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g = acceleration due to gravity
n = number of particles
n_0 = initial number of particles
SD = geometric standard deviation of particles
t = time
T = temperature, K
V = gas velocity
v_t = terminal velocity of particle in gas
z = height coordinate

Greek Letters

α_{DIFF} = particle removal coefficient due to diffusion (DIFF)
α_{SED} = particle removal coefficient due to sedimentation (SED)
η_g = gas viscosity
ρ_P = particle density

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Optimization of large or complex chemical processes often requires simplifying the system to reduce the mathematics to a form manageable by available algorithms or to reduce the time required to perform the computations. In many cases, such simplification alters the solution of the problem. Flow sheet simulation programs are ideally suited to the study of chemical processes, although the computational time is generally considered excessive for detailed optimization of complex systems by the usual procedures. This paper discusses the modifications needed to apply flow sheet simulation programs to the optimization of chemical processes. The advantages and disadvantages of the use of several optimization algorithms, including stochastic procedures, in this modified program are discussed and examples compared.

In process design optimization it is essential to have a model which accurately describes the way in which the economic desirability of a process varies as the operating conditions are changed. Since the profit and investment of a process are found from a model made up of numerous interacting parts, all the variables of the process must normally be considered simultaneously in order to find the most desirable combination of variables.

Because of the difficulties in developing accurate models of large chemical processes and the excessive time involved with executing such models for optimization purposes, most process optimization studies have had to be simplified in one way or another. Such studies have usually been limited to examination of simple processes or simplified models of complex processes.

Much of the prior work has concentrated on the application of optimization techniques rather than on the development of accurate process models. Many studies have reduced the mass, energy, and economic balance calculations normally required for detailed design purposes to general algebraic expressions containing only a few variables. Bracken and McCormick (1968) studied an alkalation process with the material balance and profit based upon regression fitted data. Friedman and Pinder (1972) optimized a gasoline polymerization process with a detailed material and energy balance model, but with the objective of maximizing the amount of product. Similarly, Gottfried et al. (1970) studied an octane isomer separation process with the economics based upon flow rates. Komatsu (1968) optimized a hydrodealkalation process by linearization of the mass and energy balances.

Perhaps the most widely studied process is the Williams and Otto (1960) plant. This model has been used to demonstrate several optimization techniques (Ahlgren and Stevens, 1966; Dibella and Stevens, 1965). These studies assumed the investment of the process to be a function of reactor volume. Considerable disagreement in this method of calculating investment was noted by Mason (1971) who found the investment from the material and energy balance data.

Numerous optimization studies have also been made of unit processes such as an absorber-stripper (Umeda and Ichikawa, 1971), a distillation column–condensor system (Zellnik et al., 1962), and a reactor (Barneson et al., 1970). Optimization of an individual unit or portion of a process is of little value in optimization of the complete process since the dependency between units must be included.

Modular computer simulation programs offer a convenient means of examining the entire chemical process. Such programs, with complete thermodynamic properties pack-

ages, may be used to produce any level of accuracy desired for even complex processes. Most of these systems are very elaborate and require considerable computational time, although extensive theoretical work is being directed toward improved computational techniques (Evans et al., 1968).

While simulation systems have been used extensively to model chemical processes, little has been done to use these programs for process optimization (Hughes, 1973). Seader and Dallin (1972) reported optimization of a toluene dealkalation plant using PACER and a student guided graphical interactive optimization procedure. Shannon et al. (1966) used a single variable optimization in connection with a PACER simulation of a sulfuric acid plant. A recent review of simulation systems (Flower and Whitehead, 1973) noted that none of the programs contained both a detailed economics capability and an automatic optimization facility.

The purpose of this study was to develop a modular process simulator that is capable of optimization of complex systems and to demonstrate its use with an example. This paper briefly reviews the program and its capabilities and presents the results of optimization of a gasoline polymerization unit. The choice of an optimization algorithm for this class of problem presents some interesting problems and the results with several algorithms are discussed.

PROPS (Process Optimization System)

Most modular simulation programs compute the material and energy balance for a process from a description of the flow diagram and equipment functions in the model. These models can be made very accurate by the use of sophisticated equipment modules and precise thermodynamic properties.

There are several additional functions that a simulation program must perform in order to be useful for optimization purposes. (a) Most processes are studied from an economic viewpoint and the simulator must be able to measure profitability. This means that equipment size, equipment investment, and process operating costs must be computed. From these data, return on investment, or some other profitability criterion can be determined. (b) To be functional, the simulator must not use excessive computer time. Significant improvements in this regard are necessary to apply most available simulation systems to optimization problems. (c) The system must be capable of carrying out repetitive simulations as directed by an optimization algorithm. (d) The accuracy of the computations must be maintained at a level compatible with the function of optimization algorithms.

The basic simulation system used in this study is CHESS (Chemical Engineering Simulation System), developed at the University of Houston. CHESS is described in detail elsewhere (Motard et al., 1969) and familiarity with this or similar systems is presumed. The modified version of CHESS, capable of optimization, is called PROPS (Process Optimization System).

The economic capabilities of PROPS have been discussed in a separate paper (Gaddy, 1974). Briefly, these capabilities include computation of the process investment, operating costs, revenue, and some profitability criterion from user supplied economic parameters, such as product prices and raw materials cost. The economic calculations are performed by separate subroutines after convergence of recycle loops.

Optimization in PROPS is accomplished by a separate subroutine which directs appropriate changes in the independent variables to the executive system. These calculations are made after the profitability is computed. Boundary constraints on the independent variables are checked before performing the computations in the simulator. Implicit constraints, involving data from the simulator, can only be checked after the simulation computations are completed. The user may supply any optimization algorithm appropriate for his problem.

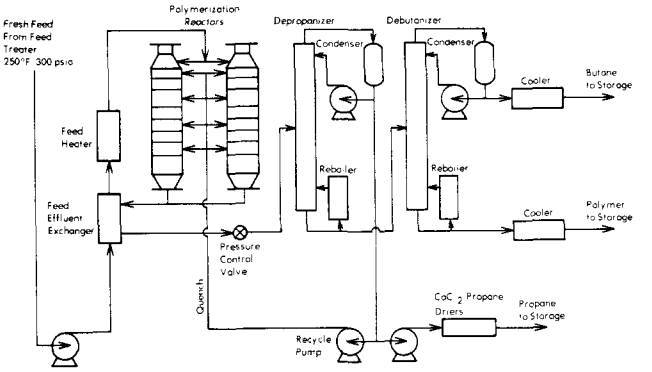

Figure 1. Flow diagram of polymerization unit.

An examination of execution times of CHESS indicated that considerable computer time was being used in determination of thermodynamic properties, convergence of recycle loops, and transfer of data. Reduction in computational times in PROPS has been accomplished by the following: (a) storage and use of material and energy balance results for initial approximations in following iterations; (b) minimization of data transfer for output; (c) re-use of calculated data that do not change in the course of an optimization run; (d) addition of simplified physical properties subroutines. Much of the computational time is used to calculate equilibrium coefficients if the Chao–Seader correlation is used. The user may choose to supply a simple, more specific, correlation that would produce equivalent accuracy. Also, the user may use curve-fitted equilibrium data. In this study, adequate accuracy was obtained by describing equilibrium coefficients found by the Chao–Seader correlation as a function of temperature and pressure.

Gasoline Polymerization Process

The process chosen for optimization in this study is the Universal Oil Products solid phosphoric acid catalyst process to produce gasoline from lighter fractions. A flow diagram of the process is shown in Figure 1.

The feed to the process is the product from a gas recovery unit and contains a mixture of light hydrocarbons. The feed is pretreated to remove hydrogen sulfide, mercaptans, and nitrogen compounds.

The treated feed enters at a temperature of 90°F and is pumped from 300 psia to 550 psia. The stream then passes through a feed/effluent exchanger where it is heated. The feed is heated further with steam and enters the polymerization reactors at approximately 360°F and 515 psia. The reactions are exothermic and require cooling between catalyst beds with propane which is recycled from the depropanizer.

The reactor effluent passes through the feed/effluent exchanger and its pressure is reduced to about 260 psia before entering a depropanizer. Liquid propane from the top of the column is used for quench in the reactors or dried and sent to storage.

The bottoms from the depropanizer enters a debutanizer at 90 psia. The overhead butane product is condensed, cooled, and sent to storage. The bottoms product, gasoline, is also cooled and sent to storage. The specification on the bottoms product includes a maximum vapor pressure of 10 psia.

Table I. Economic Analysis of Gasoline Polymerization Process

	$/yr
Investment = $499,562	
Working capital = $123,967	
Revenue	
Gasoline product	$ 631,568
Butane product	164,700
Propane product	389,200
	$1,185,494
Operating cost	
Variable costs	
Utilities	64,525
Raw materials	613,366
Operating supplies	15,731
Fixed costs	
Labor	62,196
Supervision	12,439
Payroll burden	18,658
Overhead	31,098
Maintenance	24,978
Taxes and insurance	12,489
Depreciation	40,873
Interest	62,352
Other costs	
Sales and adv.	11,855
Administration	35,565
Product distribution	35,565
Research and development	23,710
Total operating cost	$1,065,469
Earnings before taxes	120,025
Net earnings	60,012
Cash flow = $100,886	
Return on Investment = 12.01%	
Payout = 4.95 years	

This process was simulated by Friedman (1971) for the purpose of process optimization. There are several reasons for choosing the gasoline polymerization process for an optimization study. First, it is a typical chemical process consisting of a reactor with recycle and product separation units. Second, this process is complex from the standpoint of optimization because of a large number of variables and constraints. The process computations are also complicated by the rate equations in the polymerization reactions which must be solved by numerical integration. This process represents a particularly difficult situation for optimization by flow sheet simulation, since implicit constraints on the reactor temperature are involved. Third, this process is one of the few full-scale simulations reported in the literature and extensive data is available so that a detailed simulation can be made.

Simulation and Optimization of Gasoline Polymerization Process

For purposes of checking the model, the flow sheet presented in Figure 1 was simulated by PROPS using the optimum conditions found by Friedman and Pinder (1972) in a similar study of this process. These results, presented in Table I, show a plant investment of about $500,000 with annual operating costs of $1,065,500 for a plant processing 1700 barrels per day. In computing the investment, a constant reactor cost of $60,000 was used. This follows the approach used by Friedman and is considered realistic since flow rates and, hence, space velocities are nearly constant.

Guthrie (1970) estimated the investment for this size polymerization process as $500,000 with an operating cost of $1,033,000. These data verify the economic accuracy of the simulation.

This study deals mainly with process design optimization; however, simulation models may also be used for optimization of existing processes. Friedman studied the polymerization process with a simulation model that had no economic capabilities. Therefore, in that study, the operating cost had to be a constant and the objective function was the amount of product produced. It is interesting to compare the use of this objective function with a study using net earnings as the objective.

This optimization problem can be stated as

$$\text{maximize: net earnings} = f(X1, X2, \ldots, X9) \quad (1)$$

Subject to: $0.43 \leq X1 \leq 1$; $0 \leq X2 \leq 1$; $0 \leq X3 \leq 1$; $0 \leq X4 \leq 1$; $1.05 \leq X5 \leq 1.5$; $1.1 \leq X6 \leq 1.7$; $650 \leq X7 \leq 840$; $750 \leq X8 \leq 860$; $200 \leq X9 \leq 300$; $X10 = 1 - X1$; $0 \leq X11 = 1 - X2 - X3 - X4$; $760 \leq X12 \leq 945$; $760 \leq X13 \leq 945$; $760 \leq X14 \leq 945$; $760 \leq X15 \leq 945$; $X16 \leq 42$; $X17 \leq 24$; where: $X1$ = fraction recycle split; $X2$ = fraction quench split in first reactor bed; $X3$ = fraction quench split in second reactor bed; $X4$ = fraction quench split in third reactor bed; $X5$ = depropanizer reflux ratio; $X6$ = debutanizer reflux ratio; $X7$ = feed/effluent exchanger outlet temperature, °R; $X8$ = feed heater outlet temperature, °R; $X9$ = depropanizer pressure, psia; $X10$ = propane product split; $X11$ = fourth quench split; $X12$ = first reactor bed temperature, °R; $X13$ = second reactor bed temperature, °R; $X14$ = third reactor bed temperature, °R; $X15$ = fourth reactor bed temperature, °R; $X16$ = number of depropanizer trays; and $X17$ = number of debutanizer trays.

The function f in eq 1 represents all the equations in the simulator leading to computation of net profit. The optimization involves nine independent variables, $X1$ through $X9$. Implicit constraints on variables computed during the simulation were checked in the simulator with violations resulting in a return to the optimization subroutine.

In order to obtain a comparison with Friedman's work, net earnings was computed by PROPS using a constant investment, which is consistent with the concept of an existing plant. The complex method, described later, was used as the optimization procedure. The independent variables were chosen to be the recycle and quench splits, tower reflux ratios, exchanger outlet temperatures, and the tower pressure as given in eq 1 above. Other less important variables might also have been studied. Pressure in the debutanizer might be considered; however, this column has a narrow allowable pressure range and is outside the recycle loop. Thus, the optimum debutanizer pressure might be determined after optimization of the other variables without altering the validity of the results.

Dilution of the feed with propane is necessary in this process when the olefin concentration increases. Reactant concentration and catalyst activity were kept constant in this study, but might be considered as stochastic variables in the process. The physical constraints imposed on the equipment are also given in eq 1. Reactor temperatures must be kept below 945°R. The depropanizer and debutanizer columns had 42 and 24 trays, respectively. Other equipment constraints were not defined.

Friedman and Pinder (1972) used the complex method to optimize this process with only the quench and recycle splits ($X1$ through $X4$) as independent variables and with the objective of maximizing the amount of product. A comparison of these two studies is given in Table II. It is noted that the two optimum points are considerably different although the profitability is increased only about 3% when net profit is used as the objective function. While the optimum for the Friedman study was well assured (Friedman and Pinder, 1972), no effort was made to ensure that the net earnings of $128,452 for this study was, indeed, the maximum. This comparison demonstrates (not surprising-

Table II. Comparison of Optimization of a Polymerization Process with Different Objective Functions

	Optimum value	
	Friedman study	This study
Net earnings	$125,887	$128,452
Product produced, mol/hr	40.57	40.21
Feed conversion, %	92.9	92.0
Recycle split, $X1$	0.602	0.614
Quench splits, $X2$	0.016	0.037
$X3$	0.333	0.547
$X4$	0.464	0.381
$X11$	0.187	0.035
Depropanizer reflux, $X5$	...	1.05
Debutanizer reflux, $X6$	...	1.27
Feed temperature, °R, $X7$	710	822.71
Heater temperature, °R, $X8$	815	830.21
Depropanizer pressure, psia, $X9$	265	207.33

ly) that different and less profitable process optimization results can result unless a realistic economic objective function is chosen.

Process Design Optimization

In approaching this problem from a process design standpoint, equipment sizes would no longer be constrained and the investment becomes an important economic parameter. This problem, with the same independent variables, can be stated in terms of the return on investment, ROI, as

$$\text{maximize: ROI} = f(X1, X2, \ldots, X9) \qquad (2)$$

subject to: $0.43 \leq X1 \leq 1$; $0 \leq X2 \leq 1$; $0 \leq X3 \leq 1$; $0 \leq X4 \leq 1$; $1.05 \leq X5 \leq 1.5$; $1.1 \leq X6 \leq 1.7$; $650 \leq X7 \leq 840$; $750 \leq X8 \leq 860$; $200 \leq X9 \leq 300$; $X10 \leq 1 - X1$; $0 \leq X11 \leq 1 - X2 - X3 - X4$; $760 \leq X12 \leq 945$; $760 \leq X13 \leq 945$; $760 \leq X14 \leq 945$; $760 \leq X15 \leq 945$; where the variables are the same as previously defined.

Optimization Algorithms

Many different optimization algorithms have been used in process design optimization. Two of these methods which have proven successful in solving large problems are the complex and pattern search methods (Adelman and Stevens, 1972; Friedman and Pinder, 1972; Mason, 1971). These methods were applied to the problem given in eq 2. A third method, the adaptive random search, was also tried. A brief description of each of these methods follows.

1. Complex Method. The complex method was developed by Box (1965) and a modified version developed by Friedman (1971) was used in this study. The complex consists of a number of vertices greater than the number of independent variables. The point with the lowest objective function is dropped and the centroid of the remaining points is computed. The lowest point is projected through the centroid using an expansion factor. If the objective function at the new point is worse, new points closer to the centroid are evaluated until an improvement is achieved. As the optimum is approached, the complex is required to contract and is considered to have converged when the centroid ceases to move a significant distance.

2. Pattern Search. The pattern search technique was developed by Hooke and Jeeves (1961). The pattern search makes exploratory moves on all variables, one at a time. The variable is increased according to a specified or calculated step size. If an improvement is made, the next variable is considered. If no improvement results, the variable is decreased in search of improvement. Once all variables have been considered, a change in each variable is made in the direction of improving the objective and the pattern is once again formed. In order to handle the reactor temperature constraints with the pattern search, the ROI was reduced when the temperatures exceeded 945°R. This penalty of the ROI had the effect of creating a steep ridge along the constraint. Other penalty function methods were also considered, but were not applicable to this problem.

3. Adaptive Random Search. The pseudo or adaptive random search chooses new values of the independent variables in the region about the best value objective function. The expression suggested by Gall (1966) is given in eq 3

$$X_i = X_i^* + (X_{i_{max}} - X_{i_{min}})\,(2\theta_i - 1)^k \qquad (3)$$

where X_i = new value of independent variable $X1$, $X2$, etc.; X_i^* = value of variable X_i which produced the highest objective function; $X_{i_{max}}$ = maximum value of variable X_i; $X_{i_{min}}$ = minimum value of variable X_i; θ_i = random number; and k = distribution exponent.

The new value of variable X_i is found from the best known point, X_i^*, and a random sample from the range $(X_{i_{max}} - X_{i_{min}})$. θ_i is a random number between zero and unity. This procedure moves toward the optimum by successively replacing the X_i^* with improved values as they are located.

The exponent k determines the variance of the distribution of new search points. If k is unity, an exhaustive random search is performed. k may have values of 1, 3, 5, 7, 9, etc. When a better point is found, it replaces the last reference point, X_i^*, and the search is continued. In this study, the search was initiated with k at a value of 3. After 20 improved points, k was changed to 5, and after 20 more points, the value increased to 7, where it remained for the rest of the run.

Optimization Results

In order to compare the effectiveness of the three search techniques, two starting regions were used. The method of applying the techniques consisted of starting the search at one of the two regions and continuing to search for 4 min of IBM 370/165 time. After this time, any desired changes were made and the search restarted at the point where it had previously stopped. The search techniques were not restarted if convergence was obtained or little further movement was expected.

There were two changes made in the process during some of the optimization runs. The feed heater was removed from the process when its heat duty became negligible. Also, the depropanizer pressure in most cases was allowed to exceed the propane storage pressure of 300 psia, which required replacing the product pump by a valve.

Table III shows the results of optimization from the first starting region, while the results obtained using the second starting region are given in Table IV. In every case, the optimization runs produced a different end result. Further study indicates that the 14.93%, found by the adaptive random search, is the optimum ROI, or very near the optimum. As might be expected, the maximum ROI is obtained when the amount of recycle is very near its minimum value (corresponding to a recycle split of approximately 0.43) and the maximum amount of product at that recycle is produced. As noted, each of the runs converged near one of the upper reactor temperature constraints which results in near maximum feed conversion.

A comparison between the results of the adaptive random search and the pattern search, shown in Table IV, indicates the importance of making the most efficient distribution of the recycle quench stream. In the case of the pattern search results, the reactor effluent temperature is

Table III. Results of Optimization Searches from First Starting Point

Variable	Starting value[a]	Complex method	Hooke and Jeeves pattern search	Adaptive Random search
	A. Independent Variables			
$X1$	0.65	0.5788	0.5983	0.4522
$X2$	0.14	0.0190	0.1783	0.0002
$X3$	0.36	0.1033	0.3307	0.5839
$X4$	0.25	0.6520	0.3151	0.1575
$X5$	1.1	1.0853	1.0608	1.0535
$X6$	1.3	1.1820	1.1000	1.1000
$X7$	720	740.35	823.69	760.60
$X8$	840	780.97	...	...
$X9$	250	262.00	333.74	319.90
	B. Dependent Variables			
$X10$	0.35	0.4222	0.4017	0.5478
$X11$	0.25	0.2257	0.1760	0.2583
$X12$	899	844.63	873.97	815.99
$X13$	925	939.12	917.95	852.82
$X14$	944	918.27	940.05	923.77
$X15$	932	919.92	945.03	944.54
Feed Conversion (%)	92.0	91.0	92.0	89.0
ROI (%)	11.32	12.97	13.62	14.36
CPU time IBM 370/165		7.21	8.00	11.70
Total functional evaluations		203	269	204

[a] Only one of the beginning points for the complex search.

Table IV. Results of Optimization Searches from Second Starting Point

Variable	Starting value[a]	Complex method	Hooke and Jeeves pattern search	Adaptive random search
	A. Independent Variables			
$X1$	0.614	0.5596	0.5107	0.4647
$X2$	0.0375	0.0154	0.0032	0.0100
$X3$	0.547	0.3021	0.2664	0.2506
$X4$	0.381	0.3757	0.2105	0.3675
$X5$	1.05	1.0742	1.0962	1.1189
$X6$	1.27	1.2969	1.1621	1.2311
$X7$	823	790.30	760.85	761.17
$X8$	830	...	...	...
$X9$	207	302.59	336.44	326.68
	B. Dependent Variables			
$X10$	0.386	0.04404	0.4893	0.5353
$X11$	0.035	0.2888	0.5199	0.3720
$X12$	916	864.15	815.97	815.74
$X13$	919	922.53	882.12	890.48
$X14$	923	944.47	944.96	941.12
$X15$	944	938.98	929.12	944.92
Feed Conversion (%)	92.0	92.0	90.4	90.8
ROI (%)	12.03	14.08	14.24	14.93
CPU time (min) IBM 370/165		6.57	8.00	12.00
Total functional evaluations		155	277	198

[a] Only one of the beginning points for the complex search.

below the maximum value of 945°R; thus more recycle than necessary is used. Due to this added dilution and cooling, less product is produced and equipment sizes are larger. This inefficient use of recycle is the primary difference between the results of the pattern and adaptive random search results, shown in Table IV.

The objective function has a steep gradient toward the upper temperature constraint. This occurs because decreasing recycle causes both a lower investment and a higher revenue. The higher revenue is the result of higher reactor temperatures and more gasoline production. The objective function has a small gradient along the temperature constraints, as indicated by the points in Tables III and IV, all of which lie near a temperature constraint. Thus, each search procedure would be expected to move quickly toward the temperature constraint, and must then follow the constraint to find the optimum.

The first complex run resulted in an early encounter with one of these temperature constraints. Movement along the constraint was accompanied by continued contraction of the complex. Finally, the step size was so small that inherent errors in the material and energy balance computations prohibited further movement. The second complex run also moved along one of the temperature constraints, where it contracted and failed to move to the optimum. The modified complex method worked well in the region of the constraints, as reported by Friedman (1972). However, Friedman started his search much closer to his optimum, thus requiring less movement along constraints. Also, the added variables and different objective function used in this study may adversely influence the constraint following ability of the complex method.

Both pattern search runs failed when the reactor temperature constraints were encountered. By moving the independent variables one at a time, little improvement would be expected. The step sizes were decreased when the constraint was encountered and only little further movement was obtained. Additional runs with the pattern search using different tolerance limits and different penalty functions did not improve the results with this method. It appears that the constraints are nonlinear and would probably pose a problem to even the best constraint following techniques.

The adaptive random search generally makes larger changes in the independent variables than the complex or pattern search. A larger step size requires more computational time to converge recycle loops. Therefore, while fewer function evaluations were required by the adaptive random search than the pattern method and about the same number as the complex, more CPU time was used.

The random search technique does seem to have the ability to follow nonlinear constraints to the optimum. The first random search run was stopped after 11.7 min of CPU time, where it was very close to the optimum. The second run converged to the optimum. In the region of a constraint whose shape is nonlinear or unknown, a random move may be as good as any other. Patterned moves result in violation of the constraint and eventual failure of the method. Random movement, while inefficient, guarantees eventual success.

There are several advantages that can be summarized about the adaptive random search technique when applied to process optimization problems: (1) the technique is fairly simple to apply; (2) the technique will follow constraints (or ridges); (3) the method is appropriate for multi-modal problems; (4) the method can be applied to discrete variables and discontinuous objective functions.

While this method did find the proper optimum, it examines more of the uninteresting portions of the objective function region, and consequently, is somewhat inefficient. The choice of the exponent, k, in eq 3 affects the success and efficiency of this method. The first adaptive random search run might have been more successful in converging to the proper optimum if the exponent in eq 3 had been increased slowly allowing more of the region to be examined.

A small exponent will assure success but requires more time. Further study will be needed to define a general and perhaps more efficient method of handling this exponent for complicated problems. Study of additional problems of this type will also ascertain the usefulness of this method. While stochastic search techniques may never be as efficient in solving simpler optimization problems, these procedures may be found to be the best means (perhaps in conjunction with conventional techniques) of optimizing complex chemical processes.

Summary

It has been shown that complex process optimization studies can be carried out using flow sheet simulation programs with realistic economic criteria. These studies were completed in 7–12 min of IBM 370/165 computer time with minor modifications to an existing simulation system. As expected, process optimization with an economic objective function produces different results from optimization of the same process using an objective function from material or energy balance data. The adaptive random search method, while inefficient, found the optimum in this problem. The complex and pattern search methods failed because of their inability to follow constraints.

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Calculation of High-Pressure Phase Equilibrium from Total Pressure–Liquid Composition Data

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A numerical method is presented to calculate vapor compositions from isothermal total-pressure data up to the critical region. The method uses the isothermal general coexistence equation based on the Gibbs–Duhem equation and the Redlich–Kwong equation of state (Prausnitz modification) to the calculation of fugacities of components in high-pressure mixtures. Calculated results for 22 systems are in good agreement with experimental data.

Introduction

Van Ness et al. (1973) described the numerical methods by which one may accomplish the reduction of binary vapor–liquid equilibrium data at constant temperature and low pressure to yield a correlation of the liquid-phase activity coefficients and suggested that the recommended method for data reduction is the one based on just P–x data. Recently some authors extended this method to the calculation of high-pressure phase equilibrium from P–x data. Won and Prausnitz (1973) used Barker's method for binary systems containing one supercritical component. They expressed the binary activity coefficient equation with three parameters in the unsymmetric convention as a function of composition. Christiansen and Fredenslund (1975) presented an extension of the method of Van Ness et al. (1973) to high-pressure systems using the orthogonal collocation method. Several investigators have discussed numerical integration of the coexistence equation to calculate vapor compositions at low pressures (for example, Van Ness, 1964). Lu et al. (1968, 1974) applied this method to ternary systems up to 8 atm using the virial equation of state. Manley and Swift (1971) utilized the isothermal general coexistence equation and the Redlich–Kwong equation of state to obtain relative volatilities of propane–propene mixtures up to 22 atm.

The purpose of the present work is to extend the isothermal general coexistence equation to high-pressure binary vapor–liquid equilibria up to the critical region of interest because it is unnecessary to assume a particular liquid-phase model. Extension to high-pressure systems requires