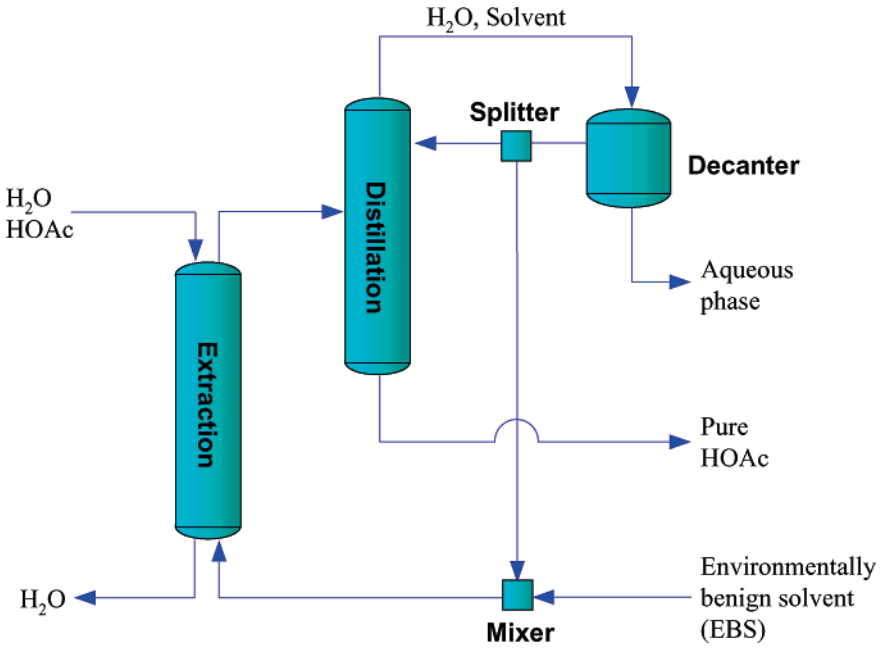

FIGURE 11. Acetic acid extraction process as a case study (from Eastman Chemical Company).

observed that this process has few degrees of freedom. Because of this, a slight variation in feed not only results in loss of HOAc purity and yield but also results in a big environmental problem due to acetic acid concentrations in effluent.

This section presents a case study of designing this separation system. To apply Principles 1 and 2, in this case study, the design starts at the initial stage of chemical or material selection. Obviously, this integration poses several challenges including the exponential growth of chemical and process design combinations and uncertainties in the group contribution models for chemical synthesis, and multiple objectives. This case study utilizes all the algorithmic stages (loops) of Figure 3 to obtain greener and cost-effective designs.

The goals of this process design are to achieve a high HOAc recovery yield, high process flexibility, and low environmental impacts. The coupled chemical and process synthesis involves integration of environmentally benign new solvent (EBS) selection and IPS recycling. EBS selection is an approach used to generate candidate solvent molecules that have desirable physical, chemical, and environmental properties. Computer-aided molecular design (CAMD) (*37*, *38*) is commonly used for EBS selection. CAMD, based on the reverse use of group contribution methods, can automatically generate promising solvent molecules from their fundamental building blocks or groups. The group contribution method is a forward problem; if we know a molecule, we can estimate its physical, chemical, biological, and health-effect properties based on its groups. In contrast, CAMD is a backward problem: if we know desired properties or regulation standards, we can find molecules that satisfy these properties or standards by combining groups. While the integrated design of this process is published in ref *39*, the current paper aims to describe the design approach and the integrated framework (Figure 2) in terms of the principles of green engineering. It also presents and analyzes two Pareto surfaces that meet the flexibility needs for uniformly varying feed of 5% and 10, respectively. instead of normally distributed feed variation presented earlier.

EBS Selection under Uncertainty. To replace the current EBS molecules or to design a new one, there are several criteria to be considered such as (a) distribution coefficient (m); (b) solvent selectivity (β); (c) solvent loss (S_L); (d) physical properties; (e) toxicology data such as LC_{50} and LD_{50}; (f) environmental properties such as persistence, BCF (bioconcentration factor), and reactivity; and (g) cost. For extraction processes, the final selection of solvents will generally be dominated by m and β. These solvent selection criteria are functions of γ^{∞}, the infinite dilution activity coefficients, and MW, molecular weights of raffinate, solute, and solvent. The symbols A, B, and S represent the raffinate, solute, and solvent phases, respectively. Significant uncertainties exist in predicting the infinite dilution activity coefficients using the UNIFAC equation (*40*). However, many of these uncertainties are difficult to characterize as (i) group interaction parameters are generated from the available experimental data of various chemicals, resulting in scattered interaction parameters; (ii) highly nonlinear correlations exist between these parameters; (iii) in general, the parameter estimation step results in multiple solutions due to multiple local optima. Therefore, characterizing uncertainty is considered to be an important but difficult step. In this case study, uncertainties were present in more than 1800 interaction parameters in the UNIFAC model (derived from DECHEMA; *15*, *16*) used to predict the solvent selection objectives for the acetic acid problem. These uncertainties were collapsed in terms of three parameters. Thermodynamics is used to identify three kinds of interactions: organic/water (log-normal distribution), organic/organic (log-normal distribution), and water/organic (normal distribution). This division considers the difference between properties of water and those of organic chemicals. To characterize these uncertainties in an earlier work (*39*), we defined an uncertainty factor (UF), the ratio of the experimental γ^{∞} to the calculated γ^{∞}, and divided γ^{∞} and the UF into three categories: organic/water, water/organic, and organic/organic. This results in the following mathematical formula-

tion for the EBS selection problem:

$$\min -\frac{1}{N_{\text{samp}}}\sum_{j=1}^{N_{\text{samp}}}\left[\frac{\xi_j^1\ \gamma_{\text{B,A}}^{\infty}}{\xi_j^3\ \gamma_{\text{B,S}}^{\infty}}\right]\frac{\text{MW}_\text{A}}{\text{MW}_\text{S}} \tag{12}$$

subject to

$$\beta = \frac{1}{N_{\text{samp}}}\sum_{j=1}^{N_{\text{samp}}}\left[\frac{\xi_j^2\ \gamma_{\text{A,S}}^{\infty}}{\xi_j^3\ \gamma_{\text{B,S}}^{\infty}}\right]\frac{\text{MW}_\text{S}}{\text{MW}_\text{A}} \geq 7.0$$

$$S_\text{L} = \frac{1}{N_{\text{samp}}}\sum_{j=1}^{N_{\text{samp}}}\left[\frac{1}{\xi_j^1\ \gamma_{\text{B,S}}^{\infty}}\right]\frac{\text{MW}_\text{S}}{\text{MW}_\text{A}} \leq 0.058$$

$$47 \leq T_{\text{BP}}\ (^\circ\text{C}) \leq 118$$

$$2 \leq N_1 \leq 10$$

$$1 \leq N_2^{(i)} \leq 24, \quad \forall\ i \in N_1$$

$$\xi^1 \sim \log N(2.92, 5.94), \quad \text{organic/water}$$

$$\xi^2 \sim N(1.08, 0.37), \quad \text{water/organic}$$

$$\xi^3 \sim \log N(1.42, 1.14), \quad \text{organic/organic}$$

where ξ is an uncertain parameter of the UF and is imposed on the estimated γ^∞. The constraint bounds of β and S_L are based on the values of the current extracting agent, ethyl acetate. Discrete decision variables are the number of groups (N_1) in a solvent molecule and the group index ($N_2^{(i)}$) of that molecule, and by combining these decision variables one can build a unique solvent molecule. By definition, solvent selection problems are to find the optimal values of N_1 and N_2 that correspond to the best solvent molecules. The set of groups in this study (i.e., group indices) are specially designed for linear or branched hydrocarbons while aromatic, cyclic, and halogenated compounds are eliminated due to environmental concerns (Principles 1 and 2). For molecular connectivity, a simple octet rule is applied. There are 40 optimal solvents that are selected for further study. The results found that deterministic optimal solvents are significantly different than stochastic solvent molecules. Furthermore, the current popular solvent ethyl acetate is found only when the uncertainties are included in the formulation. This supports the conclusion that to obtain realistic solutions to problems, especially when the design includes chemical and process synthesis steps, uncertainties quantification and inclusion is very important.

Integrated EBS Selection and IPS Recycling Problem. The objectives of this MOP problem under uncertainty are to maximize HOAc recovery ($-Z_1$), minimize environmental impacts (Principle 1) (EI) based on LC_{50} (Z_2) and based on LD_{50} (Z_3), and maximize the process flexibility ($-Z_4$).

The mathematical formulation of this MOP problem for the EBS selection and IPS recycling case study is

$$\min Z_1 = -\frac{\text{HOAc in product}}{\text{HOAc in feed}} = f(x, y) \tag{13}$$

subject to

$$1 \leq y_1 \leq 7$$

$$3 \leq y_2 \leq 9$$

$$0.5 \leq x_1 \leq 0.95$$

$$20 \leq x_2 \leq 35$$

$$Z_2 = \text{EI} = \frac{\sum F_{\text{solvent,out}}}{\text{LC}_{50,\text{solvent}}} + \frac{\sum F_{\text{HOAc,waste}}}{\text{LC}_{50,\text{HOAc}}} \leq L_2$$

$$Z_3 = \text{EI} = \frac{\sum F_{\text{solvent,out}}}{\text{LD}_{50,\text{solvent}}} + \frac{\sum F_{\text{HOAc,waste}}}{\text{LD}_{50,\text{HOAc}}} \leq L_3$$

$$Z_4 = -\frac{\text{feasible runs}}{\text{total runs}} \leq L_4$$

$$y_i = \text{integer}$$

$$u = U[-0.05, 0.05]\ \textit{or}\ u = U[-0.10, 0.10]$$

where x and y are continuous and discrete decision variables. The continuous decision variable vector **x** based on Principles 5 and 10 is [split fraction, distillation bottom rate, EBS makeup flow rate, heat duty]^T. To reduce the entropy of the system for recycling (Principle 6), solvent with no additional azeotrope needs to be selected. Therefore, the discrete decision design vector **y** is [solvent type, distillation feed point, number of equilibrium stages]^T. As stated earlier, one of the problems of this system is that the feed variation causes significant environmental problems; therefore, flexibility in the face of feed variation is explicitly included as an objective. However, as Principle 8 states, even if flexibility in design is essential, design for worst-case scenarios is not advisable. Here, therefore, the problem selects two design surfaces, flexible for uniformly varying (u, fractional variation) feed for percentage variation of 5% and 10%, respectively. To minimize the material diversity in the existing chemical plant (Principle 9), only a small number of solvents commonly available in such a plant from the 40 optimal solvents found earlier (as this plant uses Aspen Plus; Aspen Plus databank is used as a representative for the plant) are included as candidate solvents. The candidate solvents are (1) methyl propyl ketone, (2) methyl isopropyl ketone, (3) diethyl ketone, (4) ethyl acetate, (5) methyl propionate, (6) isopropyl acetate, and (7) propyl acetate. Apart from the solvent type (y_1), other discrete decisions include the total number of stages of the extractor and the distillation column (20 and 25, respectively) and the feed point to the distillation column (y_2). Continuous decisions include the distillation bottom flow, split ratio (i.e., EBS recycle ratio), EBS makeup flow rate, and heat duties of the distillation column. The feed rate is assumed to be 100 kmol/h with the molar feed composition of 0.7/0.3 in water/HOAc, and feed variation, u, is imposed on the feed flow rates.

There is another important factor that should be considered in EBS selection and IPS recycling. In industrial practice, heat duty is critical in deciding alternatives for continuous distillation. Thus before solving the MOP problem, the proposed EBSs are also checked through the reboiler heat duty comparison in order to eliminate candidate EBSs that require high heat duty.

Pareto Optimal Solutions. The first step in solving MOP problems is to obtain a payoff table. Table 4 shows a payoff table for optimization under uncertainty, in which the variation in the feed flow rate is ± 5% and 10% of the feed flow rate and is uniformly distributed.

Figure 12 and Table 5 show the Pareto optimal solutions for EBS selection and IPS recycling problems for the two feed variations. Due to a highly discretized solution surface and large infeasible regions (in terms of yield and feasibility),

TABLE 4. Payoff Table at 5% and 10% Uniform Feed Flow Variation

		5% variation			10% variation		
k	objective	Z^*_k	Z_L	Z_U			
1	HOAc recovery	−0.9869		0.9775			
2	EI based on LC_{50}	0.9077	0.90787	1.1837	0.9077	0.9077	1.1491
3	EI based on LD_{50}	0.0251	0.0251	0.0389	0.0251	0.0251	0.0384
4	flexibility	−0.8000	−0.8000	−0.3000	−0.7000	−0.7000	−0.5000

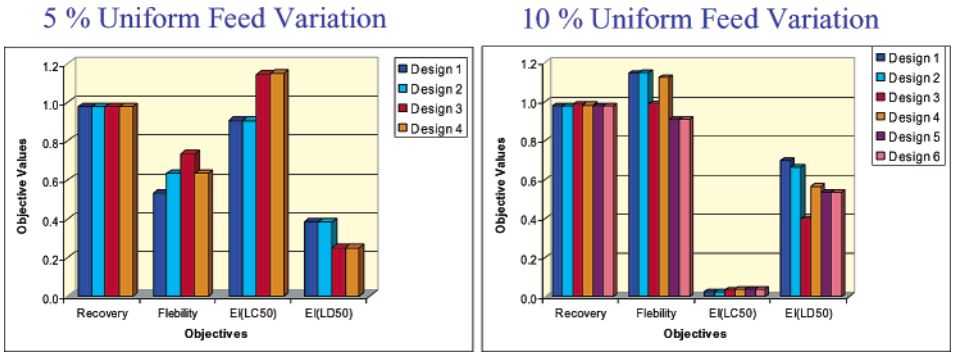

FIGURE 12. Pareto optimal solutions at 5% and 10% uniform feed flow variations.

TABLE 5. Pareto Solutions for 5% and 10% Uniform Feed Flow Variation

k	OBJ1	OBJ2	OBJ3	OBJ4	solvent	feed	splitfrac
					5% Feed Variation		
1	0.9776	1.1447	0.0250	0.7000	isopropyl acetate	6	0.8068
2	0.9775	1.1491	0.02510	0.6667	isopropyl acetate	5	0.8062
7	0.9869	0.9894	0.0337	0.4000	ethyl acetate	5	0.6540
11	0.9831	1.1254	0.0373	0.5667	ethyl acetate	8	0.6374
19	0.9761	0.9078	0.0384	0.5333	methyl propionate	6	0.6794
35	0.9761	0.9077	0.0384	0.5333	methyl propionate	3	0.6794
					10% Feed Variation		
1	0.9776	1.1447	0.0250	0.7333	isopropyl acetate	6	0.8068
2	0.9775	1.1491	0.0251	0.6333	isopropyl acetate	5	0.8062
19	0.9761	0.9078	0.0384	0.5333	methyl propionate	5	0.6794
35	0.9761	0.9077	0.0384	0.6333	methyl propionate	4	0.6794

only six designs in the face of 5% feed variation are in the tradeoff surface from the 50 optimization problems used to generate this surface. For 10% feed variation, this surface reduced further to four designs. EBS ethyl acetate (no. 4), which is the current extracting agent, has advantages in terms of two objectives: HOAc recovery ($-Z_1$) and process flexibility ($-Z_4$) for 5% feed variation. High HOAc recovery can be predicted because the distribution coefficient of ethyl acetate is the highest among the EBSs present in the Pareto optimal solutions. Hence, the popular use of ethyl acetate can be understood from these two objectives. However, for 10% feed variation, ethyl acetate is no longer in optimal design. For the environmental impact based on LC_{50} (Z_2), methyl propionate (no. 5) is the best solvent for this integrated problem. This is mainly due to the highest value of LC_{50}, 2240 mg/L. For the environmental impact based on LD_{50} (Z_3), isopropyl acetate (no. 6) is the best choice even though it does not have the highest LD_{50} value. It is found from simulation results that isopropyl acetate has the lowest fresh solvent makeup flow rate (e.g., ~0.36 vs 1.27 kmol/h of ethyl acetate). It can be seen from the formulation shown in eq 13 that the objective, Z_3, is directly proportional to the makeup solvent, and this is the main reason for the lowest Z_3 value associated with isopropyl acetate. A reduction in the demand for additional makeup isopropyl acetate reduces environmental burdens in accordance with Principle 4. The process flexibility objective is highly dependent on the distillation feed point as well as EBS molecules.

From this case study, we can see that the integrated framework can provide different and better chemical and design alternatives to decision-makers. In addition, uncertainties in CAMD models and operating conditions can play a significant role in the early design and synthesis stages.

Summary

This paper presented an integrated computer-aided framework for green engineering. The framework extends the traditional design framework to include decisions starting from chemical and material selection to management and planning. As the envelope is extended from traditional simulation step to include these earlier and later steps together and tend to increase uncertainties. Furthermore, green engineering concepts change the single goal of engineering design from profitability to include number of different and conflicting objectives that can define the sustainability in the end. Therefore, the basis of this integrated framework is efficient multi-objective optimization and uncertainty analysis methods and algorithms. The use of this algorithmic framework to solve real world problems is illustrated with two case studies. The first case study is related to synthesizing power plant as a greener and cost-effective source for energy generation that can be used to satisfy uncertain demand. The second case study deals with an important problem of waste solvents in chemical industry. This case study illustrates the importance of starting design as early as chemical selection or chemical synthesis stage.

This paper presented the power of this integrated framework and algorithms for solving problems leading to greener and profitable designs. However, the framework did not explicitly addressed questions related to LCA, industrial ecology, and socio-economic sustainability. This is because many of these issues deal with non-quantitative information. Although not fully exploited, the methods presented here have potential to include non-quantitative information also. These issues will be addressed in the future.

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