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OPTIMIZATION UNDER UNCERTAINTY IN CHEMICAL ENGINEERING

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This article presents an overview of optimization under uncertainty with application to chemical manufacturing. The article introduces the basic algorithms and methods, and presents applications related to all stages of design starting from chemical synthesis, process synthesis, to manufacturing, planning, and management.

Key Words:

1 Introduction

Deterministic optimization literature classifies problems as Linear Programming (LP), NonLinear Programming (NLP), Integer Programming (IP), Mixed Integer LP (MILP), and Mixed Integer NLP (MINLP), depending on the decision variables, objectives, and constraints. However, the future cannot be perfectly forecasted but instead should be considered random or uncertain. Optimization under uncertainty refers to this branch of optimization where there are uncertainties involved in the data or the model, and is popularly known as Stochastic Programming or stochastic optimization problems. In this terminology, stochastic refers to the randomness, and programming refers to the mathematical programming techniques like LP, NLP, IP, MILP, and MINLP. In discrete (IP, MILP, MINLP) optimization, there are probabilistic techniques like Simulated Annealing and Genetic Algorithms; these techniques are sometimes referred to as the stochastic optimization techniques because of the probabilistic nature of the method. In general, however, Stochastic Programming and stochastic optimization involves optimal decision making under uncertainties.

Table I
Weekly Demand Uncertainties

j	Demand, d_j	Probability, p_j
1	50	5/7
2	100	1/7
3	140	1/7

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The need for including uncertainty in complex decision models arose early in the history of mathematical programming. The first model forms, involving action followed by observation and reaction (or recourse), appear in ref. [1, 2] .The commonly used example of a recourse problem is the news vendor or the newsboy problem described below[3]. In the news vendor problem, the vendor must determine how many papers to buy now at the given cost and selling price per paper for a demand which is uncertain. The news vendor or newsboy problem has a rich history that has been traced back to the economist Edgeworth[4], who applied a variance to a bank cash-flow problem. However, it was not until the 1950s that this problem, like many other OR/MS models seeded by the war effort, became a topic of serious and extensive study by academicians[5].

Example: The simplest form of a stochastic program may be the news vendor (also known as the newsboy) problem. In the news vendor problem, the vendor must determine how many papers (x) to buy now at the cost of c cents for a demand which is uncertain. The selling price is s_p cents per paper. For a specific problem, whose weekly demand is shown below, the cost of each paper is c = 20 cents and the selling price is s_p = 25 cents. Solve the problem, if the newsvendor knows the demand uncertainties (Table I) but does not know the demand curve for the coming week (Table II) a-priori. Assume no salvage value s = 0, so that any papers bought in excess of demand are simply discarded with no return.

Solution: In this problem, we want to find how many papers the vendor must buy (x) to maximize the profit. Let r be the effective sales and w be the excess which is going to be thrown away. This problem falls under the category of Stochastic Programming with recourse where there is action (x), followed by observation (*profit*),

and reaction (or recourse) (r and w). We know that any papers bought in the excess are just thrown away. It is obvious that we should minimize the waste but increase the sells. Our first instinct to solve this problem is to find the average demand and find the optimal supply x corresponding this demand. Since the average demand from theT able I is 70 papers, $x = 70$ should be the solution.

Table II
Weekly Demand

i	Day	Demand,(u) di
1	Monday	50
2	Tuesday	50
3	Wednesday	50
4	Thursday	50
5	Friday	50
6	Saturday	100
7	Sunday	140

However, with this solution where supply is 70 papers per day, the newsvendor will be making a loss of 50 cents per week. This probably is not the optimal solution. Can we do better? For that we need to propagate the uncertainty in the demand to see the effect of uncertainty on the objective function and then find the optimum value of x. The above information can be transformed for daily profit as follows.

$$Profit = -cx + 5=7s_p d_1 + 1=7s_p(x) + 1=7s_p(x)$$
$$if\ d_1 \le x \le d_2 \quad \ldots(1)$$
or
$$Profit = -cx + 5=7s_p d_1 + 1=7s_p(d_2) + 1=7s_p(x)$$
$$if\ d_2 \le x < d_3 \quad \ldots(2)$$

Notice that the problem represents two equations for the objective function, eqs. (1) and (2), making the objective function a discontinuous function and is no longer an LP. The optimal solution to this problem is x = d1 = 50 providing the news vendor with an optimum profit of 1750 cents per week.

The difference between taking the average value of the uncertain variable as the solution as compared to using stochastic analysis (propagating the uncertainties through the model and finding the effect on the objective function as above) is defined as the Value of Stochastic Solution, VSS. If we take the average value of the demand, i.e. $x = 70$ as the solution, we obtain a loss of 50 cents per week, therefore, the value of stochastic solution, VSS, is 1750 - (-50) = 1800 cents per week.

Now consider the case, where the vendor knows the exact demand (Table II) a-priori. This is the perfect information problem where we want to find the solution x_i for each day i. Let us formulate the problem in terms of x_i.

Maximize $Profit_i = -cx_i + Sales(r, w, d_i)$
x_i

$$Sales(r, w, d_i) = s_p r_i + sw_i \quad \ldots(3)$$
$$r_i = min(x_i, d_i)$$
$$= x_i,\ if\ x_i \le d_i \quad \ldots(4)$$
$$= d_i,\ if\ x_i \ge d_i \quad \ldots(5)$$
$$w_i = max(x_i - d_i, 0)$$
$$= 0,\ if\ x_i \le d_i \quad \ldots(6)$$
$$= x_i - d_i\ if\ x_i \ge d_i \quad \ldots(7)$$

Here we need to solve each problem (for each i) separately, leading to the following decisions shown in Table III.

Table III
Supply and Profit

i	Day	Supply, x_i	Profit, cents
1	Monday	50	250
2	Tuesday	50	250
3	Wednesday	50	250
4	Thursday	50	250
5	Friday	50	250
6	Saturday	100	500
7	Sunday	140	700
	Average Weekly	-	2450

One can see that the difference between the two values, (1) when the news vendor has the perfect information ($2450 cents per week) and (2) when he does not have the perfect information ($1750 cents per week) but can represent it using probabilistic functions, is the Expected Value of Perfect Information, EVPI. EVPI is 700 cents per week for this problem.

The focus of this article is to provide an overview of this area of optimization under uncertainty with applications to chemical manufacturing. The aim of the newsboy is to maximize expected profit in the face of demand and/or supply. Maximizing expected profit given that there are uncertainties associated with demand and supply is a classic problem in any manufacturing industry including the chemical industry[3]. However, decision making in chemical manufacturing is not restricted to just supply and demand cost minimization problems but involves models that are linear, nonlinear, and mixed integer in nature. Moreover, there are various kinds of uncertainties typically feature in the life cycle of the process.

1. *Uncertainty with Respect to the Model Parameters:* These parameters are a part of the deterministic model and not actually subject to randomness. Theoretically their value is an exact number. The uncertainty results from the impossibility of exactly modelling the physical behaviour of the system or a phenomena.
2. *Uncertainty in the Input Variables:* This kind of uncertainty originates from the random nature and unpredictability of certain process inputs. If the technology is new then.
3. *Uncertainty in the Initial Conditions:* These types of uncertainties result due to the complications for predicting the initial conditions of the operation.

In summary, the domain of optimization under uncertainty in chemical engineering requires techniques and algorithms from stochastic linear, nonlinear, mixed integer programming. Next section provides the background[a] followed by sections on methods and algorithms for uncertainty analysis and optimization, Section 5 is devoted to applications in chemical engineering and the last section provides the summary.

2 Background

The literature on optimization under uncertainties very often divides the problems into categories such as "wait and see", "here and now" and "chance constrained optimization"[7,8] In "wait and see" we wait until an observation is made on the random elements, and then solve the (deterministic problem). This is the "wait and see" problem of Madansky[9], originally called "Stochastic Programming" by Tintner[10], is not in a sense one of decision analysis. In decision making, the decisions have to be made "here and now" about the activity levels. The "here and now" problem involves optimization over some probabilistic measure - usually the expected value. By this definition, chance constrained optimization problems can be included in this particular category of optimization under uncertainty. Chance constrained optimization involves constraints which are not expected to be always satisfied; only in a proportion of cases, or "with given probabilities". These various categories require different methods for obtaining their solutions. It should be noted that many problems have both here and now, and wait and see problems embedded in them. The trick is to divide the decisions into these two categories and use a coupled approach.

2.1 Here and Now Problems

The "here and now" problems require that the objective function and constraints be expressed in terms of some probabilistic representation (e.g. expected value, variance, fractiles, most likely values). For example, in chance constrained programming, the objective function is expressed in terms of expected value, while the constraints are expressed in terms of fractiles (probability of constraint violation), and in Taguchi's off-line quality control method[11,12] the objective is to minimize variance. These problems can be classified as here and now problems.

[a]The background information in this article is based on the chapter entitled "Optimization Under Uncertainty" from Introduction to Applied Optimization[3].

The "here and now" problem, where the decision variables and uncertain parameters are separated, can then be viewed as:

$$\underset{x}{\text{Optimize}}\ J = P_1(j(x, u)) \qquad \ldots(8)$$

subject to

$$P_2\,(h(x, u)) = 0 \qquad \ldots(9)$$

$$P_3(g(x, u) \geq 0) \geq \alpha \qquad \ldots(10)$$

Fig. 1 Different Probabilistic Performance Measures (PDF)

Fig. 2 Different Probabilistic Performance Measures (CDF)

where u is the vector of uncertain parameters and P represents the cumulative distribution functional such as the expected value, mode, variance, or fractiles. Figs. 1 and 2 show the expected value, mode, variance, and fractiles for a probabilistic distribution function. These probabilistic functionals are used to define the objective function and constraints in stochastic optimization. To obtain the value of these uncertainty needs to be propagated through the deterministic model. The generalized treatment of such problems is to use probabilistic or stochastic models instead of the deterministic model inside the optimization loop.

Fig. 3a represents the generalized solution procedure, where the deterministic model is replaced by an iterative stochastic model with a sampling loop representing the discretized uncertainty space. The uncertainty space is represented in terms of the moments like the mean, or the standard deviation of the output over the sample space of N_{samp} as given by the following equations (eqs. (11) and (12)).

$$E(z(x, u)) = \sum_{k=1}^{N_{samp}} \frac{z(x, u_k)}{N_{samp}} \quad \ldots(11)$$

$$Var(z(x, u)) = \sum_{k=1}^{N_{samp}} \frac{z(x, u_k) - \bar{z})^2}{N_{samp}} \quad \ldots(12)$$

where $\bar{z}$ is the average value of z.

Is it possible to propagate the uncertainty using moments of input uncertainties (like mean, variance) thereby obtaining a deterministic representation of the problem? This is the basis of the chance constrained programming method, developed very early in the history of optimization under uncertainty, principally by Charnes and Cooper[13]. This is discussed in the next section.

Chance Constrained Programming Method

In the chance constrained programming (CCP) method, some of the constraints likely need not hold as we had assumed in earlier problems. Chance constrained problems can be represented as follows.

$$\underset{x}{\text{Optimize}}\ J = P_1(j(x, u)) = E(z(x, u)) \quad \ldots(13)$$

subject to

$$P(g(x) \leq u) \leq \alpha \quad \ldots(14)$$

In the above formulation, eq. (14) is the chance constraint. In chance constraint formulation, this constraint (or constraints) is (are) converted into a deterministic equivalent under the assumption that the distribution of the uncertain variables, u, is a stable distribution. Stable distributions are such that the convolution of two distribution functions $F(x\text{-}m_1 = \upsilon_1)$ and $F(x\text{-}m_2/\upsilon_2)$ is of the form $F(x\text{-}dmu/\upsilon)$, where m_i *amd* υ_i are two parameters of the distribution[14]. Normal, Cauchy, Uniform, and Chi-square are all stable distributions that allow the conversion of probabilistic constraints into deterministic ones. The deterministic constraints are in terms of moments of the uncertain variable u (input uncertainties).

Maranas *et al.*[15,16] have used chance constraint programming to solve eq. (1) a chemical synthesis problem for polymer design and eq. (2) a metabolic pathways synthesis problem in biochemical reaction engineering.

2.2 Wait and See

In contrast to here and now problems, which yield optimal solutions that achieve a given level of confidence, wait and see problems involve a category of formulations that shows the effect of uncertainty on optimum design. A wait and see problem involves deterministic optimal decisions at each scenario or random sample, equivalent to solving several deterministic optimization problems.

The generalized representation of this problem is given below.

$$\underset{x}{\text{Optimize}}\ Z = z(x, u^*) \quad \ldots(15)$$

subject to

$$h(x, u^*) = 0 \quad \ldots(16)$$

$$g(x, u^*) < 0 \quad \ldots(17)$$

where u^* is the vector of values of uncertain variables corresponding to each scenario or sample.

This optimization procedure is repeated for each sample or scenario of uncertain variables u and a probabilistic representation of the outcome is obtained. These methods are also referred to as parametric programming[17].

Fig. 3b represents the generalized solution procedure, where the deterministic problem forms the inner loop, and the stochastic modelling forms the outer loop. The difference between the two solutions obtained using the two frameworks is the Expected Value of Perfect Information (EVPI). The concept of EVPI was first developed in the context of decision analysis and can be found in classical references such as Raiffia and Schlaifer[18]. From Fig. 3 it is clear that by simply interchanging the position of the uncertainty analysis framework and the optimization framework, one can solve many problems in the stochastic optimization and Stochastic Programming domain[19]. (In the above problem, there was action (x), followed by observation (*profit*), and reaction (or recourse) (r and w). Recourse problems with multiple stages (similar to the multi-period problems in chemical engineering) involve decisions that are taken before the uncertainty realization (here and now) and recourse

Fig. 3 Pictorial Representation of the Stochastic Programming Framework

actions which can be taken when information is disclosed (wait and see). These problems can be solved using decomposition methods.

As can be seen from the above description, both here and now and wait and see problems require the representation of uncertainties in the probabilistic space and then the propagation of these uncertainties through the model to obtain the probabilistic representation of the output.

3 Uncertainty Analysis and Sampling

The probabilistic or stochastic modelling[20] iterative procedure involves:

1 Uncertainty quantification which involves specifying the uncertainties in key input parameters in terms of probability distributions,
2 Sampling the distribution of the specified parameter in an iterative fashion.
3 Propagating the effects of uncertainties through the model and applying statistical techniques to analyze the results.

3.1 Uncertainty Characterization & Quantification

In general, uncertainties can be characterized and quantified in terms of probabilistic distributions. 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. Further, a normal (Gaussian) distribution reflects a symmetric but varying probability of a parameter value being above or below the mean value. In contrast, lognormal 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 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 assume the upper and lower bound of uncertain variables and hence uniform distribution is the first step towards uncertainty quantification. Most of the papers in chemical engineering use this simplistic approach and use upper and lower bounds of uncertain variables. Few studies done in refs. [19,21,22] identified most likely values and use triangular distributions. Recently, Kim and Diwekar[23-24] used extensive data obtained from DECHEMA and obtained realistic quantification of uncertainties related to UNIFAC parameters. Fig. 4 show how the uncertainties in more than 1800 interaction parameters present in the UNIFAC model are collapsed in terms of three parameters, and characterized (quantified) using probability distribution functions.

Fig. 4 Characterizing uncertainties

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.

3.2 Sampling Techniques

One of the most widely used techniques for sampling from a probability distribution is the Monte Carlo sampling technique, which is based on a pseudo-random generator used 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. Crude Monte Carlo methods can result in large error bounds (confidence intervals) and variance. Variance reduction techniques are statistical procedures designed to reduce the variance in the Monte Carlo estimates[25]. Importance sampling, Latin Hypercube Sampling (LHS)[26, 27], Descriptive Sampling[68], and Hammersley Sequence Sampling[29,30] are examples of variance reduction technique. These methods are described below.

Importance Sampling

In importance Monte Carlo sampling, the goal is to replace a sample using the distribution of u with one that uses an alternative distribution that places more weight in the areas of importance. Obviously such a distribution function is problem dependent and is difficult to find. One of the examples of importance sampling in chemical engineering is the Metropolis criterion used in molecular simulations[31].

The following two sampling methods provide a generalized approach to improve the computational efficiency of sampling.

Latin Hypercube Sampling

The main advantage of Monte Carlo methods lies in the fact that the results from any Monte Carlo simulation can be treated using 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[32]. Moreover, the error of approximating a distribution by a finite sample depends on the equidistribution properties of the sample used for U(0,1) rather than its randomness.

Once it is apparent that the uniformity properties are central to the design of sampling techniques, constrained or stratified sampling techniques become appealing[33].

Latin hypercube sampling[26, 27, 34] is one form of stratified sampling that can yield more precise estimates of the distribution function. In Latin hypercube sampling, the range of each uncertain parameter X_i is sub-divided into non-overlapping 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 in a random manner (i.e., 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. In median Latin Hypercube (MLHS) this value is chosen as the mid-point of the interval. MLHS is similar to the descriptive sampling described in ref.[28]. In Chemical Engineering LHS is used in early stochastic modelling and optimization frameworks[19,20,35].

The main drawback of this stratification scheme is that, it is uniform in one dimension and does not provide uniformity properties in k-dimensions. Sampling based on quadrature[36], cubature techniques[37], or collocation techniques[38] face similar drawback. 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. However, this transformation is possible only for limited distribution functions when the uncertain variables are tightly correlated. For highly correlated samples similar to what has been observed in thermodynamic phase equilibria, a sampling technique based on confidence region estimates[39] can be used.

Hammersley Sequence Sampling

Recently, an efficient sampling technique (Hammersley sequence sampling) based on Hammersley points has been developed Kalagnanam and Diwekar[29, 30], 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 multi-dimensions, unlike Monte Carlo, Latin hypercube, and its variant, the Median Latin hypercube sampling techniques. A qualitative picture of the uniformity properties of the different sampling techniques on a unit square is presented in Fig. 5. It is clearly observed that HSS shows greater uniformity than other stratified techniques such as LHS, which are uniform along a single dimension only and do not guarantee a homogeneous distribution of points over the multi-variate probability space. Similar behaviour is observed for correlated samples also. The implementation of correlation structures is based on the use of rank correlations[27, 34]. Some of the new variants of HSS include the HSS2 and Latin Hypercube Hammersley Sampling (LHHS)[40, 41].

Fig. 5 Sample points (100) on a unit square using (a) crude Monte Carlo sampling and (b) the Hammersley sequence sampling technique

4 Optimization Algorithms

World War II made scientists aware of numerical optimization and solutions to physics and engineering problems. Now, numerical optimization techniques constitute a fundamental part of theoretical and practical science and engineering as can be seen from the number of papers published each year in literature. Although in real world systems uncertainties cannot be ignored, the literature on optimization under uncertainty methods and/or applications is sparse as compared to any other optimization area. This can be attributed to the fact that in optimization under uncertainty area, one has to pay attention to uncertainty analysis as well as optimization. Last section described algorithms and methods for uncertainty analysis. This section presents the algorithms for Stochastic linear, nonlinear, and discrete optimization problems.

4.1 Decomposition Algorithms

Even a linear problem in optimization under uncertainty (e.g. the newsboy problem) results in nonlinearities (discontinuous function) due to the probabilistic functional. Decomposition methods is a common approach to solve such problems. In decomposition approach, the problem is decomposed into a master problem and a subproblem. The master problem is a simplified (usually) linear approximation of the complete problem and this approximation is derived from number of subproblems. First proposed for mixed integer problems Bender's decomposition[42] forms the basis for decomposition algorithms proposed for deterministic mixed integer programming and stochastic linear as well as mixed integer programming problems[43, 44]. The two main algorithms commonly used in the stochastic programming literature for stochastic linear (and mixed integer) programming with fixed recourse are the L-shaped[45-47] and the stochastic decomposition method[48,49]. The L-shaped method is used when the uncertainties are described by discrete distribution. On the other hand, the stochastic decomposition method uses sampling when random variables are represented by continuous distribution functions. Although chemical engineering applications involve large number of Stochastic linear programming (and Stochastic MILP) problems, researchers in chemical engineering have not exploited these generalized algorithms. On the other hand, chemical engineering researchers[6,50,51] have used specific structure of a particular problem (e.g. flexibility.) to derive different decomposition schemes and/or bounds[52]. The domain (flexibility) specific nature of the problem restrict the applicability of these methods.

4.2 Stochastic Nonlinear Programming

Since engineering models are usually nonlinear, and uncertainties are not restricted to uniform or normal distributions, the algorithms and approaches presented above have restrictions that limit their application potential to large-scale problems in the various domains of chemical engineering. In order to develop a more general approach, Sahin and Diwekar[53,54] proposed the Better Optimization of Nonlinear Uncertain Systems (BONUS) algorithm, which uses sampling and replaces the inner model evaluation loop with a reweighting scheme, as shown in Fig. 6. Deterministic nonlinear programming (NLP)

Fig. 6 Density estimation approach to optimization under uncertainty

problems use quasi-Newton's methods and require calculation of derivatives with respect to each decision variable, at each optimization iteration. These methods are widely used and the codes are made robust over the years. BONUS extends these algorithms to stochastic nonlinear programming problems. BONUS provides significant reductions in model iterations.

4.3 Discrete Optimization under Uncertainty

Many chemical engineering applications like chemical synthesis, process synthesis under uncertainty, and planning under uncertainty involve discrete decision variables (mixed integer problems). Although decomposition methods have been used to solve these problems, the applicability of these algorithms to solve problems of real world scale is very limited as also indicated by Birge in his recent review on stochastic programming[55]. This is mainly due to the fact that most of these methods rely heavily on convexity conditions and simplified approximations of the probabilistic functions containing uncertainties. Variants of probabilistic methods like the Stochastic Annealing algorithm[56] show great promise in this regard. Stochastic annealing and its recent variants (described briefly below) have been used to solve real world problems such as (1) nuclear waste management problem[57], (2) computer aided molecular design polymer design under uncertainty[58], (3) greener solvent selection[24], and (4) methylene chloride process synthesis[59]. This algorithm is described below.

Stochastic Annealing: An Efficient Algorithm for Combinatorial Optimization under Uncertainty

The Simulated Annealing algorithm described in Chapter 4 is used for deterministic optimization problems. The Stochastic Annealing algorithm[b]. is a variant of Simulated Annealing[56,57,60], and is an algorithm designed to efficiently optimize a probabilistic objective function. In almost all stochastic optimization problems, the major bottleneck is the computational time involved in generating and evaluating probabilistic functions of the objective function and constraints. For a given number of samples (N_{samp}) of a random variable (u), the estimate for the mean or expected value ($\bar{u}$) and the unbiased estimator for standard deviation (s) can be obtained from classical statistics[61]. For example, the error in the calculation of the expected value decreases as N_{samp} increases and is given by:

$$\varepsilon_{\mu} \alpha (N_{samp})^{-0.5} \quad \ldots(18)$$

The accuracy of the estimates for the actual mean (μ) and the actual standard deviation (σ) is particularly important to obtain realistic estimates of any performance or economic parameter. However, this accuracy is dependent on the number of samples. The number of samples required for a given accuracy in a stochastic optimization problem depends upon several factors, such as the type of uncertainty, and the point values of the decision variables[56]. Especially for optimization problems, the number of samples required also depends on the location of the trial point solution in the optimization space. Fig. 7 shows how the shape of the surface over a range of uncertain parameter values changes since one is at a different iteration (different values of decision variables) in the optimization loop. Therefore, the selection of the number of samples for the stochastic optimization procedure is a crucial and challenging problem. A combinatorial optimization algorithm that automatically selects the number of samples and provides the trade-off between accuracy and efficiency is presented herewith.

In the Stochastic Annealing algorithm, the optimizer (Fig. 3a) not only obtains the decision variables but also the number of samples required for the stochastic model. Furthermore, it provides the trade-off between accuracy and efficiency by selecting an increased number of samples as one approaches the optimum. In Stochastic Annealing, the cooling schedule is used to decide the weight on the penalty term for imprecision in the probabilistic objective function. The choice of a penalty term, on the other hand, must depend on the error band-width of the function that is optimized, and must incorporate the effect of the number of samples.

The new objective function in Stochastic Annealing, therefore, consists of a probabilistic objective value P and the penalty function, which is represented as follows:

$$\text{Min}Z(cost) = P(x, u) + b(t)\ \varepsilon_{p} \quad \ldots(19)$$

In the above equation, the first term represents the real objective function which is a probabilistic function in terms of the decision variables x and uncertain

[b] By "Stochastic Annealing" we refer to the annealing of an uncertain or stochastic function. It must be realized that the Simulated Annealing algorithm is a stochastic algorithm inherently, since the moves are determined probabilistically. However, for our purposes, we will refer to the annealing of a deterministic objective function simply as Simulated Annealing

Fig. 7 Uncertainty Space at Different Optimization Iterations

variables u, and all other terms following the first term signify the penalty function for error in the estimation.

The weighting function $b(t)$ can be expressed in terms of the temperature levels. At high temperatures, the sample size can be small, since the algorithm is exploring the functional topology or the configuration space to identify regions of optima. As the system gets cooler, the algorithm searches for the global optimum; consequently it is necessary to take more samples to get more accurate and realistic objectives/costs. Thus, $b(t)$ increases as the temperature decreases. Based on these observations, an exponential function for $b(t)$ can be devised as:

$$b(t) = \frac{b_o}{k^t} \qquad \ldots(20)$$

where b_o is small (e.g., 0.001), k is a constant which governs the rate of increase, and t is the temperature level. Remember that as the temperature level t increases the annealing temperature T decreases.

The Stochastic Annealing algorithm reduces the CPU time by balancing the trade-off between computational efficiency and solution accuracy by the introduction of a penalty function in the objective function. This is necessary, since at high temperatures the algorithm is mainly exploring the solution space and does not require precise estimates of any probabilistic function. The algorithm must select a greater number of samples as the solution nears the optimum. The weight of the penalty term, as mentioned before, is governed by $b(t)$, and is based on the annealing temperature. For example, for the nuclear waste management problem reported by Chaudhuri and Diwekar[57], the CPU time was reduced from approximately 20 days to 18 hours using a variant of the original stochastic annealing[56]. The recent variant called Hammersley Stochastic Annealing reduces the computational time further[62].

5 Applications

Problems in chemical engineering are linked to the life cycle of the process that extends from raw material selection (chemical synthesis), process development (process synthesis and design) through the planning and management of the production process as shown in Fig. 8. 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 unit operations and connections. In general, process design activities start at this level and process simulation, which is shown to be the last step in computer aided process design, predicts the behaviour of the process if it was constructed. Incorporation of pollution prevention, operability, and other concepts into design and development at the initial stages lead to processes that are less cost intensive, thereby reducing the technical and economic risks. Therefore, process synthesis remains an important step in analyzing and designing environmentally benign processes. In recent years, researchers have also realized the importance of including the chemical synthesis in the process design, and methods for solvent selection, molecular design are gaining importance[24]. Most of the current systems analysis approaches focus on the simulation step. This is because several simulation programs (like the ASPEN simulator used in chemical industries[63] and models are available to describe these basic phenomena. However, this is the last step in decision making, as it predicts the behaviour of the plant (or strategy) if it was constructed (or implemented). As the envelope extends to include process synthesis, chemical synthesis, or management and planning considerations, the ability to include uncertainties become important. The left hand corner of the figure shows the objectives or goals of this integrated design

process. Unlike the traditional process design where engineers are looking for low cost options, objectives of optimization in this framework is not restricted to maximizing profit but includes several other criteria like reliability, flexibility, operability, controllability, environmental and ecological impacts, safety, and quality need to be considered at the different stages of analysis as described in the next section.

5.1 Stochastic Objectives and Constraints

The formulation of objective function is one of the crucial steps in the application of optimization to a practical problem[64]. This subsection is devoted to the different stochastic objectives and constraints used in various chemical engineering applications.

The earliest work related optimization under uncertainty in chemical engineering used the "here and now" formulation where expected value of cost is used as the objective function for a given level of risk[65-67]. Soon researchers realized the importance of including operability considerations like feasibility and flexibility[68-71] in the optimal design problem. Flexibility is concerned with the problem of ensuring feasible steady-state operation over a variety of operating conditions. On the other hand, reliability is concerned with the probability of normal operation given that failures can occur, while safety is concerned with hazards that are consequence of failure. The other aspects of operability are controllability which is dealing with the concept of quality and stability of the dynamic response of the system.

Earlier approaches to obtaining flexible design dealt with finding over design factors[67]. By introducing the concept of flexibility index, Swaney[71] provided a well structured optimization problem that could be easily converted to a mini-max deterministic problem. This concept formed the basis for large number of papers in this area and is explained below. Flexibility index is defined as a scaler matrix whose value for any fixed design characterizes is equal to the size of the region of feasible operation in the space of uncertain parameters. The basic assumption behind the definition of flexibility index is that the uncertainty parameters are varying within upper and lower bounds with equal

Fig. 8 Uncertainty Space at Different Optimization Iterations

probability (equivalent to uniform distribution). These parameters are assumed to be varying independently. Geometrically, this approach corresponds to inscribing within the feasible region a hyper-rectangle which is centered at the nominal point. The size of the feasible region is then characterized by the lengths of the sides of the rectangle, which in turn define the lower and upper bounds of the parameter. This hyper-rectangle then defines the actual ranges for each uncertain parameter over which the feasible operation can be guaranteed. The maximum hyper-rectangle that can expand around the nominal parameter point touches the boundary at a vertex of the hyper-rectangle. Straub[36] extended this concept further to stochastic flexibility expressing it in terms of probability of feasible operation. The design for "optimal flexibility" falls under the category of "here and now" problem. On the other hand, the flexibility index or stochastic flexibility with multiperiod optimization problems involve "wait and see" decisions and solution of a deterministic optimization problem for each scenario so that one gets a probabilistic representation of optimal solutions.

The problem of flexibility is studied extensively in the chemical engineering literature. In fact many researchers use flexibility synonymous to uncertainty analysis. For example, in a recent paper Hene *et al.*[17] categorize solution techniques for optimization under uncertainty into three categories, namely, (1) multiperiod, (2) stochastic programming, and (3) parametric programming. It should be noted that these categories are related to the "optimal flexibility" and "flexibility index" problems and cannot be generalized for all optimization under uncertainty problems in engineering or operations research. Further, it should be remembered that the flexibility is one of the concept in this field and is still an abstract measure as pointed out in a recent paper by Pekny[72]. It is easy to understand that why problem of flexibility gained so much attention in the chemical engineering literature. This problem is a well structured problem amenable to solutions using deterministic approaches with decomposition[6,50,51] or using new approximation to derive the probabilistic functions describing the effect of uncertainties[73]. Further, the concept of flexibility is also extended to include reliability and controllability in a similar fashion, demanding similar approaches. However, controllability also deals with the concept of quality control. This concept is derived from quality engineering and is described below.

The aim of control system is to keep the process output specifications on target, despite changes in the process input. In such an approach, the control engineer is often presented with difficult control problems that may require extensive and expensive modifications to both process and control system hardware to obtain satisfactory performance of the control system. Furthermore, the effectiveness of the control system is highly dependent upon the nominal values of the operating variables and the mechanical design which are set by the designer of the processing unit. Parameter design methodology is an off-line quality control method, popularized by G Taguchi[11], for designing products and processes that are robust to uncontrollable variation at the design stage. In parameter design, Taguchi's stated objective is to find settings of the product or process design parameters which minimize an average quadratic loss function defined as the average standard deviation of the response from a target value. The rapid growth of interest in the Taguchi approach over the last few years led to a great expansion in the number of published case studies relating to different areas of industrial activities[74]. Although the popularity of Taguchi approach seems to be pervasive in all engineering branches, application of this procedure to chemical industries has not been widely reported until 1990. Boudriga[75] presented one of the first systematic studies of using different statistical approaches to the problem of off-line quality control for chemical processes. Diwekar and Rubin[12] posed this problem as a stochastic optimization problem where the objective is to minimize output variance from the specified nominal value. This approach is the basis of robust design. Recently, a similar approach (objective function) was used for dynamic models[76]. However, this approach is derived from financial literature using the mean-variance optimization models for portfolio optimization[77].

In view of growing environmental concerns, there is a critical need for designing large chemical processes with environmental considerations. Earlier design under uncertainty studies[19,21] focused on design for environment, included environmental considerations as probabilistic constraints in terms of risk of exceeding the specified emission limits. These papers considered the end-of-pipe treatments like new environmental control technology designs. Nowadays, industries are practicing the art of pollution prevention, which 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. This also means instead of including environmental considerations as constraints, they should be included as objectives like minimum environmental impacts. Environmental impacts can be classified in terms several indexes related to ozone depletion, global warming potentials, human and aquatic toxicity, photochemical oxidation, and acid rain potentials. Current methodologies, such as the generalized waste reduction algorithm (WAR), provide a first step towards evaluating these impacts[78, 79] (Table IV). However, the problem of uncertainties becomes more important than before when one has to address the issues of accuracy and the relative weights of these impact indexes. Environmental impacts must also be weighted and balanced against other concerns, such as their cost and long-term sustainability. These multiple, often conflicting, goals pose a challenging and complex optimization problem, requiring multi-objective optimization under uncertainty as considered in some recent papers[59,78,80].

Table IV
Environmental Impacts in the WAR Algorithm

Name	Meaning
HTPI	human toxicity potential by ingestion
HTPE	human toxicity potential by exposure
ATP	aquatic toxicity potential
TTP	terrestrial toxicity potential
PCOP	photochemical oxidation potential
ARP	acid rain potential
GWP	global warming potential
ODP	ozone depletion potential

Environmental considerations are also translated into specific objectives for problems like expected value of solvent selectivity in the solvent selection problem[23,24], and minimizing expected value of "glass" formed in vitrification of nuclear waste problems[57].

5.2 Chemical Synthesis

Chemical synthesis involves search for molecules possessing desired physical, chemical, biological and health properties for easy manufacture of products. Group contribution methods rely on experimental data and theoretic formulations to assign numerical values to chemical groups, which form the basis building blocks for computer aided chemical synthesis. By combining these building blocks, it is possible to determine a wide range of characteristics for any given chemical. The reverse approach, Computer Aided Molecular Design (CAMD) uses group contribution techniques to determine physical characteristics by generating test molecules using primary building blocks.

A basic diagram of CAMD is shown in Fig. 9, where there is a set of groups as a starting point. These groups are uniquely designed to generate all possible molecules by exploring all combinations. The properties of each group and/or the interaction parameters between groups can be theoretically calculated, experimentally obtained, or statistically regressed. For example, from this set of groups, solvent molecules can be generated by group combinations. Once molecules are generated, the properties of the molecules are predicted based on the properties of their groups in order to determine whether or not they satisfy the specified criteria. This method can generate a list of candidate solvents with reasonable accuracy within a moderate time scale. There are three main CAMD approaches: generation-and-test, mathematical optimization, and combinatorial optimization approaches. All methodologies for CAMD are exposed to uncertainties that arise from experimental errors, imperfect theories or models and their parameters, improper knowledge, or ignorance of systems. In addition, available group parameters may not be present, and current Group Contribution Models (GCM) cannot estimate all necessary properties. However, only a few papers have focused on uncertainties in CAMD and these are described below.

Maranas[15] has developed a technique for designing polymers under uncertainty. This approach uses MINLP formulations, where the chance constraints represent the probability of meeting the target values. Following traditional Chance constrained programming techniques, a deterministic equivalent is obtained. Two formulations are presented: (1) Stochastic Property Matching, identifies molecules that meet all characteristics with a given probability α, (2) Stochastic Property Optimization determines the molecules that have a maximum value for a given property with probability α while all other probabilities are met with given probability β. Tayal and Diwekar[58] presented a generalized framework to solve the same polymer design problem based on HSS sampling and stochastic annealing. The framework allowed them to study; (1) impact of uncertainties, (2) effect of various probability distributions including stable and non-stable distributions (as CCP

Fig. 9 A basic diagram of CAMD based on group contribution methods

does not allow non-stable distributions), mixed distributions, and (3) different forms of objective functions. The framework presented a set of solutions to choose from instead of a single optimal solution, providing flexibility to the designer.

Sinha *et al.*[81] proposed that locally optimal solutions to the traditional CAMD problem are potential sources of uncertainties. To bypass this, a global optimization algorithm is presented. The CAMD is modelled as a MILP, and a case study is presented.

Kim and Diwekar[23,24] have analyzed solvent selection using a CAMD approach that selects environmentally benign molecules through group combination tools. This is the first study where the uncertainties in group contribution methods are systematically characterized using available literature and experimental data. New variants of stochastic annealing are developed and used to find environmentally benign solvents. They also coupled process synthesis along with chemical synthesis to obtain environmentally friendly and cost effective solutions[82].

5.3 Process Synthesis and Design

Process synthesis translates the chemical synthesis to a chemical process. It involves decisions about process unit operations and connections. In general, process design activities start at this level and process simulation, which is shown to be the last step in computer aided process design, predicts the behaviour of the process if it was constructed.

One of the main goals in synthesis problems is to establish methodologies for selecting optimal flowsheet configurations. Approaches to process synthesis problems essentially fall under the following areas:

1. Thermodynamic approach.
2. Evolutionary methods.
3. Heirarchial approach, based on intuition and engineering judgment.
4. Optimization approach based on mathematical programming techniques.

The optimization approach to process synthesis involves (a) formulation of a conceptual flowsheet incorporating all the alternative process configurations (superstructure) and (b) identification of an optimal design configuration based on optimal structural topology and the optimal parameter level settings for a system to meet specified performance and cost objectives. Once the superstructure is known, combinatorial optimization methods like MINLP algorithms can be used to solve the synthesis problem. The first step in the solution of the process synthesis problem is to develop the superstructure containing all alternative designs to be considered for the optimal solution. The design of new processes are, however, complicated by the fact that technical and economic uncertainties arise, which lead to uncertainties in the prediction of plant performance and overall plant economics. An example where such technical and economic uncertainties occur and are not treated or characterized rigorously, is in the design of integrated environmental control processes for advanced power systems[20]. Since the conceptual design of any chemical process involves the identification of possible flowsheet configurations, design methods must also address the issues of process synthesis under uncertainty, as it has important implications on process viability, and other quality measures such as controllability, safety, and environmental compliance.

The literature in the area of process synthesis and process design under uncertainty have been concentrated

on two focused application areas: (1) pollution prevention by design, and (2) designing for flexibility.

The earlier papers in design under uncertainty with pollution prevention focus dealt with integrated environmental control systems for coal based power systems. The work continued and extended to address synthesis problems in this area[19-21]. Nuclear waste management posed a very hard synthesis problem[83]. This is a large scale, real world problem related to the environmental restoration of Hanford site. Conversion of high-level radioactive waste into glass is crucial to the disposal of toxic waste dumps generated over 40-50 years at the Hanford nuclear waste site. The procedure essentially consists of mixing the sources of wastes into blends, to which appropriate glass formers (frit) is added to make glass. The objective is to maximize the amount of wastes per glass log, by keeping the amount of frit added to a minimum. Processibility and durability conditions require that certain restrictions on crystallinity, solubility and glass properties are met. Increasing the number of wastes, increases the combinatorial size of the problem. The combinatorial, non-convex nature of the problem was hard to solve even for the deterministic optimization methods. Uncertainties associated with the tank contents and models caused further problems and demanded new algorithms[57]. The new stochastic annealing algorithm provided optimal and robust solution to this problem in the face of uncertainties with reasonable computational time. A multi-objective extension of this problem to include policy aspect was possible due to these new algorithms. Dantus and High[59] also used this new algorithm for methylene chloride process synthesis.

As stated earlier, process flexibility is an area that received significant attention, as it ensures that processes are operational and safe when exposed to variations in operating conditions. The studies include distillation network design, heat exchanger network synthesis[51], reactor network synthesis[73], and batch processing plant design and operation for waste treatment[84].

5.4 Management Scheduling and Planning

Most the problems in management, scheduling, and planning include combinatorics (discrete choices and decisions) and uncertainties. Pekny recently reviewed this area in his paper entitled “Algorithms architectures to support large-scale, process systems engineering applications involving combinatorics, uncertainty, and risk management[72]. These problems belong to batch processing due to time dependent nature of these chemical processes. Batch processing is generally used in high-value added, low volume speciality chemicals and pharmaceuticals. Uncertainties abandon in batch plant operation. Although batch processing is faced with all kinds of uncertainties, most of the literature in this area deal with demand uncertainties.

In general the scheduling problem is to determine a time-based assignment of tasks to equipment so that no process constraints are violated. The problems in the domain of process scheduling and planning can be conveniently described by resource-task-equipment network. The process design and retrofit problems adds longer time horizons to the scheduling problems and includes decisions regarding additions of equipments. Supply chain management problems extends the scheduling problem in the spatial dimension and considers the coordinated management of multiple facilities and the shipment of materials through an associated transportation network. The product and research pipeline management problem has much overlap both with supply chain management and process scheduling problems. These problems are closely related to pharmaceutical industries where new drugs and products are invented regularly. Obviously these problems have great deal of uncertainty. Research management in general is also related to prioritization and reducing uncertainties. The chemical engineering literature is concentrated in problems in batch scheduling and planning including design and retrofit problems. For details, please see ref.[72]. Supply chain management problems are rare[85], and research management problems have only recently being studied in our domain[22,86,87].

6 Summary

Optimization under uncertainty involve probabilistic objective functions and constraints. These problems can be categorized as (1) here and now problems, and (2) wait and see problems. Many problems involve both here and now, and wait and see decisions. The optimization under uncertainty problems encountered in chemical engineering are complex, and models involved are linear, nonlinear, and discrete in nature. These problems require variety of algorithms and methods to solve for complete array of decisions related to various stages of design and analysis. Apart from expected profit and cost, chemical engineering literature considered various performance indices for

operability, environmental considerations, and quality control. Flexibility and feasibility objectives are most prominently figured in chemical design due to the specific problem structure presented by these performance measures. Uncertainties are inherent in design, operation, control of chemical plants and in the future we will see many articles in the area of uncertainty characterization and quantification, new algorithms for discrete and nonlinear optimization under uncertainty, and multi-objective considerations.

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