From Nonlinear Programming Theory to Practical Optimization Agorithms: A Process Engineering Viewpoint

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FROM NONLINEAR PROGRAMMING THEORY TO PRACTICAL OPTIMIZATION ALGORITHMS: A PROCESS ENGINEERING VIEWPOINT

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As process optimization becomes an established and mature technology for process simulation, analysis and operation, it becomes important to consider larger and more creative problem formulations and applications, as well as the development of efficient algorithms to tackle them. Here, some novel process optimization applications are briefly reviewed in the following areas of process design and analysis:

- ***treatment of constrained and nonsmooth simulation problems, particularly in phase equilibrium***
- ***synthesis of chemical reactor networks through the application of targeting strategies***
- ***more efficient strategies for process optimization and postoptimality analysis***
- ***treatment of uncertainty through multiperiod optimization problems***
- ***the role of automatic differentiation tools in process optimization***

An outline of the concepts behind each of these topics will be presented and process examples are briefly described in order to demonstrate the effectiveness of these optimization-based applications.

Introduction

Over the last few years there has been renewed interest in optimization methods for a broad range of tasks in process engineering. Process optimization has always been a natural task for every process engineer, but only recently have reliable and efficient optimization tools been integrated into the engineers toolkit. As these tools are further applied, the size and complexity of the applications will certainly increase, but also the types of applications will change, much the same way that the scope of process simulation has evolved and broadened. In particular, the efficient performance of optimization tools will sharpen optimization problem formulations from vague, poorly defined descriptions to precise and clear tasks. Moreover, with frequent application the purpose of an optimization study will shift from a single optimal design to a decision-making tool where "what-if' questions can be explored at a higher level

In this paper, a few applications and examples are described to reflect this philosophy and to highlight recently developed optimization approaches for novel and untypical applications. A special class of optimization algorithms, Successive Quadratic Programming with reduced space decomposition, was reviewed in Biegler (1992) and Schmid and Biegler (1992). An important aspect of these algorithms is that they can be tailored to the structure of specific process applications, such as separation and reaction systems. Because of the availability and easy applications of these and other related optimization tools, new problems and applications can be addressed readily. In this paper, for example, through relatively simple reformulations with optimization methods, results are obtained on problems that are difficult to handle with existing simulation tools. In the following sections we consider a number of process applications that are not normally considered through an optimization framework. For these we stress the use of optimization strategies as a tool that guides decision-making *at a higher level* and handles many of the tedious lower-level decisions automatically.

In the next section, we consider the application of Successive Linear Programming strategies for constrained *simulation* problems. Here a process simulation problem can easily incorporate variable bounds and inequality constraints. Moreover, many combinatorial aspects of simulation problems including nonsmooth functions, checkvalves in flow networks and phase changes in vapor-liquid equilibrium can be addressed through the addition of inequalities and linear penalty terms. A constrained simulation method is briefly summarized with examples. In addition, simulations of a column *below* the minimum reflux ratio are described.

Section three then explores a different approach to reactor network synthesis, based on targeting concepts driven by nonlinear programming. Over the last decade, process synthesis has yielded a wealth of applications for novel optimization-based strategies; examples abound for energy and separation networks. While a survey of process synthesis is beyond the scope of this paper, the concept of attainable regions is outlined here for reactor networks. To aid in this synthesis process, simple nonlinear programs are formulated to explore the attainable region in higher dimensions. Moreover, this optimization-based approach can be integrated within larger process problems in order to synthesize a reactor network that accounts for interactions with the flowsheet.

Section four deals with flowsheet optimization and briefly sketches the advantages of obtaining analytic derivatives from the process simulator. Here, benefits for optimization include drastic reductions (up to 80%) in computational effort, in addition to more reliable performance. There is also an important side benefit, a straightforward and cheap method for post-optimality analysis. Based on the structure of reduced Hessian methods, sensitivity of the optimal flowsheet is obtained with, at most, a few additional flowsheet passes. This analysis yields second order sufficiency tests, directions along which the objective function is insensitive or nonunique, and changes in the minimizer as a result of changes in external parameters. A typical process example is summarized for illustration. With this capability, one can also consider the related problem **of** optimization under uncertainty, and formulate it as **a** multiperiod design problem. Here each design scenario is **incorporated as a** set **of constraints in the optimization problem and a much larger problem results. Fortunately, efficient decomposition strategies have been developed for these problem classes so that the computational effort increases only linearly with the number of periods.**

Finally, the paper concludes with a brief summary of future developments and directions. These can be classified as better methods and interfaces for optimization modeling as well as a changing perspective toward optimization as a tool for a broad range of process applications. This change is driven by the awareness of better tools coupled with a shift in the designer's education, from optimization methods to more sophisticated problem formulations.

Constrained Simulation through Successive Linear Programming

For the past thirty years, Newton's method has been the standard algorithm for solving nonlinear equations in process engineering. Through clever problem implementation and initialization, it is virtually the only method used for large-scale, equation-oriented process simulations. While this method has generally been successful, its disadvantages are also well-known. In particular, poor starting points, ill-conditioned problems and singularities lead to poor performance and failure of the method. Moreover, on typical process problems ($h(x) = 0$) the variables, x, are usually confined to physically well-defined regions (e.g., lower and upper bounds, $1 \leq x \leq u$) and inequality constraints ($g(x) \leq 0$) can often be derived in order to isolate desirable solutions. Such restrictions are difficult to incorporate systematically within a Newton solver; therefore we consider an algorithm where we replace the linear equations within each Newton iteration, $h(x^k) + Vh^T(x^k)(Ax) = 0$, with the following linear program (LP):

$$\begin{aligned} \underset{d}{\text{Min}} \quad & \sum_j (P_j^+ + n_j) \\ \text{st} \quad & h(x^k) + Vh^T(x^k)\, d = p - n \\ & l \leq x^k + d \leq u \\ & p,\ n \geq 0 \end{aligned} \qquad (1)$$

where p and n are artificial variables that are forced to zero at the solution and d is the search direction in x. Duff et al. (1987) developed an LP-based algorithm that uses a trust region approach. For bounded regions, we also note that global convergence can also be enforced through a line search procedure. Moreover, Bullard and Biegler (1991) proved the following properties for a Constrained Successive Linear Programming (CSLP) algorithm:

•*The algorithm converges quadratically (as fast as Newton's method) near the solution*

•*The merit function* $\backslash L(X) = \sum_j T\ |hj\ (xj)| + \pounds g_k(*i)_+$ *will at a^wa y^s decrease for d^O.*

•*A descent direction d and improved points can always be obtained for a non-zero solution of the LP*

•*The algorithm terminates at a non-solution point only in the case of a pseudosolution, in which d = 0 and \i(xi) *0. Systematic methods to recover from pseudosolutions are described in Bullard and Biegler (1991).*

Thus, while there is no guarantee that the method will converge under all conditions (a global optimization algorithm is required for this.) the approach can handle most singularities and always remains within variable bounds. In Bullard and Biegler (1991) we provide a summary of this approach on 68 test cases, many of which are process examples. Here we compared the CSLP approach with the results reported in Buzzi-Ferraris and Tronconi (1986) and Swaney and Wilhelm (1989); in most cases our results were quite favorable. In addition, results are obtained for MINOS (which for these problems is essentially a sparse Newton solver). Here CSLP was successful on all problems while MINOS fails on 23. Also, our approach required fewer function evaluations than MINOS on 42 out of the remaining 45 problems.

In addition, the constraint handling features of **CSLP lend** another advantage **to** process simulation. Here process **equations and** relations with **nonsmooth terms (e.g., absolute values, floor functions** and **max operators) can cause difficulties for Newton-based solvers. On the other hand, these can** be **handled through straightforward reformulations that involve inequality constraints in CSLP. For example, an absolute value term in y can be rewritten as z = max(y,-y) and reformulated by the** following inequalities:

$$z \pounds\ y, \quad z \pounds -y, \quad (Xi-X_2)y \wedge\ z, \quad 0 \leq X i, X_2 \leq l \qquad (2)$$

Note that the *X* variables ensure that at least one of the elements in the max operator is active. This approach was applied in Bullard and Biegler (1992a) to pipe networks with (on/off) checkvalves as well as fluid flow problems with laminar/turbulent transitions. In both cases, combinatorial decisions in the model are made automatically through appropriate constraint activity from the max operators. As a result, only a single simulation is required here and no corrective decisions are needed by the designer. Moreover, the number of CSLP iterations (equivalent to Newton iterations) required for these problems is similar to those for the corresponding "smooth" simulation.

Finally, we consider a simplified case of vapor-liquid equilibrium where transitions may occur from/to one and two phase regions. Within a modular simulation engineering such problems are handled procedurally by first calculating bubble and dew points. In nonprocedural environments (e.g. equation oriented steady-state, multi-stage or dynamic), this becomes much more difficult and expensive to handle. Using a penalty successive linear programming (PSLP) formulation, on the other hand, one can derive a simple, automatic strategy to handle phase transitions. This approach is supported by two arguments:

•the PSLP approach is equivalent to performing a Gibbs free energy minimization of the vapor-liquid system. This was proved in Bullard and Biegler (1992b) and can also be extended to more complex multi-phase systems

•the PSLP approach can be visualized intuitively by introducing a new parameter (such as a *pseudo-pressure)* and observing that in the single and two phase regions a consistent set of equations results. As a result single phases can be viewed as bubble or dew points evaluated at "pseudo-

pressures".

Here we summarize this approach and illustrate it with some simple examples.

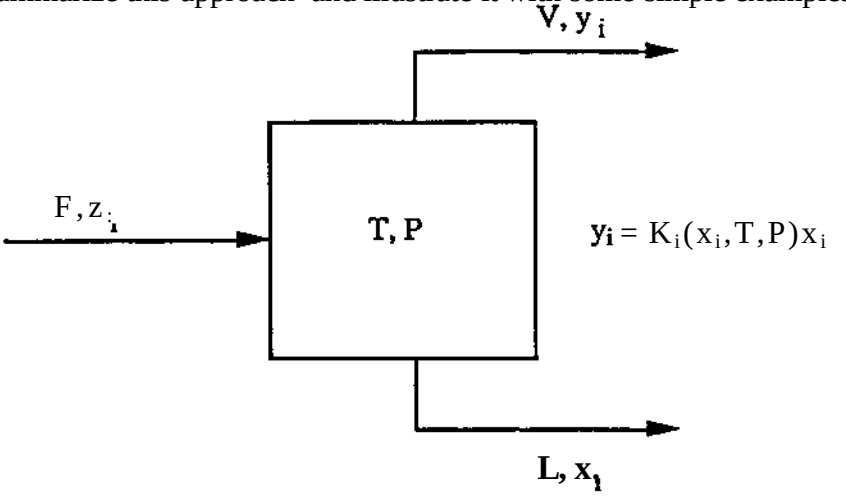

Figure 1. Isothermal flash operation.

Consider the simple flash unit in Figure 1 with the following set of vapor-liquid equilibrium equations. For the moment we assume that vapor fugacity and liquid activity coefficients are independent of pressure (in a more general formulation this assumption is not required). Here we have:

$$z_i F - x_i L + y_i V = 0, \qquad i = 1,\ldots n$$
$$F-(L + V) = 0 \qquad (3)$$

$$y_i - K_j(P, T, x)\, x_i = 0, \qquad i = 1,\ldots n$$
$$\sum_{i=1}^{n} y_i = 0 \qquad \sum_{i=1}^{n}$$

where the notation is defined from Figure 1. Introducing a pseudo-pressure variable, Pp. within the equilibrium expression and its absolute deviation (5) from the specified pressure, Ps,leads to the following relations:

$$\delta \geq P_S - P_P \qquad (4)$$
$$\delta \geq P_P - P_S$$
$$\delta \geq 0$$
$$y_i - K_i(P_P, T, x)\, x_i = 0$$

In the two phase region, (3) and (4) reduce to the square system

$$8 = 0$$
$$P_s = P_p$$
$$Z_j F = X_i L + y_i V, \qquad i = 1,\ldots n$$
$$F = L + V \qquad (5)$$

$$y_i = K_i(P_P, T, x)\, x_i \quad i = 1,\ldots n$$
$$\sum_{i=1}^{n} x_i - \sum_{i=1}^{n} y_i = 0$$

For the single phase liquid region, this formulation reduces to:

$$V = 0$$
$$8 = P_s - P_P$$

$$z_i = x_i$$
$$F = L \qquad (6)$$
$$y_i = K_i(P_p, T, x_i)\, x_i$$
$$\sum_{i=1}^{n} x_i - \sum_{i=1}^{n} y_i = 0$$

and Pp is the bubble point pressure. A similar reduction occurs for the single vapor reqion where Pp becomes the dew point pressure. The following optimization problem allows us to obtain these solutions:

$$\begin{aligned} \text{Min} \quad & 5 \\ \text{st} \quad & h(x, y, L, V, P_P) = 0 \\ & 5 \geq P_S - P_P \\ & 8 \geq P_P - P_S \\ & 5 \geq 0 \\ & 0 \leq L, V \leq F \\ & 0 \leq x_i, y_i \leq 1 \end{aligned} \qquad (7)$$

where h(x, y, L, V, Pp) = 0 are the flash equations given in (3). This NLP has a vertex solution and can be solved through PSLP by solving the following linear program at each iteration (instead of taking a Newton step):

$$\begin{aligned} \min \quad & \sum_j (p_j + n_j) + \omega\, \delta \\ \text{st} \quad & h_j + V\, h_j\, d = p_j - n_j \\ & 5 \geq P_S - P_P \\ & 8 \geq P_P - P_S \\ & 8, p_j, n_j \geq 0 \\ & 0 \leq L, V \leq F \\ & 0 \leq x_i, y_i \leq 1 \end{aligned} \qquad (8)$$

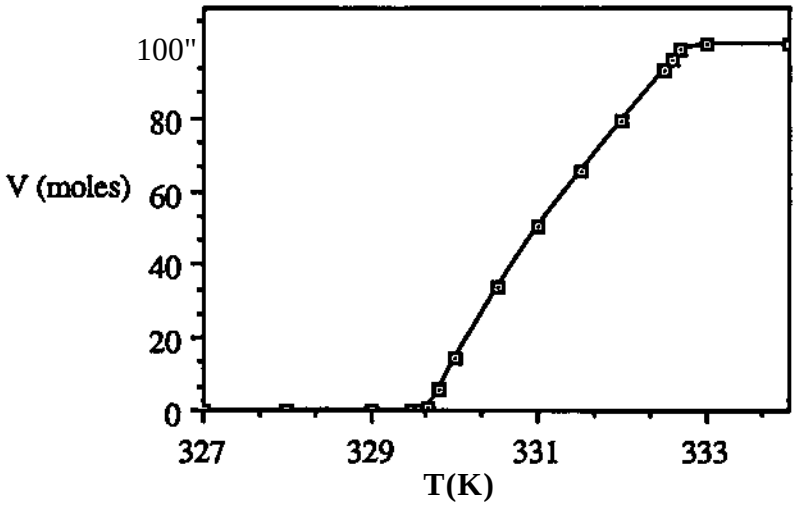

Figure 2. Vapor flowrate versus temperature for Nonideal Flash (Methanol, Acetone, Methyl Acetate, Benzene, Chloroform)

where o is a small positive constant The application of this approach on a small nonideal IP flash is presented in Figure 2 (see Bullard and Biegler, 1992b, for more details). Note here that the vapor flow rate increases as a function of temperature, from zero at the bubble point to the feed rate at the dew point Our single problem formulation captures all of these characteristics.

This approach has been demonstrated on many examples including ideal and nonideal mixtures and even retrograde condensation (Bullard and Biegler, 1992b). More importantly, however, it can easily be incorporated into multi-stage separation systems to describe limiting behavior of equilibrium-staged columns. Here the familiar mass-equilibrium-summation-heat (MESH) equations are modified with pseudo-pressure variables on each tray (the i^{th} tray), in a similar manner as in (7). An objective function is formed through summation of the penalty variables (80 and the combined system is solved by the PSLP approach.

The advantage of this strategy is seen for distillation columns that are specified below the minimum reflux ratio or below a minimum heat duty. In these cases, the PSLP approach will yield solutions with dry trays or vaporless trays, respectively. For example, the (methanol, acetone, methyl acetate, benzene, chloroform) column described in Figure 3 exhibits the following output concentrations in Table 1 as a function of the reflux specification. Note that below the minimum reflux (about 0.1), PSLP allows the tray above the feed to be dry and thus the liquid path is broken.

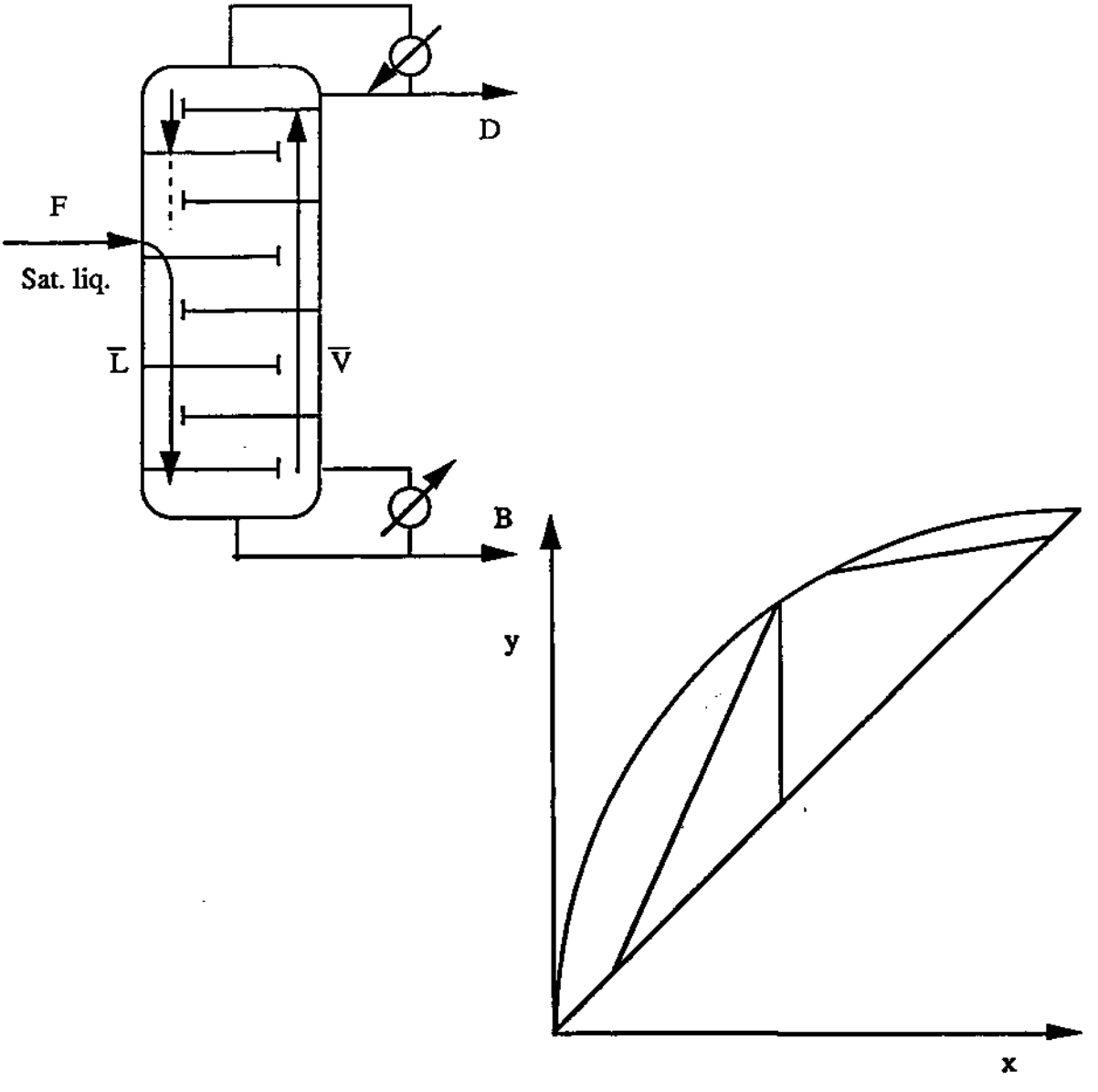

Figure 3. The McCabe-Thiele diagram (lower) illustrates the distillation case having low reflux and highboilup rate with saturated liquid feed When reflux ratio is below its minimum value, liquid flow becomes zero on trays above the feed

Reflux ratio	bottom product					top product				
	xM	xA	xMA	xB	xC	xM	xA	xMA	xB	xC
8.5	0.013	0.350	0.053	0.283	0.301	0.373	0.482	0.044	0.065	0.035
7.0	0.010	0.356	0.055	0.281	0.298	0.377	0.472	0.042	0.068	0.041
6.0	0.009	0.340	0.055	0.280	0.296	0.379	0.465	0.041	0.070	0.044
5.5	0.008	0.362	0.056	0.279	0.294	0.380	0.461	0.041	0.071	0.047
4.5	0.007	0.367	0.056	0.278	0.291	0.382	0.453	0.040	0.073	0.052
4.0	0.006	0.373	0.057	0.276	0.287	0.384	0.443	0.039	0.076	0.058
3.0	0.006	0.391	0.057	0.275	0.284	0.384	0.437	0.038	0.078	0.063
2.5	0.007	0.385	0.058	0.274	0.281	0.383	0.431	0.038	0.080	0.068
2.0	0.008	0.389	0.058	0.272	0.277	0.380	0.424	0.037	0.083	0.076
1.5	0.013	0.389	0.058	0.269	0.271	0.372	0.418	0.037	0.088	0.085
1.0	0.025	0.391	0.058	0.264	0.262	0.353	0.415	0.038	0.096	0.099
0.75	0.036	0.391	0.057	0.260	0.256	0.335	0.415	0.038	0.103	0.108
0.10	0.075	0.393	0.055	0.240	0.236	0.271	0.411	0.042	0.135	0.141
0.001	0.075	0.393	0.055	0.240	0.236	0.271	0.411	0.042	0.135	0.141
5E-05	0.075	0.393	0.055	0.240	0.236	0.271	0.411	0.042	0.135	0.141
4E-05	0.075	0.393	0.055	0.240	0.236	0.271	0.411	0.042	0.135	0.141

Table 1. Top and bottom liquid mole fractions of methanol, acetone, methyl acetate, benzene, and chloroform obtained by PSLP. Note the constant compositions below a reflux ratio of 0.1. Here tray 13 (above the feed) is liquidless.

Finally, the equivalence of PSLP to Gibbs minimization can also be extended to multiphase systems. Therefore, future work will extend this strategy to more complex separation systems, such as heterogeneous distillation and liquid-liquid extraction. In addition, the conceptual simplicity of this strategy (replace the Newton step by a linear program) allows application to any equation-solving environment (steady-state or dynamic) and thus leads to more reliable and powerful simulation strategies for complex process models.

Targetting for Reactor Networks using Optimization Tools

Process synthesis has yielded a wealth of applications for optimization-based formulations. Examples of linear and nonlinear programming formulations can be found in the synthesis of heat exchanger networks (Gundersen and Naess, 1988) and mixed integer formulations (with discrete decision variables) are widespread for energy systems, separation sequences and the synthesis of total flowsheets. A detailed review of these approaches is beyond the scope of this paper and excellent surveys of these approaches can be found elsewhere (e.g, Grossmann, 1990). Moreover, research in this area proceeds at a healthy pace through the efforts of Floudas, Grossmann, Pibouleau, Westerberg and many others. In this section we discuss the application of simple NLP formulations to a particularly difficult process problem, the synthesis of reactor networks. Unlike the synthesis of energy or separation systems, this area has seen relatively little development and still contains a number of open, unresolved problems. Moreover, as with many optimization-based approaches to process synthesis, most research relating to reactor networks has concentrated on superstructure optimization (Chitra and Govind, 1985; Pibouleau et al, 1988; Kokossis and Floudas, 1990; Achenie and Biegler, 1990). With this approach, a network is constructed that captures a large family of potential solutions, to be determined by a (mixed integer) optimization strategy.

While the superstructure approach has been useful in discovering innovative and improved networks for complex reaction mechanisms, this approach can suffer from three limitations. First, one is seldom certain that the proposed superstructure is rich enough to capture **the** "best" reactor network. Second, modeling equations tend to be nonlinear and therefore lead to nonconvex optimization problems (unlike MILP formulations for energy and separation systems); possibilities

for local optima with poor characteristics are likely. Finally, multiple networks can be derived that yield identical performance characteristics. (For example, compare a network with two tubular reactors in parallel to a single reactor with an intermediate exit stream.) In addition to finding a local optimum, the synthesis procedure may also yield a reactor network that is more complicated than necessary. To avoid these limitations, the alternative (and often complementary) approach of reactor targeting can be extremely useful. Using an analogy with heat exchanger network synthesis developed initially by Linhoff and coworkers (Linnhoff et al., 1982), targeting provides realistic bounds on system performance *before* the network is constructed.

For reactor networks, such bounds or targets can be developed through the concept of attainable regions initially proposed by Horn (1964). More recently, Glasser, Crowe and Hildebrandt (1987) developed powerful geometric properties for reactor networks, and derived necessary conditions for which the attainable region is closed and cannot be extended by additional reactors. In developing a constructive approach, Glasser et al show that the attainable region, created by the operations of reaction and mixing, is a convex hull of reactor trajectories. This region can only be extended by rate vectors within the convex hull pointing outward (extension by a plug flow reactor) or rate vectors outside the convex hull projecting backwards into the convex hull (extension be stirred tank or recycle reactors). By searching the attainable region, a network is derived constructively and extended until the attainable region is complete. Any point in the attainable region can then be realized from the reactors used in the construction and thus the reactor network is no more complicated than it needs to be.

The geometric targeting approach was applied to isothermal reactors with two to four species. Later studies (Hildebrandt, Glasser and Crowe, 1990; Hildebrandt and Glasser, 1990) extended this approach to residence time optimization and nonisothermal systems. However, the chief advantage of the geometric approach, visualizing the attainable region, is also its limitation. To date, problems have only been solved that could be plotted in two (and in some cases, three) dimensions. More complex reaction mechanisms cannot be treated completely with this constructive, geometric approach.

On the other hand, the principles that govern this strategy can also be adapted **to** an optimization-based **framework. Here, one can explore higher dimensions through nonlinear programming formulations. An attainable region is first constructed using limiting assumptions about the system** and **further extensions to this region can then be found by solving small nonlinear programs. To outline this approach, consider an isothermal system described by an arbitrarily complex reaction** mechanism.

Figure 4:: Segregated flow model

If we assume that the reactions take place only in segregated flow, as shown in Figure 4, the optimization problem can be given by:

$$\text{Max} \quad J(X_{exit} > t)$$

$$\frac{dX_{seg}}{dt} = R(X_{seg}), \quad X_{seg}(0) = X_o$$

$$X_{exit} = \int_0^{t_{max}} f(t)\, X_{seg}(t)\, dt, \quad \int_0^{t_{max}} t\, f(t)\, dt = X, \quad \int_0^{t_{max}} f(t)\, dt = 1 \qquad (9)$$

where t is the age of the molecule in the system, f(t) is the residence time distribution, X_{seg} is the dimensionless concentration of molecules in the segregated environment, R(X) is the dimensionless rate vector, x is the mean residence time and Xexit is the exit concentration. Here, the objective function, J, is specified by the designer and can be any function of Xexit and x. One can see that the differential equation system can be solved offline for X_{seg} if XQ (feed concentration) is

constant. Once X_{seg} is determined, Gaussian quadrature is applied on finite elements in t and we have:

Max J (Xexit, t) (10)

EiZj w(j)f(i,j)oc(i) = 1

x = SiEjwG)f(ij)t(ij)a(i)

X_{exit} = 2iEjw(j)f(i,j)$X_S$eg(ij)a(i)

Here, f(i,j) and X_{se}g(i,j) correspond to the profile values in the i^[1] finite element and j ^ [1] quadrature point; i is the index of finite elements; j is the index of the quadrature points; w(j) and a(i) are constants that denote the Gaussian quadrature weights and the fixed length of the i^[1] finite element, respectively. Note that the constraints in (10) are linear and if the objective function is either yield or selectivity, problem (10) is simply a linear program (UP).

Solution of this LP will yield an optimal isothermal reactor network under the assumption of segregated flow; these solutions consist of at most two parallel plug flow reactors (PFRs). Often this assumption alone will generate an optimal network; Balakrishna and Biegler (1992a) derive convexity conditions for the PFR trajectories for which a segregated flow solution is sufficient. If these convexity conditions are not satisfied, small NLPs can be solved and the goal is now to find additional (mixed) reactors that allow extensions to the attainable region. From the assumption of segregated flow and global solutions resulting from the LP, it is clear that no further PFRs can be found that improve the objective. To find a continuous stirred tank reactor that allows these extensions, one need only solve the following problem:

Max JCSTR (Xexit) dD

X_S = £i Zj wG) f (ij) X_{seg} (i,j) cc(i)

X_{exit} = X_S + TR(X_{exit})

$\Sigma_i \Sigma_j w(j) f(i,j) \alpha(i) = 1.0$

$\tau < \tau_{max}$

where t and X_{ex}it refer to the CSTR extension and Xs is the output from the segregated region. Similarly, a recycle reactor extension that improves the objective can be found by:

Max Jrr (Xexit) (12)

s.t. X_S = EiEj w(j)f(ij)X_{se}g(ij)a(i)

X_{exit} = $\Sigma_i \Sigma_j$ w(j) f_r(i,j) X_{rr} (i,j) α(i)

$\Sigma_i \Sigma_j$ w(j) f (i,j) α(i) = 1.0

Ei Lj wG) fr(ij) a(i) = L0, Zi Zj wG) f_r(ij) t(ij) a(i) = x < x_{max}

with the residence time distribution, f_r, dimensionless concentration, Xn> and Xexit defined for the recycle reactor extension, A new candidate region is then formed by the convex hull of either of these reactor extensions coupled with the segregated flow region. As illustrated in Figure 5 this strategy continues until no further extensions can be found. Further details of this approach are presented in Balakrishna and Biegler (1992a). Here it is interesting to note that this optimization based approach is equivalent to geometric targeting as long as the extensions to the attainable region yield monotonic improvements in the objective function. Since the geometric approach considers all extensions to the attainable region (not just those that improve the objective), it is possible that nonmonotonic improvements in the objective can lead to better designs with the geometric approach. On the other hand, the optimization-based targeting approach has conceptually no limitations on the problem dimension that can be considered.

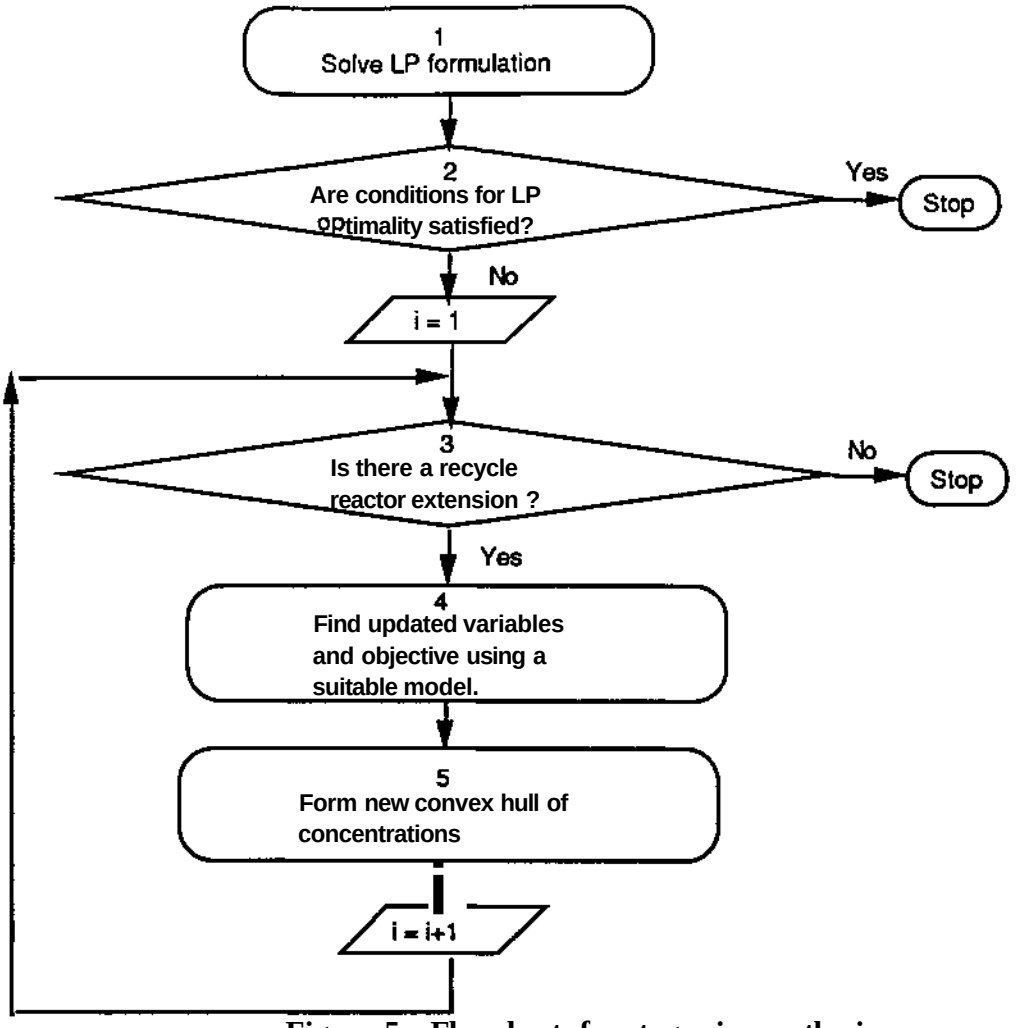

Figure 5: Flowchart for stagewise synthesis

To illustrate the optimization-based targeting approach, consider the isothermal Denbigh reaction with the following mechanism:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$A \xrightarrow{k_3} D$$

The dimensionless reaction rate vector for components A,B,C,D,E respectively, is given by R(X) = $[-X_A(k_3 + k_1X_A),\ k_1X_A^2 - X_B(k_4X_B + k_2),\ k_2X_B,\ k_3X_A,\ k_4X_B^2]$, where $k_1 = 6.0\ s^{-1}$, $k_2 = k_3 = 0.6 s^{-1}$, $k_4 = 0.6\ s^{-1}$, $C_{AO} = 6$ mol/L, $C_{DO} = 6$ mol/L The objective here is to maximize the yield of product C subject to 95% conversion of A. Following the stagewise approach in Figure 5, we observe a CSTR extension from the seg flow model, which gives a C yield of 3.726 mol/1 with a CSTR residence time of 3505 sec. The residence time in the segregated environment is 0.766 sec (with a Dirac delta function for f(t), which corresponds to a PFR). No further extensions are observed beyond this point. By mixing Xexit with the feed 95% conversion of A can be achieved, which corresponds to a C yield of 3.54 mol/lit. Glasser et. al (1987) observe similar results with a CSTR with infinite space time.

Finally, an important advantage to optimization-based targeting is that it can be integrated within larger process synthesis formulations. In particular, designing a reactor network that interacts with the separation and energy systems in a process flowsheet can be done straightforwardly and efficiently - without proposing a reactor network in advance. Here the problem formulations described above are extended to include interactions with the rest of the flowsheet and the approach described in Figure 5 follows as before. To illustrate this concept, consider the Williams and Otto process illustrated by the flowsheet in Figure 6.

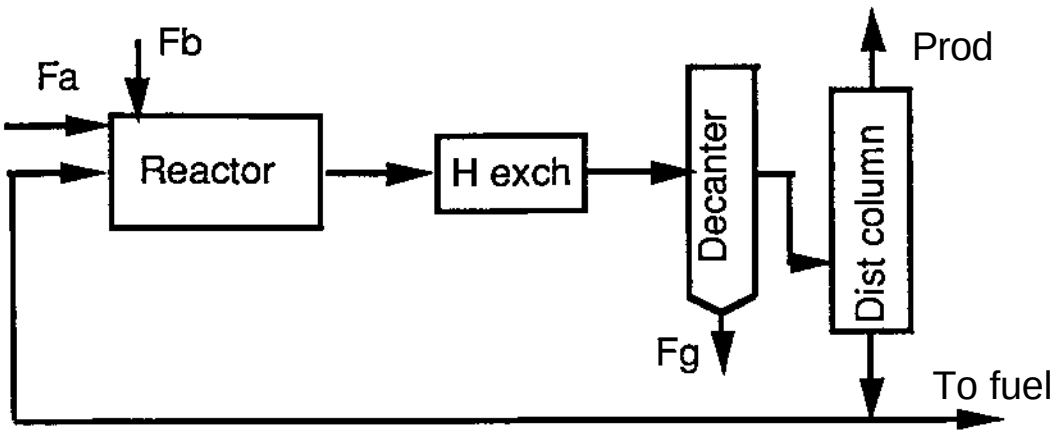

Figure 6: Williams and Otto Flowsheet

The plant consists of a reactor, a heat exchanger to cool the reactor effluent, a decanter to separate a waste product G, and a distillation column to separate product P. A portion of the bottom product is recycled to the reactor, and the rest is used as fuel. The following reactions are involved in the * manufacture of compound P:

$$A + B \rightarrow C, \qquad C + B \rightarrow P + E, \qquad P + C \rightarrow G$$

with rate vectors summarized in Balakrishna and Biegler (1992a). Decision variables include the reactor temperature, residence time and the purge fraction. In previous studies, the reactor was specified as a CSTR and the return on investment (ROI) was maximized. Here we replace the CSTR with a segregated flow targeting model embedded within the flowsheet. It should be noted, however, that the targeting problem is slightly complicated by a nonconstant feed vector; a discretization of (9) is solved here. As defined in previous studies, the ROI objective function includes all raw material and separation costs for the plant and a maximum ROI of 130% can be obtained with a fixed CSTR model. With the targeting model integrated within the flowsheet, an ROI of 278% was obtained. Moreover, no CSTR extensions can be found that improve the ROI; here the optimal network is just a PFR with a residence time of 0.0111 hr. These results indicate that significant savings can be obtained by integrating the reactor with the flowsheet, even with simple targeting models.

Balakrishna and Biegler (1992b) have extended this approach to nonisothermal reaction systems as well. Here, in addition to defining and extending candidate attainable regions through nonlinear programming formulations, optimal temperatures and temperature profiles are determined that allow for general heating and cooling strategies. Also, this NLP formulation can easily be coupled to synthesis strategies for heat exchanger networks, by appending the targeting formulation of Duran and Grossmann (1985). As a result of this approach, optimal reactor and heat exchanger networks can be derived simultaneously and trade-offs between raw material conversion, energy and capital costs are considered and optimized directly. Balakrishna and Biegler (1992b) illustrated this simultaneous reactor and energy targeting approach on a process flowsheet with a van de Vusse-type mechanism. As a result of the simultaneous strategy, overall raw material conversion to product increased from 49.6% to 61.5% and the profit was over 90% higher when compared to a sequential strategy, with the best reactor targeting strategy followed by energy integration! Interestingly, both approaches lead to single plug flow reactors but with only small differences in temperature profiles. Note again, that the compact nature of the targeting formulation (as opposed to a large superstructure of reactors) leads to a tractable optimization problem for a complex process.

Uncertainty and Optimal Flowsheets

In many design studies the process model and optimization problem specification may be subject to uncertainty. Consequently, it is often argued that the optimal solution may not be reliable and of little value to the designer. As optimization tools become more reliable, efficient and user-friendly, the ability to obtain multiple optimization cases quickly becomes an effective counter to this argument Also, the results of the optimization study can reveal additional information other than an

optimal design. In this section we explore two optimization-based tools, postoptimalty analysis and multiperiod optimization, in order to cope with process uncertainty.

Once an optimum design is obtained, one is frequently interested in the sensitivity of the objective function and the optimal decisions. Questions such as "Is the optimum flat?", "What are the binding constraints?", "How does the objective change if I relax this constraint?" are often asked and these can be resolved either by examination of the Kuhn-Tucker multipliers or by running additional cases. Additional sensitivity analysis is not only possible, but is often quite inexpensive, compared to the cost of obtaining the optimum solution. Indeed, such an analysis is a standard tool in linear programming. Extensions of this approach have been made to nonlinear programming as well, particularly in the context of SQP. To illustrate this analysis, consider the following general optimization problem:

$$\begin{aligned} &\text{Min } f(x,p) \\ &\text{s.t. } h(x,p) = 0 \\ &l(p) \le x \le u(p) \end{aligned} \qquad (13)$$

where p are specified parameters, and 1 and u are bounds on x. First order Kuhn-Tucker conditions for this system are given by:

$$\begin{aligned} &V_x L(x, X, \backslash i) = Vf(x) + Vh(x)\, A. + jiu - \mathbf{w} = 0 \\ &h(x,p) = 0 \\ &0 \le \wedge i_u, \ [i\backslash; \quad l(p) \le x \le u(p) \\ &\mu_u^T (u(p) - x) = 0; \ \mu_l^T (x - l(p)) = 0 \end{aligned} \qquad (14)$$

where L(x, *X*, |i) is **the Lagrange function. To** address **the problem of sensitivity of the optimum, we** also consider **the second order Kuhn-Tucker sufficient conditions; i.e., the reduced Hessian of the Lagrange function, $Z^T V_{xx} L(x, A, \backslash i)$ 7+ must be positive definite at the optimum. Here the Z matrix lies in the null space of (all of) the active constraint gradients and a strict local optimum requires positive curvature of the Lagrange function, in the space spanned by the degrees of freedom of the problem. All other variables are determined by the set of active constraints, provided they are linearly independent. Since there are generally few degrees of freedom for process optimization, evaluating the reduced Hessian in this space is inexpensive, even if it needs to be determined by finite difference. Evaluating the eigenvalues of this matrix quickly resolves the questions of positive curvature or leads to the following considerations.**

Are any eigenvalues zero or very small? **Under these conditions, one can argue that the objective function is relatively insensitive (flat) in a neighborhood about the optimum. For zero eigenvalues, a ridge of nonunique optima can often be found along the corresponding eigenvector, which can be explored to gain further insight about the problem.**

Are any eigenvalues negative? **Because most NLP methods are constructed to find only first order Kuhn-Tucker points, second order conditions are rarely checked. This is also true among SQP and reduced gradient methods that use line searches. In the case of saddle points (indefinite systems with positive and negative eigenvalues), it is easy to restart the problem by moving along a direction of negative curvature (e.g. the eigenvector corresponding to the negative eigenvalue) and solve the problem again. Because any step along this direction leads to an immediate decrease in the objective, any reasonable optimization method is guaranteed not to revisit the saddle point, and to move to an improved point**

Related questions deal with parametric sensitivity of the optimum solution, particularly with respect to parameters that cannot be specified with certainty. Here we may be interested in sensitivities of the optimal decision vector as well as the change in the objective. The sensitivity analysis follows directly from the first order Kuhn-Tucker conditions. If the active constraints are independent at the optimum, differentiating these conditions implicitly with respect to p leads to the following expressions:

$$V_{xp} L(x, X, \backslash i) + V_{xx} L(x, X, \backslash i)\, VpxT + Vh(x)\, VpXT + (V_p \wedge_u - V_{pW})T \ll 0 \qquad (15)$$

$V_p h(x,p)T + V_x h(x,p)Tv_p xT = 0$
$V_p x_b = Vpl(p)$ or $Vpu(p)$

where Vpx is the sensitivity of the minimizer to p and xb are the bounded variables at the optimum.

These equations easily lend themselves to decomposition. First, note that bounded variables (xb) have sensitivities given directly by the sensitivities of the bounds. The remaining variable sensitivities can be determined by partitioning them into dependent components, py, which lie in the range space Y of Vh, and independent components, pz, which lie in the null space Z of Vh^T. The combined contribution to the remaining (free) variables Xf is given by $V_p xf = Ypy + Zpz$. Similar concepts are developed in Fiacco (1982) and Ganesh and Biegler (1987). The resulting sensitivity equations are therefore:

$$V_p x_N = Vpl(p) \text{ or } V_p u(p) \qquad (16)$$
$$p_Y = -(V_x h(x,p)TY)\text{-}l(V_p h(x,p)T + V_x h(x,p)T\, V_p x_N)$$
$$PZ - -(ZTv_{xx}L(x,p)\, Z)\text{-}l\; ZT[V_{xp}L(x,p) + V_{xxN}L(x,p)\, V_p x_N T + V_{xx}L(x,p)\, \mathbf{Ypy})]$$
$$\mathbf{V_p Xf = - p_Y + Zp_Z}$$

Note that sensitivities within **the** range space are given directly by **the** gradients of **the** equality constraints while sensitivities for the independent variables also require the reduced Hessian matrix. Thus the only additional information that is required at an optimal point is the derivative information on the right hand side **and** possibly **the** reduced Hessian (if second derivatives **are not** used for optimization). These **are** readily obtained with a few additional perturbations. Finally, once the sensitivities in **the optimal decision variable vector are determined, estimated changes to the objective** function, **with respect to finite parameter perturbations, can be determined through a Taylor** series **expansion. A detailed description of this approach is provided in Wolbert et al (1992).**

Ganesh and Biegler (1987) applied this approach to small flowsheeting problems. More recently, Wolbert (1992) refined this approach and implemented it within the PROSIM simulation environment, along with tailored RND/SQP methods (Biegler, 1992) for simultaneous optimization and recycle convergence. The PROSIM implementation has a major advantage in that derivatives for all modular inputs and outputs are calculated analytically. As a result, one of the most time-consuming steps for flowsheet optimization is streamlined. Moreover, the availability of accurate derivatives allows faster and more reliable behavior of the optimization algorithm. With an efficient RND/SQP optimization strategy Wolbert noted 70 to 80% reductions in effort when using analytical derivatives over derivatives obtained by perturbation. In addition, the availability of analytic first derivatives allows rapid calculation of reduced Hessian matrices, either for the RND/SQP algorithm or for sensitivity analysis.

Wolbert et al. (1992) analyze a number of PROSIM flowsheet examples with this postoptimality approach. To illustrate this approach, consider the ammonia process shown below. Here Wolbert (1992) showed that using analytical derivatives leads to a 74% reduction in effort for flowsheet optimization. At the solution it interesting to note that the eigenvalues for the reduced Hessian matrix (of order four) range from **10^{-10} to 10^{-4}, indicating that the optimal solution is relatively flat for the four independent directions. Moreover, as shown in Wolbert (1992), sensitivity of this optimal flowsheet to the feed and reactor conversion is nearly linear. Therefore the sensitivity analysis outlined above gives an accurate representation of the changes in objective and decision variables for this example.**

Further consideration of uncertainty can be handled through the framework of multiperiod optimization and flexibility analysis (Grossmann and Straub, 1991). While sensitivity analysis gives an indication of the effect of uncertain parameters on the optimum design, it is usually important to *guarantee* that an optimum design remains feasible for a specified range of uncertainties. Here Grossmann and coworkers have advanced the concept of process flexibility and developed sufficient conditions to guarantee feasibility for a given design. In general, this analysis applies to linear systems and can be extended to systems that meet certain convexity requirements. In addition, the flexibility of a process to parameter uncertainties has been quantified using both deterministic and stochastic measures. Finally, Pistikopoulos and Grossmann (1989) and Straub and Grossmann (1990) have developed optimization-based analysis tools that allow trade-offs of an

economic objective and flexibility or reliability, respectively. In this way one can obtain a quantitative measure for the optimal overdesign of a process.

While a detailed discussion of flexibility analysis is beyond the scope of this paper and is covered elsewhere, uncertainties for general process optimization problems can often be captured by a finite (but possibly large) set of discrete design scenarios. A useful formulation for an optimal design for these scenarios is given by the following multiperiod optimization problem:

$$\text{Min } fo(d) + \Sigma_i\, w_i\, f_i(x_i, d) \tag{17}$$

$$\text{s.t.} \quad \mathbf{hi}(x_{if}, d) = 0$$
$$li \le xi \le ui$$
$$\mathbf{l \le d \le u}$$

where wi are weights for each scenario i with the objective function terms corresponding to each period- Here the i^{th} scenario (or period) is represented by a different set of variables xi and constraints hi; coupling of the scenarios is effected through decision variables d, which are fixed for all periods (e.g., equipment parameters). Thus the optimal design represented by these decisions needs to satisfy all of the scenarios as part of the problem formulation.

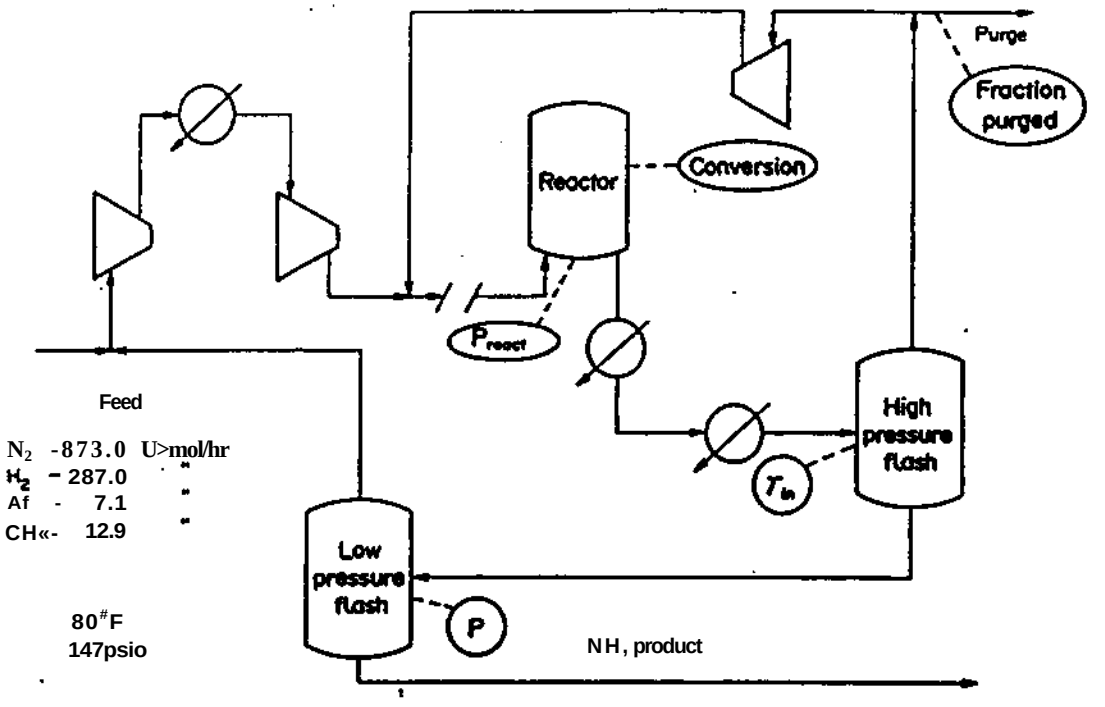

Figure 7: Ammonia Process Optimization and Sensitivity Analysis

The multiperiod approach successfully captures the concept of a reliable optimal design as long as the uncertainty of the process can be represented by discrete scenarios. However, note that the problem size increases directly with the number of design scenarios. Application of a general purpose optimization strategy can be expensive here because the computational effort generally increases polynomially (quadratically or even cubically) with the size of the optimization problem. To remedy this drawback, NIP decomposition strategies have been developed to allow for faster performance. Grossmann and Halemane (1982) developed a projection/restriction strategy for inequality constrained systems that generally has linear performance characteristics with respect to

the number of periods. More recently, Varvarezos et al. (1992) developed an efficient OA/RLP (Outer Approximation/Relaxed Linear Programming) strategy for convex problems and even extended this to problems with discrete decision variables. Comparisons on batch design and planning problems showed that this approach was several times faster than conventional NLP and MINLP solvers.

Currently, we are extending the DSQP strategy developed for EVM (errors-in-variables method) estimation problems to multiperiod problems in (17). As described in Tjoa and Biegler (1992) DSQP can be ten to a hundred times faster than MINOS or SQP on larger paramter estimation problems. EVM problems have the same structure as (17), but here the challenge remains to deal with bound activity on xi as well. Interior point (or barrier) formulations seem to **be** promising for this task.

With this approach global and superlinear convergence properties of the SQP algorithm still hold and an efficient decomposition strategy is applied period by period. Consequently, the effort required by the optimization algorithm increases only linearly with the number of periods and the effort per period is **comparable** to **that** required for an efficient single period optimization. Consequently, with improvements in process optimization interfaces **and** models, **as well as NLP** strategies for multiperiod problems, **it is** clear **that** solving problems like (17) **will not be** difficult **for** larger systems. Thus, optimal **and** flexible designs can **be** generated relatively **easily and quickly in** the future.

Summary and Future Directions

As optimization strategies **are further developed, more attention can be paid to novel problem formulations with a wider scope of process application. This paper addresses a few applications of novel formulations that are now realizable as a result of better algorithms* First we describe constrained simulation problems (systems of equations with inequality constraints) that can be addressed systematically and solved efficiently through Successive Linear Programming strategies. This approach allows nonsmooth problems, such as pipe networks with checkvalves and multiphase equilibrium systems, to be addressed. Next we consider optimization formulations to probe higher dimensions in reactor network synthesis. Here geometric concepts for network targeting were invoked in order to define an attainable region. Constructing this region was enabled by defining a region sufficient for segregated flow reactors and then extending it by allowing mixed reactors that improve the objective function. This concept has the further advantage that it can be integrated within larger process models with interactions from energy and separation subsystems. Finally, the ability to obtain optimal solutions quickly leads us to reconsider uncertainties in the process model and their effect on the desired solution. Here it was shown that sensitivity of the optimal solution to specified parameters can be obtained only at the cost of a few function evaluations, once the optimum is available. A typical process example was briefly described to illustrate this approach. Also, accurate treatment of design uncertainty can be performed through multiperiod optimization. Here several design scenarios are incorporated within the optimization problem and these are all satisfied by the final design. While the resulting optimization problem becomes larger than for the single design case, NLP-based decomposition strategies are briefly sketched above which yield optimal designs efficiently.**

Future work in process optimization can be expected to evolve along the following paths:

- ***optimization and modeling strategies for larger and more complex process systems***
- ***novel and more creative optimization applications.***

In Biegler (1992) optimization strategies were presented that could be tailored to the structure of process models. This allows a more efficient approach to large, complex systems. Similar reduced SQP strategies have been considered for finite element models in shape optimization for mechanical parts, aerospace systems and materials processing (Kodiyalam, 1992; Rüigertz, 1992; Ghattas and Orozco, 1992; Kupfer and Sachs, 1992). Moreover, with the development of more efficient interfaces and modeling tools, the development of these strategies will be made easier.

A key aspect to these tools is the availability of accurate derivative information. The importance of accurate derivatives was illustrated dramatically for process optimization by Wolbert. Moreover, a number of derivative generating codes are currently available or under development, that can be used directly with existing FORTRAN-based process models (see Griewank and Corliss, 1991, for a survey). In general, these tools parallel the model's calculation sequence with a derivative calculation that applies the chainrule to the sequence and handles the bookkeeping to keep track of intermediate values. Such strategies are preprocessors or coprocessors that use the model's FORTRAN source code directly and generate derivative FORTRAN code that is run along with the model. Examples of these include:

- ***JAKE-F,*** *which has seen many applications but is limited to a subset of FORTRAN (Hillstrom, 1982)*
- ***DAPRE,*** *which has been developed for use with the NAG library (Pryce and Davis, 1987)*
- ***ADOL-C,*** *which is implemented very efficiently using operator overloading features of C++ (Griewank et al, 1990)*
- ***ADIFOR,*** *the most recent development (Bischofet al, 1992), which uses a source transformation approach within the ParaScope environment (Callahan et al, 1988). This environment is used for dependency analysis among the variables as well as parsing the FORTRAN code .*

In ADIFOR, for example, an adiabatic flash block was processed and Jacobian matrices were calculated by an ADIFOR-generated derivative code, for all outputs with respect to all **inputs.** No changes were required in the original model and the total time for evaluating both the flash block and its Jacobian was only twice that of evaluating the function. A number of similar examples were solved in other disciplines with up to a 70-fold increase in **performance. Future development and** application of ADIFOR as well as other tools will deal with calculation of higher derivatives, undoubtedly for use in optimization algorithms as well as nonlinear analysis.

Creative problem formulations that result from the evolution of powerful optimization **tools extend** far beyond traditional optimal designs. **As noted in the third section, optimization formulations were** used **to "see[11] in higher dimensions in order to determine attainable regions. For example, a simple tubular reactor can frequently be found to be an optimal network, without further model refinement or complexity. Similarly, these approaches can be used to evaluate the goodness of a process model. Here, instead of building and refining a process design or control model to describe a base case, it is more useful to observe the behavior of the process model in the desired (optimal?) direction of the process. By using the optimization strategy within the model-building loop one can determine whether:**

- ***many sophisticated modeling details are unnecessary in order to identify the optimum, or***
- ***the current model is inadequate in order to predict or extrapolate to optimal process performance.***

Closer examination can then uncover misleading assumptions, limiting correlations or transitions to other mechanisms. Of course, this is only possible if there is a quick turnaround for optimization modeling and solution.

Finally, advancing the use of optimization tools also needs to be guided by an educational component. As noted in numerous studies in process synthesis, the success of process optimization is driven equally by efficient and precise problem formulations as well as efficient algorithms. Examples of equivalent process models and representations with great differences in computational effort have been described by Grossmann (1990). In addition, appropriate guidelines for optimization modeling are developed in Amarger et al. (1992) and Grossmann (1992). Awareness of these guidelines, as well as greater knowledge (advantages and limitations) of current optimization tools will change the engineer's perspective toward optimization strategies and lead to their greater appreciation as indispensible design and analysis tools.

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