Optimal Synthesis of Reactor-Separator Systems by Nonlinear Programming Method

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The optimum computer-aided design (CAD) of chemical engineering processes can generally be stated as a large-scale mixed-integer programming (MIP) problem, where the integer variables represent the process topology and the continuous variables are referred to the design parameters of unit operations. Processes involving reactors and separators are in common use in chemical engineering, so this study is restricted to the optimum CAD of such processes. This optimization problem can be defined as: Given a set of goal products (composition, flow rate, pressure, and temperature), systematically synthesize a process leading to this production at a minimum total annual cost (sum of investment and operating costs) from known reactants and reaction paths. In order to reduce the combinatorial aspect of the problem, only well-stirred tank reactors and simple distillation columns (a simple separator splits a single feed into two product streams) not thermally coupled are considered. The structure and the operating conditions are simultaneously optimized by using a Lagrangian-based algorithm, where the linearized subproblem is solved with a large-scale projected reduced gradient procedure. The synthesis of a benzene chlorination process illustrates this approach.

Previous Work

The optimal solution is searched within a superstructure developed by means of structural parameters (Ichikawa et al. 1969; Nishida and Powers, 1978). The structural changes in the superstructure are represented by continuous variables, and so the synthesis problem becomes a large-scale nonlinear programming problem. Five main classes of algorithms (Lasdon, 1981; Ladson and Warren, 1983) can be used to solve this type of problem:

1. Direct-search algorithms (Box, 1965; Luus and Jaakola, 1973), which can be used to solve small-scale problems with inequality constraints.
2. Successive linear programming (SLP) methods (Griffith and Stewart, 1961), which linearize any nonlinear criterion and constraints about some base point.
3. Successive quadratic programming (SQP) procedures (Biggs, 1975), which solve a sequence of quadratic programs.
4. Generalized reduced gradient (GRG) algorithms (Abadie, 1968; Abadie and Guigou, 1969), which solve the NLP by means of a sequence of reduced problems.
5. Augmented Lagrangian methods, which convert the original NLP to a sequence of unconstrained minimization problems of the augmented Lagrangian function (i.e., Lagrangian function in which exterior penalty terms are added). An alternative consists in defining the augmented Lagrangian by using only the nonlinear constraints and by solving a sequence of linearly constrained problems (Murtagh and Saunders, 1976, 1978, 1980; Pibouleau et al., 1985a).

From the comparative studies, realized on mathematical problems by Colville (1970), Himmelblau (1972), Lasdon et al. (1978), Sandgren and Ragsdell (1980), Schittkowski (1981), and Pibouleau et al. (1985b), the efficiency of GRG and augmented Lagrangian methods can be noted; that is why an augmented Lagrangian-based procedure has been retained (Pibouleau et al., 1985a, b) for solving the synthesis problems presented below.

Problem Formulation

The technico-economic criterion associated to the process is the total annual cost C, representing the sum of investment costs C_I and operating costs C_{op}. The investment cost C_I is the sum of three main items:

- FOB (free on board) costs for all reactor equipment: cost of vessels, platforms, ladders, and agitators; for distillation columns, costs of shells, trays, platforms, ladders, and internals; costs of heat exchangers and compressors
- Equipment installation costs (direct and indirect costs)
- Contingencies.

The annual operating cost C_{op} is computed by adding the three following terms:

- Annual energy cost and the cost for utilities; the latter is the annual cost of the frigories and calories needed for reboilers, condensers, and reactors
- Annual labor-related cost (operating labor, operating supervision, plant overhead cost)
- Annual cost of raw materials

Among the great number of published works, the choice of a set of correlations to compute the above costs was a difficult task. Attention must be focused in choosing recent correlations in order to get a coherent set with regard to the outputs of the design procedures. The correlations employed for calculating the various costs are given by Floquet (1986); see also the supplementary material. So for a process involving r reactors and d distillation columns, the total annual cost is the following:

$$C = \sum_{i=1}^{r} (C_{li} + C_{opi}) + \sum_{j=1}^{r} (C_{lj} + C_{opj}) \tag{1}$$

The structural parameters defining the process structure are the split fractions of streams (connections reactor-reactor or column-reactor) and the recovery rates of the feed components into the distillate of each column. By using this representation, a feed stream component may exit in the two outputs of a column, so nonsharp separations are handled. The solution of the synthesis problem must begin with an important formulation task, in order to get an optimization problem expressed in a standard continuous NLP form.

The enumeration of the optimization variables is made as follows.

Reaction Level

1. Operating pressure and temperature of each reactor
2. Component molar flows of the output stream of each reactor
3. Component molar flows of the input feed stream of the first reactor
4. Structural parameter defining the split fraction of the output stream of each reactor

So, for a given number r of reactors in series and a number N of components, the number n_r of optimization variables for the reaction level is (Floquet, 1986):

$$n_r = r(N + 3) + N - 1 \tag{2}$$

Separation level

In order to obtain a finite number of separators, it is assumed that the lightest and the heaviest components of the feed are not distributed between the column outputs. The lightest (heaviest) component exists only in the top (bottom) product. So it is shown (Pibouleau and Domenech, 1986) that the number d of columns is given by:

$$d = 2^{(N-1)} - 1 \tag{3}$$

The optimization variables associated with a distillation column are the following:

1. Operating pressure and reflux ratio
2. Structural parameters defining the recovery rates of intermediate components into the distillate
3. Structural parameters representing the split fractions of the top and bottom components that are recycled toward the reactor sequence

The number n_s of optimization variables for the separation level is equal to:

$$n_s = \sum_{i=1}^{(N-1)} 2^{(i-1)}(2r + N + 1 - i) \tag{4}$$

The range of values of all the variables mentioned above is bounded: all the structural parameters lie between 0 and 1, and all the design variables are physically bounded.

The set of constraints can be partitioned into three subsets (Floquet, 1986):

1. Inequality (linear) constraints on structural parameters; the number m_{li} of these constraints is given by:

$$m_{li} = 2^N - 2 + \sum_{i=1}^{(N-3)} 2^{(i-1)}(N - i - 2) \qquad \text{if } r > 1 \tag{5a}$$

$$m_{li} = \sum_{i=1}^{(N-3)} 2^{(i-1)}(N - i - 2) \qquad \text{if } r \le 1 \tag{5b}$$

2. Nonlinear equality constraints giving, for each reactor, the output stream composition as a function of the input stream and the design variables; the number of these constraints is:

$$m_{nle} = r \cdot N \tag{6}$$

3. For each component a production constraint (nonlinear equality) may be imposed; so the number m_{nle} becomes:

$$m_{nle} = r \cdot N + N \tag{7}$$

The implicit nonlinear criterion, Eq. 1, contains some discontinuities essentially due to:

- Corrective factors in cost evaluation (type of equipment, inflation)
- Specifications; for example, when a component in the feed stream of a column reaches a given purity specification, this separator and all its successors are removed from the superstructure and some costs are set to zero. Furthermore, when compressors are introduced into the process, the criterion discontinuously increases. These discontinuities can be approximated by continuous functions defined by Pibouleau and Domenech (1986).

Example: Synthesis of a Benzene Chlorination Process

The benzene chlorination process studied in this section is shown in Figure 1. The chemical reactions considered into the reaction level are the following:

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$
$$C_6H_5Cl + Cl_2 \rightarrow C_6H_4Cl_2 + HCl$$
$$C_6H_4Cl_2 + Cl_2 \rightarrow C_6H_3Cl_3 + HCl$$

Insofar as the other chlorination reactions concern insignifi-

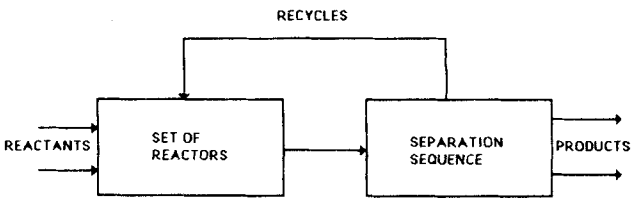


Figure 1. Flowsheet of the benzene chlorination process.

Table 1. Variation of Total Number of Variables and Constraints with Number of Reactors

	No. of Reactors, r			
Constraints	1	2	3	4
n	40	75	96	117
m	6	24	28	32

cant amounts of reactants, they are not taken into account. The monochlorobenzene is produced in liquid phase in a sequence of continuous stirred-tank reactors (CSTR's) whose design has been studied by several authors (Agnello and Williams, 1960; Bodman, 1968; Barona and Prengle, 1973; Wild et al., 1980) for fixed operating conditions. The reaction rate constants are given by the classical Arrhenius law (Bodman, 1968). Because all the reactions are exothermic, the heat is removed in internal coils. The number of reactors r is an important parameter of the problem, and it is assumed that its value lies between 1 and 4, as indicated by Rose (1981).

After the reaction level, the product (monochlorobenzene) is separated in the separation level from the unreacted benzene recycled toward the reactors, and from the by-products of the reactions (di- and tri-chlorobenzene; DCB, TCB). The produced hydrochloric acid is eliminated at the reaction level output by a stripping operation, whose cost is not taken into account. The kinetic data and the correlations and economic data are given by Floquet (1986); see also the supplementary material. The problem consists in determining the optimal process for a total production of monochlorobenzene of 30.10^6 kg/yr.

The linear inequality constraints are transformed into linear equality constraints by introducing slack variables. For processes involving one to four reactors, the total numbers of variables and constraints are reported in Table 1. For a process containing two reactors, the superstructure is shown in Figure 2. The streams are defined in the supplementary material.

Since the recycle streams are defined by structural parameters (splitting fractions of recycled components) considered as decision variables, the convergence of the simulation procedure is always assured during the search. In order to reduce the number of iterations, the search was initialized in each case (r = 1 to 4) with the best solution found by a discrete procedure (Floquet et al., 1985). The optimal processes determined by minimizing the augmented Lagrangian function are shown in Figure 3, where the values of the main design parameters (temperatures, conversions, volumes, and number of trays) are reported. In all cases, the operating pressures and the ratios $t = R/R_{min}$ are found to be 1 atm and 1.2, respectively, and the molar fractions of TCB in each stream are very low (less than 10^{-3}). For the four processes, the optimal value of the cost, the number of iterations, the maximum value of constraints, the number of crite-

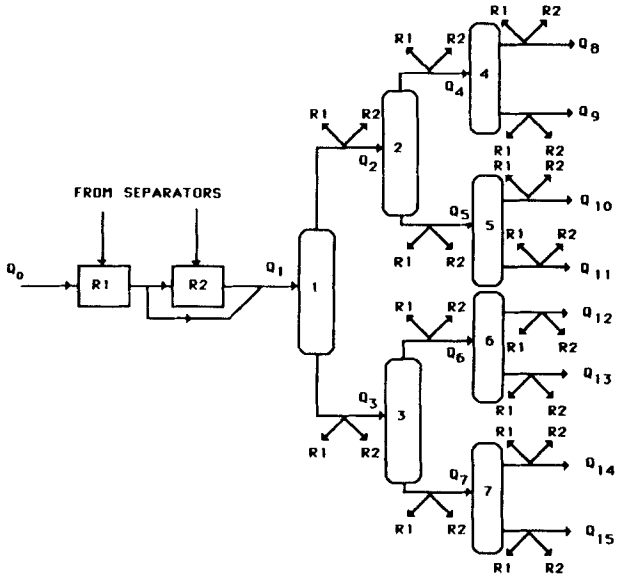
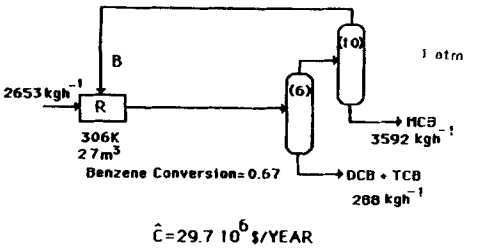
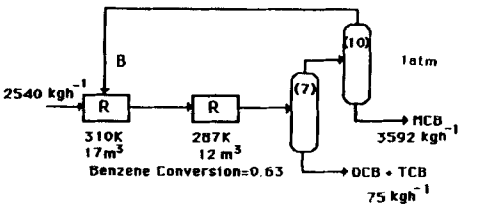


Figure 2. Superstructure for a process involving two reactors and four components.

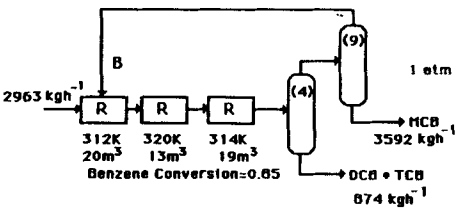


$\hat{C}$=29.7 10^6 $/YEAR

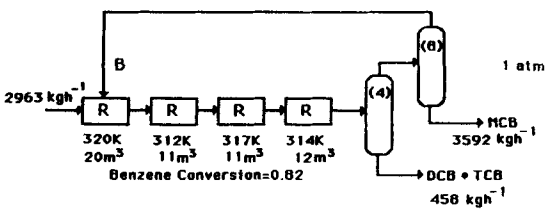


$\hat{C}$=29.8 10^6 $/YEAR

Figure 3a.



$\hat{C}$=29.8 10^6 $/YEAR



$\hat{C}$=30.8 10^6 $/YEAR

Figure 3b

Figure 3. Continuous solution for r = 1 to 4: optimal processes.

Table 2. Continuous Solutions for $r = 1$ to 4

No. of Reactors, r	Opt. Cost $\hat{C} \times 10^6$ \$/yr	Iteration No.	Max. Value of Constraints	No. of Criterion Calls	CPU Time IBM 3081 s
1	29.7	132	10^{-4}	14,009	360
2	29.8	78	10^{-5}	13,728	2,650
3	29.8	78	10^{-5}	17,004	4,890
4	30.8	36	10^{-4}	9,360	3,750

rion calls, and the CPU time on an IBM 3081 are given in Table 2. The important values of the number of criterion calls are due to the fact that the gradient vector was computed by using central finite differences. The central memory requirement is about 180 kbytes. From Table 2, it can be noted that when the number of iterations decreases, the CPU time increases. This is due to the fact that the criterion and constraints are more complex. The optimal costs $\hat{C}$ of the various processes are very close, but for reasons of simplicity the plant involving only one reactor may be chosen.

In the costing procedure, the cost of distillation columns is preponderant with regard to the cost of reactors; so it seems that small variations in the number of reactors do not perceptibly change the criterion value.

Notation

C = total annual cost of process, \$/yr
C_I = investment cost, \$/yr
C_{op} = operating cost, \$/yr
$\hat{C}$ = minimum cost, \$/yr
d = number of distillation columns of process
m = total number of constraints, $m < n$
m_{li} = number of linear inequality constraints
m_{nle} = number of nonlinear equality constraints
N = number of components
n = total number of variables
n_r = number of variables in reaction level
n_s = number of variables in separation level
R = operating reflux
R_{min} = minimum reflux
r = number of reactors

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