LITERATURE CITED

Aidarous, S. E., M. R. Gevers, M. J. Installe, "Optimal Sensor's Allocation for a Class of Stochastic Distributed Systems," *Int. of Control*, **22**, 197 (1975).

Athans, M., "On the Determination of Optimal Costly Measurement Strategies for Linear Stochastic Systems," *Automatica*, **8**, 397 (1972).

Bucy, R. S., and P. D. Joseph, *Filtering for Stochastic Processes with Applications to Guidance*, Interscience, New York (1978).

Colantuoni, G., and L. Padmanabhan, "Optimal Sensor Locations for Tubular-Flow Reactor System," *CES*, **32**, p. 1035 (1977).

Johnson, C. D., "Optimization of a Certain Quality of Complete Controllability and Observability for Linear Dynamical Systems," *J. Basic Eng.*, ASME Trans., Series D-229 (1969).

Jorgensen, S. B. and K. Clement, "Experimental Investigation of Reaction Zone Control in a Fixed Bed Reactor," *Chem. Eng. with Per Soltoft*, p. 69, Danish Technical Press, Copenhagen (1977).

Jutan, A., J. P. Tremblay, J. F. Macgregor, and J. D. Wright, "Multivariable Computer Control of a Butane Hydrogenolysis Reactor, Part I: State Space Reactor Modelling," *AIChE J.*, **23**, p. 732-742 (1977a).

Jutan, A., J. F. MacGregor, and J. D. Wright, "Multivariable Computer Control of a Butane Hydrogenolysis Reactor, Part II: Data Collection, Parameter Estimation and Stochastic Disturbance Identification," *AIChE J.*, **23**, 742-750 (1977b).

Jutan, A., J. D. Wright, and J. F. MacGregor, "Multivariable Computer Control of a Butane Hydrogenolysis Reactor, Part III: On-Line Linear Quadratic Stochastic Control Studies," *AIChE J.*, **23**, 751-758 (1977c).

Kumar, S., and J. Seinfeld, *Optimal Location of Measurements for Distributed Parameter Estimation*, IEEE **AC-23**, 690 (1978a).

Kumar, S., and J. H. Seinfeld, *Optimal Location of Measurements in Tubular Reactors*, Chem. Eng. Sci., **33**, 1507 (1978b).

Kushner, H., *Introduction to Stochastic Control*, Holt Rhinehardt and Winston, Toronto (1971).

MacGregor, J. F.: "Optimal Discrete Stochastic Control Theory for Process Applications," *Can. J. Chem. Eng.*, **51**, 468 (1973).

Mehra, R. K., "Optimization of Measurement Schedules and Sensor Designs for Linear Dynamic Systems," IEEE **AC-21**, 55 (1976).

Meier, L., J. Peschon, and R. M. Dressler, "Optimal Control of Measurement Subsystems," IEEE, **AC-12**, 528 (1967).

Mellefont, P. J., and R. W. H. Sargent, "Optimal Measurement Policies for Control Purposes," *Int. J. Control*, **26**, 595 (1977).

Mellefont, P. J., and R. W. Sargent, *Selection of Measurements for Optimal Feedback Control*, Ind. Eng. Chem. Process Des. Dev., **17**, 549 (1978).

Mitchell, T. J., "An Algorithm for the Construction of *D*-Optimal Experimental Designs," *Technometrics*, **16**, 203 (1974).

Muller, P. C., and H. I. Weber, "Analysis and Optimization of Certain Qualities of Controllability and Observability for Linear Dynamic Systems," *Automatica*, **8**, 237 (1972).

Omatu, S., S. Koide, and T. Soeda, "Optimal Sensor Location Problem for a Linear Distributed Parameter System," IEEE **AC-23**, 665 (1978).

Wynn, H. P., "The Sequential Generation of *D*-optimum Designs," *Ann. Math. Statist*, **B 35**, 1655 (1970).

Yu, T. K., and J. H. Seinfeld, "Observability and Optimal Measurement Location in Linear Distributed Parameter Systems," *Int. J. Control*, **18**, 785 (1973).

Manuscript received November 26, 1979; revision received March 12, and accepted April 10, 1980.

The Synthesis of Distillation Trains with Heat Integration

Due to rising energy costs, there is an increasing need to include the goal of energy conservation as an integral part of process synthesis. This paper discusses the problem of finding the optimum sequence of distillation columns for separating a multicomponent mixture, when heat exchange is permitted between the columns. The major difficulties are associated with the nonserial nature of the problem, the large combinatorial variety and the size of the optimization task. The synthesis strategy presented here overcomes these problems by the use of a bounding technique together with the Lagrangian theory from nonlinear programming. Accurate lower bounds on the optimal costs permit the elimination of nonoptimal sequences with minimal computational effort.

MANFRED MORARI
and
DON C. FAITH, III
Chemical Engineering Department
University of Wisconsin
Madison, Wis. 53706

SCOPE

Distillation is probably the most widely used method of separation in industry. U.S. distillation energy consumption for 1976 is conservatively estimated as two quads (1 quad = 10^{15} Btu), which is nearly 3% of the entire national energy consumption (Mix et al., 1978). In a recent study, the energy usage of 45 refineries and 226 chemical plants was surveyed (Prengle et al., 1974) and almost everywhere distillation was a major energy consumer. In petroleum refineries, crude and vacuum distillation was found to account for 22.5 to 51% of the total energy consumption. Thus, it is obvious that any small enhancement of efficiency can have a major impact on the national energy situation.

The techniques of vapor recompression and using the heat of condensation of an overhead stream in the reboiler of a neighboring column have been known for almost a century. However, systematic design methods which make maximum use of these ideas of heat integration or thermal coupling are still lacking. The problem of synthesizing optimal separation trains for multicomponent mixtures has attracted much attention recently. A survey is given by Hlavacek (1978). Heat integration between separators or with other streams in the plant has not been considered in these publications. Very elegant results on the so-called heat exchanger network synthesis problem have appeared recently (Linnhoff and Flower, 1978). Much of the earlier work in this area has been reviewed by Nishida et al. (1977).

All correspondence should be addressed to Morari.

Unfortunately, the synthesis of distillation trains with heat integration between the columns cannot be accomplished by a straightforward combination of separation train and heat exchanger network synthesis. Choosing the optimal separation train without heat integration and developing the optimal heat exchanger network a posteriori for the selected sequence generally do not leat to the optimal heat integrated flowsheet. Therefore, an entirely new approach is called for.

A very efficient and quite general technique involving a minimum number of assumptions has been developed and is presented in this paper. The method is algorithmic in nature and is based on a bounding strategy. The bounds are obtained with the aid of the Lagrangian theory of nonlinear programming. This combination allows one to arrive at the globally optimum solution without requiring an exhaustive enumeration of all the possibilities, as was suggested in earlier studies. The method is tested on the five-component hydrocarbon mixtures studied by Rathore et al. (1974 a,b).

CONCLUSIONS AND SIGNIFICANCE

Process synthesis does not only involve the search for the optimal design parameters, but even more important the development of the optimal processing structure. The structural decision is often based on rules of thumb or on an exhaustive enumeration of all the possibilities. New results developed in the present work allow one to make rational nonheuristic-based choices about the optimal sequence of separators and the optimal heat exchanger network between the distillation columns without resorting to the *brute force* overall optimization problem.

The new technique has been proven to be very effective on an example problem of a five-component hydrocarbon mixture. The number of possible heat exchanger networks increases rapidly with the number of components to be separated. The new method generates accurate lower bounds on the optimal costs without considering all the possible heat exchanger networks. Therefore, the computational complexity increases only slowly with the number of components in the mixture. The detailed analysis necessary for the development of this technique has made it also possible to identify and estimate the key variables (temperature difference and heat load in intercolumn heat exchanger) determining the optimal operation of thermally coupled columns.

Process synthesis is the specification of the chemical and physical transformations and the selection and interconnection of equipment to implement these transformations, to convert available raw material into more desirable final products on an industrial scale. This procedure, which is equivalent to the generation of the process flowsheet, was formulated in a systematic fashion for the first time by Rudd and his students (Siirola and Rudd, 1971; Siirola et al., 1971). They decomposed the overall problem into a series of interacting subproblems: reaction path synthesis, species allocation, task specification, task integration and equipment design. The reaction path synthesis problem and particular task specification and task integration problems have been studied extensively since.

Examples of tasks are separation, cooling-down/condensing, and heating-up/vaporizing of process streams. An example of task integration is the combination of heat sources and heat sinks in a plant in order to reduce the utility consumption. In general task specification and task integration are carried out iteratively. For example a sequence of separators to separate a mixture into its constituent components is specified and the heat sources (e.g., condensers) and heat sinks (e.g., reboilers) are identified. In the next step heat integration is attempted. Then the designer returns to the task specification step and tries a different sequence of separators and so on until the *optimal* separation train including heat integration has been found.

PROBLEM DEFINITION AND DISCUSSION

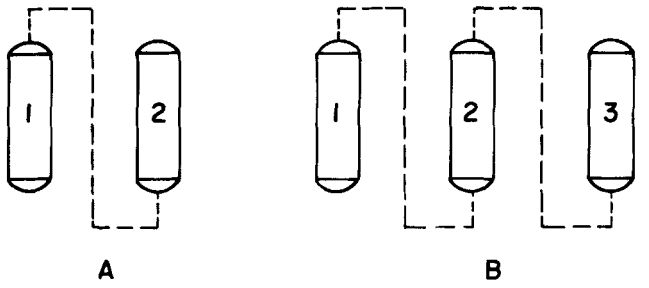
Many techniques for synthesizing separation sequences have been developed over the last decade. They can be classified into: 1) heuristic methods (*rules of thumb*), 2) algorithmic techniques, and 3) evolutionary strategies.

The heuristic approach (e.g., Seader and Westerberg, 1977) is used to reduce the combinational complexity of the problem, and narrows the search over the most promising alternatives by involving *rules of thumb*, so it does not guarantee optimality. Nevertheless, it has been used extensively. Algorithmic techniques have used the principle of optimality (e.g., Hendry and Hughes, 1972) variations of the branch and bound search (e.g., Westerberg and Stephanopoulos, 1975; Rodrigo and Seader, 1975) and other methods. They are mathematically rigorous and therefore provide the optimal solution. Evolutionary strategies combine some aspects of heuristic and algorithmic techniques and can lead to the optimal solution if the evolutionary rules are properly chosen (e.g., Stephanopoulos and Westerberg, 1973; Nath and Motard, 1978).

All those methods take implicitly or explicitly advantage of the strictly serial problem structure. The cost of a separator separating N components into two sets of M and N-M components is completely independent of *later decisions* on how the two mixtures resulting from the first separation are further separated into their constituent components. The total separation cost is simply obtained by adding the investment and operating cost of the different separators.

Significant progress has also been achieved in the area of heat exchanger network synthesis. The problem definition is chosen such that this task is isolated from the remaining synthesis problem: the physical state of a set of process streams has to be changed from a specified initial state to a specified target state (that is, the streams have to be heated up, vaporized, condensed, cooled down), and the optimal network to accomplish this task is to be designed. By fixing the initial and final conditions the network synthesis can be carried out separately from the remaining process.

The big challenge of the thermally integrated separation synthesis problem is that none of the two basic assumptions mentioned above is satisfied:



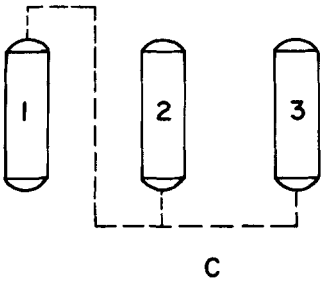


Figure 1. Some possible heat match structures between distillation columns. The dotted lines indicate reboiler (condenser) matching between the corresponding columns. For more detailed examples see Fig. 6.

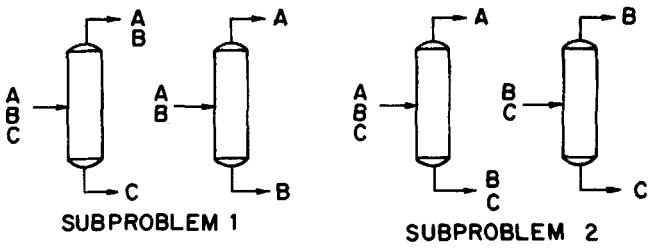


Figure 2. The two two-column subproblems for a three-component separation.

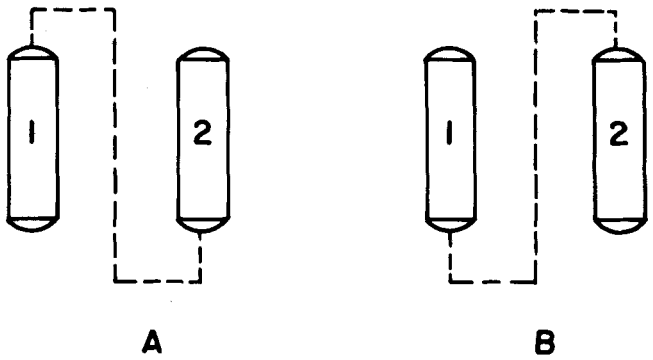


Figure 3. The two possible heat matches for a two-column subproblem.

1) The problem has a nonserial structure. Assume that the four-component mixture *ABCD* is separated into *A* and *BCD* by distillation. The operating and investment costs of this column depend on how *BCD* is separated further downstream. If *BC* is separated from *D* in the next column, it might be possible to use the heat of condensation of *BC* for supplying some or all the heat for separating *A* from *BCD* assuming that the two columns operate at different pressures. This fact prohibits the use of all the established heuristics, branch and bound searches, and evolutionary strategies.

2) The initial and final states of the heat sources and sinks are not prespecified but variable: by changing the column pressure, the dew point and boiling point change and consequently the temperatures at which energy is available and needed respectively. The pressure changes lead also to the need for different utilities and different column designs and are therefore not free but have costs associated with them. It is therefore impossible to separate the heat exchangers from the associated distillation columns and to arrive at a meaningful network.

A further point is worth mentioning. In all discussions on heat exchanger network synthesis, the operating costs were found to dominate the overall costs and thereby a network featuring maximum energy recovery is usually at least close to optimal. Linnhoff et al. (1979) attributed this, from an industrial point of view, unrealistic result to the fact that in all problems steam is available at one pressure only. In order to yield realistic results, this assumption is not used in the present work. We found then, that it is generally not desirable to change the column pressures to extreme values just in order to recover as much energy as allowed by the pressure constraints. Due to the resulting high (low) pressures, the remaining energy not obtained by integration has to be supplied (removed) by utilities at such a high (low) temperature level that this *maximal heat integration* becomes uneconomical.

PREVIOUS WORK

Due to these complications only one paper has appeared in the literature so far which provides some valuable insight into the general problem of synthesizing thermally coupled distillation trains (Rathore et al., 1974 a,b). A case study for four- and five-component hydrocarbon mixtures with different relative concentrations has been presented by Freshwater and Ziogou (1976). Umeda et al. (1979) give an outline for reducing the problem to a heat exchanger network synthesis problem and their approach suffers from the difficulties mentioned above.

Very imaginative schemes for treating ternary mixtures were suggested by Petlyuk et al. (1965) and were the subject of subsequent case studies by Stupin and Lockhart (1972) and Doukas and Luyben (1978). A detailed study for ternary hydrocarbon mixtures was prepared by Tedder and Rudd (1978). The problem has been reviewed by Siirola (1978) and some early attempts by one of the authors were reported before (Sophos et al., 1978).

Because of its importance the work by Rathore et al. (1974) will be discussed in more detail. They limit the types of heat integration between columns to those shown in Figure 1. Reboiler-Condenser matches are considered exclusively. Stream splitting between several columns is allowed (Figure 1*c*) and a column can be matched at both ends (Figure 1*b*). The columns may operate at different pressures. In order to allow the application of dynamic programming, the problem was reformulated to yield sequential information flow. In addition to considering single separators without heat integration, multiple separator subproblems are defined, where heat integration is allowed within the subproblem.

A three-component mixture, for example, has two two-column subproblems shown in Figure 2. For each subproblem two forms of heat integration are possible (Figure 3). For three-column subproblems many more forms

Table 1. Enumeration of Groups of Separation Subproblems

Number of Components	Number of Coexisting Subproblems 1	2	3	4	5	6
2	1					
3	4	2				
4	10	15	5			
5	20	63	56	14		
6	35	196	336	210	43	
7	72	504	1314	1650	792	132

of heat integration exist and the complexity continues to increase rapidly with the subproblem size. The number of independent subproblems for different numbers of components has been evaluated by Siirola (1978) as shown in Table 1. Note that the number of one-column subproblems (first entry in row) is equal to the number of distinct separators. The last entry in every row is the number of distinct flowsheets (without heat integration).

Rathore et al. (1974) find first for each subproblem the optimal solution including heat integration. Then, they combine the different subproblem solutions by dynamic programming to yield the optimal solution of the overall problem. Unfortunately, dynamic programming often yields an infeasible solution and cannot be applied. Even if it works the computational advantages are minimal, because the major effort goes into the solution of *all* the subproblems and not into their combination where dynamic programming is useful. While only a small reduction of the synthesis effort was accomplished by the aforementioned authors, they provided a very valuable elucidation of the topological features of the problem through the definition of a stream matrix and the development of feasibility rules.

An *exclusion principle* was also stated to eliminate the need for evaluating higher sets of interacting subproblems. Can we determine from the economic (in)feasibility of the two matches in Figure 4*a*,*b* that the three-column match in Figure 4*c* is economically (in)feasible? Let us define the profit associated with an energy match m as:

$$P_m \equiv (C_1^0 + C_2^0) - (C_{1m}^0 + C_{2m}^0) \qquad (1)$$

where C_{im}^0 and C_i^0 are the optimal costs of the separator i with and without match respectively. If $P_m < 0$, the match can be discarded as uneconomical. Denote the pressure range of Column 2 within which match a (Figure 4*a*) is feasible on thermodynamic grounds by R_a. Denote the pressure range for match b (Figure 4*b*) likewise by R_b. Match c (Figure 4*c*) will be feasible for the Column 2 pressure in the range $R_a \cap R_b$. Quite clearly

$$P_{ma}(R_a \cap R_b) \leq P_{ma}(R_a)$$

and

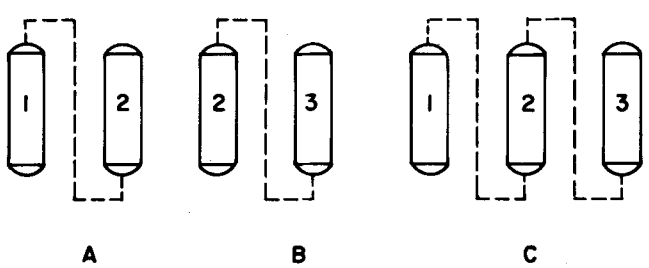


Figure 4. The *exclusion principle* is formulated to allow the elimination of structure C, when A and B are economically infeasible.

$$P_{mb}(R_a \cap R_b) \leq P_{mb}(R_b)$$

and by adding

$$P_{ma}(R_a \cap R_b) + P_{mb}(R_a \cap R_b) \leq P_{ma}(R_a) + P_{mb}(R_b) \qquad (2)$$

From this inequality, Rathore et al. (1974*b*) concluded that if matches a and b are economically infeasible [$P_{ma}(R_a) \leq 0$, $P_{mb}(R_b) \leq 0$] the triple column match c is also infeasible. This assumes that the left hand side of Eq. (2) is equal to P_{mc}. However, it can be shown easily that it is possible to have

$$P_{mc} \geq P_{ma}(R_a \cap R_b) + P_{mb}(R_a \cap R_b) \qquad (3)$$

and therefore this conclusion is not correct in general.

As in most previous work we use list techniques for the representation of the separation operations. A ranked list is a list of components of the initial mixture in decreasing order of relative volatility. Thus, in a five-component mixture *ABCDE*, *A* is the most volatile and *E* the least volatile component. For our task of developing a method for synthesizing distillation trains with heat integration, we make the following assumptions:

A1. Each column operates at high recovery.
A2. The volatility order does not change with changes in pressure.
A3. Only heat matches of the type shown in Figure 1*a* and 1*c* are considered. In other words, condenser/reboiler matching is allowed exclusively and a column must not be matched at both ends (Figure 1*b*).

A1 can be somewhat relaxed as we will discuss later; A2 is satisfied in the majority of practical cases. A3 might seem restrictive but it was found that matches as in Figure 1*b* are rarely economical. Column 1 has to be at a strongly elevated pressure and/or Column 3 is at a strongly reduced pressure; thus, requiring expensive utilities. Other matches which are commonly used like bottom product-feed heat exchange are of lesser importance, because they involve sensible heat only. We made a number of further assumptions solely to simplify our example calculations. They are not inherent to the method and the necessary modifications for their relaxation will be discussed below.

A4. Only cooling water, no refrigerant is used.
A5. The steam costs are approximated by a continuous function dependent on pressure.
A6. The cost of changing the temperature and pressure of streams as they pass between columns are negligible.
A7. Vapor recompression is not used.
A8. Feeds and products are saturated liquids.
A9. Only total condensers and reboilers are employed.

The remainder of the paper is organized as follows: Lagrangian theory forming the backbone of our developments is reviewed and an important extension is derived. Subsequently, we explain how to apply these theorems to the practical problem of interest. The presentation of the example problem is succeeded by an extensive discussion.

LAGRANGIAN THEORY

We could present the review of the Lagrangian theory in complete generality, but we prefer to carry out the developments with reference to the particular synthesis problem. When we refer just to the order of separation operations, we will speak of *separation sequences* or simply *sequences*. As an example, Figure 5 shows all possible sequences for separating a four-component mixture. An index is associated with each separation and each se-

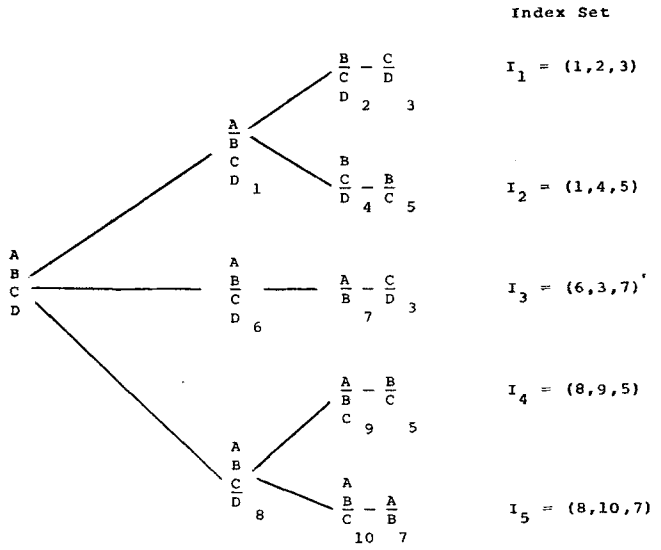


Figure 5. All feasible separation sequences for a four component mixture.

quence is identified uniquely by an index set. For each separation train different structures of heat exchangers between the columns are possible. We will term this topological property the *interconnection structures*. A separation sequence including a particular heat exchanger network will be referred to as a *separation flowsheet* or simply a *flowsheet*. To find the optimal flowsheet we have to search over all sequences, all interconnection structures, and finally over all design parameters. The overall synthesis problem can therefore be expressed mathematically as:

$$\underset{m}{Min}\ \{\underset{k\epsilon K^m}{Min}\ [\underset{u}{Min}\ \phi^{m,k} = \sum_{i\epsilon I_m} \phi_i(x_i,u_i,z_i)]\} \tag{4}$$

$$m = 1,2,\ldots M$$

$$s.t.:\ f_i(x_i,u_i,z_i) = 0 \tag{5}$$

$$y_i = g_i(x_i,u_i,z_i) \tag{6}$$

$$z_i = \sum_{j\epsilon I_m} T^k_{ij}\, y_j \tag{7}$$

where

- ϕ_i = objective function (investment and operating cost for column and heat exchangers) of column with index i.
- x_i = dependent variables of column i.
- u_i = independent variables of column i.
- z_i = interconnection variables, input to column i.
- f_i = state equations describing column i (dim f_i = dim x_i).
- y_i = interconnection variables, output of column i.
- M = number of distinct separation sequences.
- I_m = index set of sequence m.

The k^{th} interconnection structure is defined uniquely by the Boolean matrix T^k. The matrix T^k_{ij} is the identity matrix, when the output variable of Column j is an input variable to Column i and is zero otherwise. K^m is the set of indices denoting all possible interconnection structures for the sequence m. The innermost optimization determines the best parameter values for a fixed sequence and a fixed heat integration network. The middle optimization finds the best heat integration network and the outer optimization finds the best sequence. Define problem $P1$ as:

$$\underset{u}{Min}\ \phi^{m,k}(x,u,z) \tag{8}$$

$$(P1)\qquad s.t.\ \ f_i(x_i,u_i,z_i) = 0 \tag{5}$$

$$z_i = \sum_{j\epsilon I_m} T^k_{ij}\, y_j \tag{7}$$

That is, $P1$ is the fixed sequence, fixed structure parametric optimization problem. Let the optimal solution be obtained for the parameters $(x^{m,k}, u^{m,k}, z^{m,k})$ and denote the optimal value of the objective function by:

$$\Phi^{m,k} = \phi^{m,k}(x^{m,k}, u^{m,k}, z^{m,k}) \tag{8a}$$

and

$$\Phi = \underset{m}{Min}\ \{\Phi^m\} = \underset{m}{Min}\ \{\underset{k\epsilon K^m}{Min}\ \{\Phi^{m,k}\}\} \tag{9}$$

Define the Lagrangian for $P1$ by:

$$\begin{aligned} L^{m,k} &= \sum_{i\epsilon I_m} \phi_i(x_i,u_i,z_i) + \lambda_i^{kT}\left(\sum_{j\epsilon I_m} T^k_{ij} y_j - z_i\right) \\ &= \sum_{i\epsilon I_m} \phi_i(x_i,u_i,z_i) + \sum_{j\epsilon I_m} \lambda_j^{kT} T^k_{ji}\, y_i - \lambda_i^{kT} z_i \\ &\equiv \sum l_i^k(x_i,u_i,z_i,\lambda^k) \end{aligned} \tag{10}$$

and formulate problem $P2$ as:

$$H^{m,k}(\lambda^k) = \sum_{i\epsilon I_m} \left\{ \begin{array}{l} \underset{u_i,\, z_i}{Min}\ \{l_i^k(x_i,u_i,z_i,\lambda^k)\} \\ s.t.\ f_i(x_i,u_i,z_i) = 0 \end{array} \right. \qquad (P2)$$

$$\equiv \sum_{i\epsilon I_m} h_i^k(\lambda^k) \tag{11}$$

and finally the dual problem $P3$ as:

$$\underset{\lambda^k}{\text{Max}}\ H^{m,k}(\lambda^k) \qquad (P3)$$

$P2$ and $P3$ define the two level optimization problems discussed in detail by Lasdon (1970). A solution can be obtained by guessing values of λ^k and solving $P2$ for a fixed λ^k. Then λ^k is updated successively in order to find a solution of $P3$. Usually a gradient technique is used for the stepwise improvement of λ:

$$\lambda_i^k,\ \text{New} = \lambda_i^k,\ \text{Old} + \epsilon\left(\sum_{j\epsilon I_m} T^k_{ij}\, y_j - z_i\right)$$

where $\epsilon > 0$.

It can be shown (Lasdon, 1970) that if the Lagrangian function $L^{m,k}$ has a saddlepoint, the solution of $P2$ and $P3$ is also the solution of $P1$. The existence of a saddlepoint is guaranteed if the objectives ϕ_i and all constraints are convex. Note that by substituting $P2$ and $P3$ for $P1$, we replace one large optimization problem ($P1$) with a large number of independent variables by a set of several smaller problems ($P2$) involving only single separators. These small problems have to be optimized repeatedly, however, in order to solve ($P3$). We observe that this method will be efficient if the dimension of the interconnection variable z which has to be introduced is small and if the dual problem $P3$ converges fast.

Theorem 1 (Lasdon, 1970). Any solution of $P2$ forms a lower bound on the optimal value of the objective function as:

$$H^{m,k}(\lambda^k) \leq \Phi^{m,k} \quad \forall k \tag{12}$$

At the optimum, that is, for properly chosen multipliers and if a saddlepoint exists, inequality (Eq. 12) will become an equality. Theorem 1 allows one to obtain a lower bound on the optimal cost of a separation train by assuming values for λ^k and performing single column optimizations. The bound will be the better, the closer the chosen λ^k is to the one at the optimum. The theorem can also be interpreted in economic terms by regarding the columns as independent decision-makers who buy and sell commodities (z and y respectively) among each other at prices λ.

For any prices, the total costs arising for all the companies will form a lower bond on the optimal costs. Supply will equal demand for correctly chosen prices. These considerations led us to the following extension of the theorem. If we are just interested in obtaining a lower bound on the costs, the chosen market structure (who sells to whom) is irrelevant. If all the commodities are bought at the lowest and sold at the highest possible price, a *lower lower bound* on the optimal costs will be obtained. This idea can be expressed as follows.

Theorem 2. Assume $z \geq 0, y \geq 0$ * then for all $k \epsilon K^m$

$$\Phi^{m,k} \geq \sum_{i \epsilon I_m} \left\{ \begin{array}{l} Min\ \phi_i(x_i, u_i, z_i) + \underline{\lambda}_i^T y_i - \bar{\lambda}_i^T z_i \quad ** \\ u_i, z_i \\ s.t.\ f_i(x_i, u_i, z_i) = 0 \end{array} \right.$$

where

$$\underline{\lambda}_i \leq \sum_{j \epsilon I_m} \lambda_j^{kT} T_{ji}^k \qquad \forall k \epsilon K^m \tag{13}$$

$$\bar{\lambda}_i \geq \lambda_i^k \qquad \forall k \epsilon K^m \tag{14}$$

Proof. Assume that (x^k, u^k, z^k) solve $(P2)$ for a specified λ^k as:

$$\sum_{i \epsilon I_m} \phi_i(x_i^k, u_i^k, z_i^k) + \sum_{j \epsilon I_m} \lambda_j^{kT} T_{ji}^k y_i^k - \lambda_i^{kT} z_i^k \leq$$

$$\leq \sum_{i \epsilon I_m} \phi_i(x_i, u_i, z_i) + \sum_{j \epsilon I_m} \lambda_j^{kT} T_{ji}^k y_i - \lambda_i^{kT} z_i$$

$$\forall x, u, z \text{ satisfying } f_i(x_i, u_i, z_i) = 0, i \epsilon I_m.$$

Then it follows from Eqs. (13) and (14), and the assumption $z \geq 0, y > 0$ that:

$$\sum_{i \epsilon I_m} \phi_i(x_i^k, u_i^k, z_i^k) + \underline{\lambda}_i^T y_i^k - \bar{\lambda}_i^T z_i^k$$
$$\leq \sum_{i \epsilon I_m} \phi_i(x_i^k, u_i^k, z_i^k) + \sum_{j \epsilon I_m} \lambda_j^{kT} T_{ji}^k y_i - \lambda_i^{kT} z_i$$

and by Theorem 1, the conclusion of the theorem becomes obvious.

In order to obtain an even more conservative bound, we can invoke

Corollary 1. Theorem 2 also holds for $\underline{\lambda}$ and $\bar{\lambda}$ chosen such that

$$\underline{\lambda}_i \leq \sum_{j \epsilon I_m} \lambda_j^{kT} T_{ji}^k \qquad \forall k \epsilon K \tag{15}$$

$$\bar{\lambda}_i \geq \lambda_i^k \qquad \forall k \epsilon K \tag{16}$$

where $K = \bigcup_{m=1}^{M} K^m$

Assume that we have obtained reasonable estimates of all vectors λ^k ($k \epsilon K^m$, $m=1, \ldots M$) by a technique to be discussed later. Theorem 1 allows to compute a lower bound on the optimal cost of each possible flowsheet with each possible heat exchanger configuration. Theorem 2 provides a lower bound on the optimal cost of a separation sequence regardless of the form of heat integration.

The bound is less accurate than that obtained from Theorem 1 but much less single column optimizations will be necessary. Corollary 1 gives an even more conservative bound with even less single column optimizations. From an economic point of view, Corollary 1 means a further simplification of the market structure from Theorem 2. In Theorem 2, a column is treated differently when appearing in different sequences: Corollary 1 does not make this distinction.

Synthesis Procedure

This forms the basis of the synthesis procedure:

1) Choose a flowsheet (separation sequence and heat exchanger network) on the basis of heuristics. The (optimal) cost for this flowsheet will form the upper bound on the optimal solution of the synthesis problem.

2) Estimate the multipliers λ for all interconnections in all sequences.

3) Compute a lower bound on the optimal costs of the different sequences by using Corollary 1. If the lower bound of a sequence exceeds the upper bound, the sequence can be discarded as uneconomical.

4) Try to improve the upper bound by computing the cost for the sequence with the lowest lower bound found in Step 3. Discard any sequences whose lower bound exceeds the new upper bound.

5) Compute a lower bound on the optimal cost of the different sequences by using Theorem 2. If the lower bound of a sequence exceeds the upper bound, the sequence can be discarded as uneconomical.

6) Try to improve the upper bound and discard any sequences whose lower bound exceeds the new upper bound.

7) Compute a lower bound on the optimal cost of the remaining flowsheets by using Theorem 1. If the lower bound of a flowsheet exceeds the upper bound, the flowsheet can be discarded as uneconomical.

8) Try to improve the upper bound and discard any flowsheet whose lower bound exceeds the new upper bound.

9) Try to improve the multipliers λ and return to step 7 until the optimal flowsheet has been found.

This procedure will be effective if complete sequences can be discarded in steps 1 to 6, thus avoiding the evaluation of all the different flowsheets. This efficiency will depend on the chosen upper bound and the initial guesses for the multipliers λ.

Variations of this synthesis algorithm are possible — how often to improve the upper bound, how often to update the multipliers, etc. However, we found this structure to be most efficient. The Lagrange multipliers λ express the sensitivity of the objective to a change in the constraints at the optimum (Wilde and Beightler, 1967) and can be found via the solution of the adjoint equations (Westerberg, 1973) or directly from the sensitivity interpretation.

*Vector inequalities are to be understood component wise; e.g., $z \geq y$ is equivalent to $z_i \geq y_i, \forall i$.

**Note that for the economic interpretation ($-\lambda$) are the prices of the *commodities*.

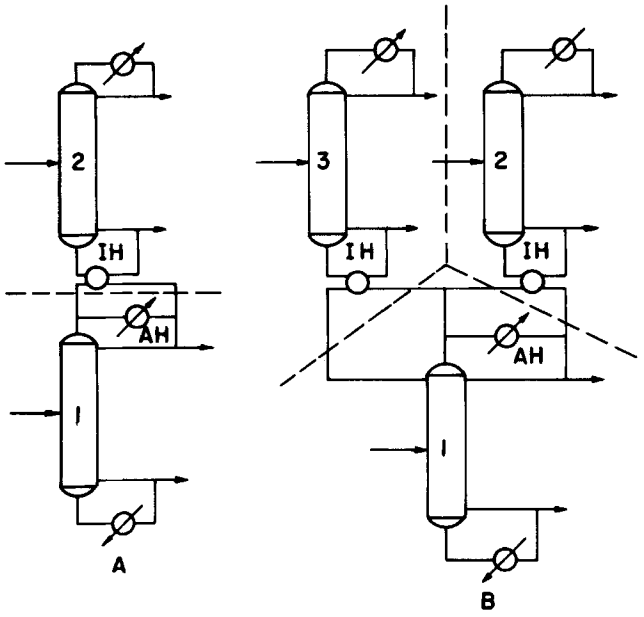


Figure 6. Examples of the application of the *Decomposition Rule* (IH = Intercolumn Heat Exchanger; AH = Auxiliary Heat Exchanger).

$$\lambda_i^k = \frac{\delta \Phi^{m,k}}{\delta z_i} \Bigg) \quad f_j(x_j, u_j, z_j) = 0 \qquad \forall j \epsilon I^m \tag{17}$$

$$z_j = \sum_{s \epsilon I^m} T_{js}^k y_s \qquad \forall j \epsilon I^m, j \neq i$$

Here, the derivative is to be understood as the constrained derivative (Beveridge and Schecter, 1970); that is, it is taken such that all the constraints listed above remain satisfied. Eq. (17) is a convenient way to determine λ in a complex system where adjoint equations might be difficult to derive.

Though the numerical value of λ depends on scaling, we will make the following qualitative definition. We call two subsystems weakly- (strongly-)coupled, if the multiplier associated with the interconnections has a small (large) absolute value. Neglecting the influence of the interconnections in weakly-coupled subsystems has only a minor influence on the optimal value of the objective.

DECOMPOSITION OF THE FLOWSHEET AND ESTIMATION OF THE LAGRANGE MULTIPLIERS

The flowsheet should be decomposed such that the number of interconnection variables which have to be defined is as small as possible and that the multipliers associated with the interconnections can be easily estimated. We experimented with a variety of decomposition schemes and finally arrived at the following.

Decomposition Rule

Each subsystem should consist of a distillation column, one reboiler and one condenser. These heat exchangers can use either utilities or other process streams as the source (sink) of energy.

Examples are shown in Figure 6. This rule would fail, if heat loads for different columns were identical. This is an extremely rare coincidence, never encountered in our example calculations. Besides, an auxiliary reboiler or condenser would always be installed because of operability considerations.

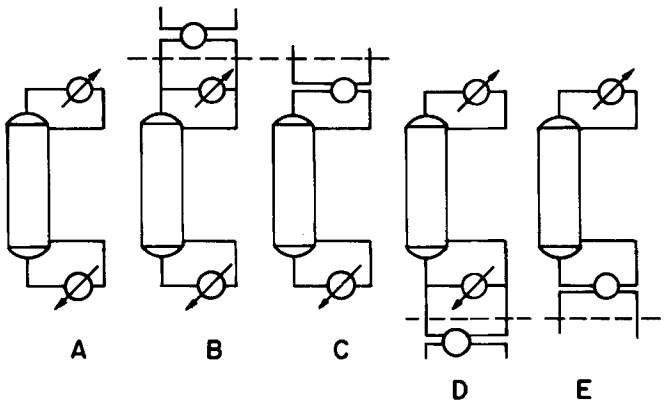


Figure 7. Five possible subsystems formed by a distillation column.

Only two interconnection variables are needed across each subsystem boundary: (1) the temperature of the stream with the auxiliary heat exchanger (AH) and (2) the heat load of the intercolumn heat exchanger (IH). As an example, the sublagrangians for system A in Figure 6 are:

$$\text{Column 1: } l_1 = \phi_1 + \lambda_T T_1 - \lambda_Q Q_2^* \tag{18}$$

$$\text{Column 2: } l_2 = \phi_2 - \lambda_T T_1^* + \lambda_Q Q_2 \tag{19}$$

where

ϕ_i = objective function of column i.
T_1 = temperature of condensing stream of column 1.
Q_2 = heat load of intercolumn heat exchanger of column 2.

Interpreted from an economic point of view, Column 1 sells the temperature T_1 of its condensing stream at a price $(-\lambda_T)$ and buys heat Q_2^* from Column 2 at a price $(-\lambda_Q)$. A similar interpretation holds for Column 2. The sublagrangians for system B in Figure 6 can be derived in the same manner:

$$\text{Column 1: } l_1 = \phi_1 + (\lambda_{T_2} + \lambda_{T_3}) T_1 - \lambda_Q (Q_2^* + Q_3^*) \tag{20}$$

$$\text{Column 2: } l_2 = \phi_2 + \lambda_Q Q_2 - \lambda_{T_2} T_1^* \tag{21}$$

$$\text{Column 3: } l_3 = \phi_3 + \lambda_Q Q_3 - \lambda_{T_3} T_1^* \tag{22}$$

Each column can form a maximum of five distinct subsystems (Figure 7) depending on the type of heat match. To find the *lower lower bound* for a column, Theorem 2 (or Corollary 1) has to be applied to each configuration B-E. The *lower lower bound* is the smallest of the minimized sublagrangians A-E. However, the column with the largest heat load in the sequence will never participate in matches of type C and E; the column with the smallest heat load in the sequence will never need an auxiliary reboiler or condenser as in B and E.

The number of single-column optimizations required by Theorem 2 (or Corollary 1) will, therefore, always be less than or equal to the number of possible matches. The simplification offered by the proposed technique will be the more significant the larger the number of components in the mixture. The multipliers λ can be estimated by applying Eq. (17). Assume, for example, that the heat exchanger costs are given by the commonly used power law expression, $K(Q/\Delta T)^p$:

where

K,p = constants.
Q = heat load.
ΔT = temperature difference.

then the objective functions for system A in Figure 6 would be:

$$\phi_1 = \phi_1 + K\left(\frac{Q_1 - Q_2}{T_1 - T_u}\right)^p + C_u\,(Q_1 - Q_2) \qquad (23)$$

$$\phi_2 = \phi_2' + K\left(\frac{Q_2}{T_1 - T_2}\right)^p \qquad (24)$$

where T_u, C_u are the utility cost and temperature respectively. From physical reasoning, it is easy to see that ϕ_1' is independent of Q_2 and ϕ_2' is independent of T_1 and that the constrained derivatives (Eq. 17) reduce to partial derivatives. Therefore,

$$\lambda_T = \frac{\partial}{\partial T_1}\left[K\left(\frac{Q_2}{T_1 - T_2}\right)^p\right] \qquad (25)$$

$$\lambda_Q = \frac{\partial}{\partial Q_2}\left[K\left(\frac{Q_1 - Q_2}{T_1 - T_u}\right)^p - C_u Q_2\right] \qquad (26)$$

evaluated at the optimum. To obtain initial estimates of the multipliers, we only have to estimate the heat loads Q_1, Q_2 and the temperatures differences T at the optimum and then apply the simple formulas (Eqs. 25 and 26). Thus, we have reduced the problem of guessing a priori values of λ to finding a heuristic for guessing optimal values of a few operating parameters.

Heuristics for Determining Optimal Operating Parameters

*H*1: Determine the heat loads Q_i by optimizing the columns separately without heat integration.

*H*2: Assume the mean temperature difference across a heat exchanger to be 11°C.

Though the reflux ratios in the columns were found to change sometimes quite significantly when heat integration was allowed, *H*1 usually offered a good approximation. The assumed ΔT in *H*2 is related to the balance between capital costs and operating costs. We used the value most often quoted in the literature [11°C (20°F)], but tried also different choices without affecting the results significantly. Because we exclude the use of a refrigerant, *H*2 would imply quite a high pressure in Column 1 in Structure B in Figure 6. Therefore, we found it advantageous to use

*H*3: When more than one *low pressure column* participates in a match, the temperature difference should be distributed with the average ΔT = 11°C. (For example, for the two intercolumn heat exchangers in Figure 6, we used ΔT = 5.5°C and 16.5°C respectively.)

It is important to emphasize that *H*1 to *H*3 are used *only* to obtain *initial* estimates for λ. During the optimization itself ΔT is free to vary as is the pressure, the reflux and consequently the heat load Q.

TECHNICAL ASPECTS OF THE BOUNDING PROCEDURE

Positivity of the Sublagrangians

If the sublagrangians l_i, $i \epsilon I_m$ defined in Eq. (10) are known to be nonnegative, it is possible to discard a sequence or a flowsheet even before all the sublagrangians have been minimized. As soon as the sum of the already minimized sublagrangians exceeds the established upper bound, the sequence or flowsheet can be eliminated because the remaining sublagrangians can only increase the lower bound. The magnitude of l_i can be varied by redefining the zero of the scale for the interconnection variables y and z. In our example problem it was impossible to guarantee the positivity; therefore, it was always necessary to evaluate all l_i, $i \epsilon I_m$. (Compare with the discussion by Westerberg and Stephanopoulos, 1976).

Positivity of the Interconnection Variables y and z

Theorem 2 and Corollary 1 are based on the assumption that for all a priori estimated, λ^k, y, and z will be positive at the minima of the sublagrangians. Again, by redefining the scale (shifting the zero), y and z can be guaranteed to be positive. For example, if we use the absolute temperature scale, the temperatures resulting from our optimization will always be positive for all reasonable choices of λ. Equivalently, if only the sign of λ_Q is chosen correctly, negative heat loads will never occur. This conservative way of choosing the temperature scale makes also the lower bounds more conservative and therefore less effective.

Assume for simplicity that the vectors y_i and z_i have the same dimension for all i and that to guarantee positivity we define $y_i = y_i + s$ and $z_i' = z_i + s$, where s is an arbitrary nonnegative vector. Assume further that the minimum of the objective defined in Theorem 2 is obtained for (x^*, u^*, y^*, z^*), then we can state:

$$\Phi^{m,k} \geq \sum_{i \epsilon I_m} \phi_i\,(x_i^*, u_i^*, z_i^*) + \underline{\lambda}_i^T y_i^* - \bar{\lambda}_i^T z_i^* + s^T \sum_{i \epsilon I_m} (\underline{\lambda}_i - \bar{\lambda}_i) \qquad (27)$$

We know from the definitions (Eqs. 13 and 14) that the last summation yields a vector with nonpositive elements. Therefore, s should be chosen as small as possible but large enough to guarantee $y \geq 0, z \geq 0$. For our synthesis problem $Q > 0$ always and $T > 0$ by selecting the cooling water temperature as the zero of the temperature scale. Note that for Theorem 1 the last term in Eq. (27) is always zero and therefore shifting the zero has no influence on the magnitude of the lower bound.

Convexity

As we remarked above, the two-level optimization method will converge only if the Lagrangian has a saddlepoint. The existence of a saddlepoint is guaranteed for

TABLE 2. OPTIMAL OPERATING CONDITIONS FOR THE 20 SEPARATORS WITHOUT HEAT INTEGRATION

Number	Column	Pressure (10^6 Pa)	Heat Load (10^9 J/h)	Cost ($/yr)
1	B/C	0.71	23.90	83400
2	D/E	0.21	49.27	156800
3	A/B	1.95	3.35	18260
4	A/BC	1.95	5.23	27350
5	C/D	0.56	12.01	49370
6	CD/E	0.37	53.25	189620
7	BC/D	0.65	16.03	65070
8	BCD/E	0.43	55.00	204940
9	B/CDE	0.70	28.26	110620
10	A/BCD	1.95	5.86	31460
11	ABC/D	0.75	16.91	71410
12	BC/DE	0.61	18.88	77570
13	AB/CDE	0.95	28.84	121070
14	ABCD/E	0.52	55.59	215990
15	B/CD	0.72	26.12	96650
16	A/BCDE	1.69	6.49	36490
17	ABC/DE	0.75	19.67	83960
18	AB/CD	0.97	26.83	106600
19	AB/C	0.98	24.82	92610
20	C/DE	0.54	15.36	63010

convex objective functions and convex constraints. We note, however, that the dual bound always forms a lower bound on the optimum regardless of nonconvexities. We further state that a *convexification* (e.g., Stephanopoulos and Westerberg, 1975b) is not possible when Theorem 2 and Corollary 1 are to be applied. Usually the influence of the *dual gap* on the objective function is small enough to be neglected for engineering calculations. However, this is not necessarily so for the minimization of the sublagrangian of a column with an auxiliary reboiler, e.g., from Eqs. (18) and (23).

$$l_1 = \phi_1' + K\left(\frac{Q_1 - Q_2^*}{T_1 - T_u}\right)^p + C_u\,(Q_1 - Q_2^*) - \lambda_Q Q_2^* + \lambda_T T_1 \qquad (28)$$

Depending on the value for λ_Q, the minimum is obtained for $Q_2^*=Q_1$, or $Q_2^*=0$. Though these bounds are correct, they can be improved by choosing a linear cost function for the auxiliary heat exchanger $A+B(Q/\Delta T)$. This is discussed in more detail by Faith (1979).

EXAMPLE

To be able to compare the efficiency of our technique with other methods presented in the literature, we used an example studied by several authors (Perry and Chilton, 1973; Rathore et al., 1974a,b; Freshwater and Ziogou, 1976): 907.2 by mol/h of the following five-component mixture are to be separated into essentially pure components (98% recovery for both keys in all columns).

Component	Feed Mol Fraction
Propane (A)	0.05
i-Butane (B)	0.15
n-Butane (C)	0.25
i-Pentane (D)	0.20
n-Pentane (E)	0.35

All the cost equations were adopted with minor modifications from Rathore et al. (1974) and are listed in the Appendix. In all our optimizations, we considered the reflux, the column pressure, and the steam pressure in the reboiler as independent variables. It should be mentioned that for this five-component mixture there exist 20 distinct separators which can form 14 different separation sequences (see Table 1). The optimal operating conditions for the unmatched separators are needed to choose the proper Lagrange multipliers for the synthesis procedure, Table 2. From these figures the optimal separation sequence without heat integration is found to be:

ABC/DE, A/BC, B/C, D/E
Annual Cost: \$351,510

Purely for demonstration purposes, we studied two cases of heat integration. In Case 1, stream splitting was forbidden, that is, only two-column matches were allowed; in Case 2, one-stream split was allowed.

Case 1: No stream splitting
- 63 two-column subproblems
- 350 flowsheets
- 126 two-column optimizations necessary for *brute force method*

Case 2: One-stream split allowed
- 63 two-column subproblems
- 56 three-column subproblems
- 574 flowsheets
- 126 two-column optimizations and
- 112 three-column optimizations (at least) necessary for *brute force method.*

Case 1

Step 1. The optimal unmatched sequence was found above. We chose quite arbitrarily some form of heat integration for that sequence and used the optimal costs as our upper bound.

B/C – A/BC, D/E – ABC/DE 318200

We will use a hyphen (–) to indicate a heat match between columns; e.g., B/C – A/BC means that the reboiler heating in column B/C is accomplished (partly) by condensing the top product in column A/BC.

Step 2. Estimation of the Lagrange multipliers. The multipliers were estimated according to Eqs. (25) and (26) using the heuristics $H1$ and $H2$.

Step 3. Lower bound calculation according to Corollary 1/Theorem 2. A column was allowed to match with all columns in branches emerging from it, Figure 5.

Step 4. Improvement of the lower bound according to Theorem 2.

Step 5. Improvement of the lower bound according to Theorem 1.

As an example, some of the results of the computations in Step 4 are shown in Table 3. We have also listed the actual costs to demonstrate the good quality of the lower bounds. We did not attempt to improve the upper bound

TABLE 3. EXAMPLE OF THE MULTIPLIER SELECTION AND THE LOWER BOUND CALCULATION ACCORDING TO THEOREM 2 FOR THE SEQUENCE ABC/DE, A/BC, D/E, B/C.

Pair Match for λ Selection	λ_T	λ_Q	Lower Bound Cost	Actual Cost (\$/yr)	% Deviation
ABC/DE-A/BC	329.77	−10228.5	112759	infeasible*	—
A/BC-ABC/DE	−329.77	− 2834.4	116521	134709	14%
ABC/DE-D/E	−776.07	− 2898.8	236054	293092	19%
D/E-ABC/DE	776.07	− 6568.8	210540	214413	2%
ABC/DE-B/C	−776.07	− 2421.7	158527	173632	9%
B/C-ABC/DE	776.07	− 6743.2	139433	142365	2%
A/BC-D/E	−329.77	− 3207.3	191991	251630	24%
D/E-A/BC	329.72	− 6568.8	175555	177851	1%
A/BC-B/C	−329.77	− 3022.1	115850	141917	18%
B/C-A/BC	329.77	− 6921.4	102918	104908	2%
D/E-B/C	884.85	− 6574.8	202890	206153	2%
B/C-D/E	−884.85	− 2850.6	213607	224822	5%

*Exceeds allowed pressure range.

Table 4. The Lower Bound Costs and the Optimal Costs of the Nine Remaining Flowsheets in Case 1 after Step 5.

	Lower Bound	Optimal Cost	% Deviation
1. D/E-C/DE, AB/CDE-A/B	314330	infeasible**	
2. D/E-A/B, AB/CDE-C/DE	309910	345630	10%
3. B/C-A/BC, D/E-ABC/DE	307010	318200	4%
4. B/C-ABC/DE, D/E-A/BC	308220	317920	3%
5. D/E-B/C, A/BC, ABC/DE	314500	317690	1%
6. D/E-B/C,BC/DE-A/BCDE	310940	infeasible**	
7. B/C-A/BCDE, D/E-BC/DE	301590	312480	1%
8. D/E-A/BCDE, B/C-BC/DE	303520	312250*	3%
9. D/E-B/CDE, C/DE-A/BCDE	310760	343110	9%

*Optimal sequence.
**Exceeds allowed pressure range.

Table 5. Operating Conditions for the Three Best Flowsheets of Case 1.

Column	Pressure (10^6 Pa)	Heat Load (10^9 J/h)	Optimal Cost
D/E-A/BCDE, B/C-BC/DE			*312250*
D/E	0.20	48.77	
A/BCDE	2.74	4.52	
B/C	0.68	23.73	
BC/DE	1.07	20.55	
D/E-BC/DE, B/C-A/BCDE			*312480*
D/E	0.20	48.77	
BC/DE	1.03	20.43	
B/C	0.70	23.86	
A/BCDE	2.74	4.73	
D/E-B/C, ABC/DE, A/BC			*317690*
D/E	0.20	48.47	
B/C	1.21	26.58	
ABC/DE	0.75	19.67	
A/BC	1.95	5.23	

in this example. After Step 5, only the nine flowsheets listed in Table 4 remained. In Table 5, the operating conditions for the three best flowsheets are shown. From here, we can continue by improving the multipliers as discussed in the section, "Lagrangian Theory," or we can select a flowsheet among these suboptimal ones according to noneconomic criteria; e.g., operability. The optimization effort compares very favorably with that required by Rathore et al. (1974):

Step	Remaining Flowsheets	Single Column Optimizations
0	350	0
3	70	148
4	66	12
5	9	36

Case 2

Step 1. Choice of upper bound. The optimal sequence from Case 1 was equipped with a three-column match of arbitrary choice and the optimal cost for this flowsheet was used as an upper bound:

D/E – (B/C, BC/DE), A/BCDE 282780

Step 2. Estimation of the Lagrange multipliers. The multipliers were estimated according to Eqs. (25) and (26) using the heuristics $H1$, $H2$ and $H3$.

Step 3. Lower bound calculation according to Corollary 1.

Steps 4 and 5. As Case 1.

Again we did not attempt to improve the upper bound. After Step 5, only the seven flowsheets shown in Table 6 remained. The operating conditions for the three best flowsheets are given in Table 7. Again the synthesis effort compares very favorably with that of other investigators:

Step	Remaining Flowsheets	Single Column Optimizations
0	574	0
3	160	124
4	39	26
5	7	18

DISCUSSION

The two level optimization method has been utilized for process synthesis before, the problem formulation and the motivation were different however. McGalliard and Westerberg (1972) judge the economic feasibility of a particular flowsheet modification from dual and primal bound calculations. Estimates of the multipliers are obtained from the unmodified initial flowsheet. The ideas are applied to the synthesis of heat exchanger networks. Westerberg and Stephanopoulos (1975) solve the separation sequence synthesis problem through a branch and bound technique employing dual and primal bounds. Zero was an efficient estimate of all the interconnection multipliers yielding excellent lower bounds. This implies that the subsystems are weakly coupled: pressure changes between columns and feed preheating have only a minor influence on the overall costs and the synthesis problem is greatly simplified.

The major novelty in this work is the development and effective application of Theorem 2 (Corollary 1). In conjunction with the decomposition rule and the heuristic for estimating multipliers, it allowed entire separation sequences to be discarded without a painstaking detailed optimization of all the possible heat exchanger networks.

Table 6. The Lower Bound Costs and the Optimal Costs of the Seven Remaining Flowsheets in Case 2 after Step 5.

		Lower Bound	Optimal Cost	% Deviation
1. D/E-(B/C, ABC/DE),	A/BC	273010	279380*	2%
2. D/E-(ABC/DE, AB/C),	A/B	248390	280860	12%
3. D/E-(AB/CDE, C/DE),	A/B	263870	290460	9%
4. (A/B, AB/CDE)-D/E,	C/DE	269350	334380	19%
5. (C/DE, AB/CDE)-D/E,	A/B	258350	346740	25%
6. D/E-(C/DE, B/CDE),	A/BCDE	261700	296000	12%
7. D/E-(B/C, BC/DE),	A/BCDE	275220	282780	3%

*Optimum sequence.

Table 7. Operating Conditions for the Three Best Flowsheets of Case 2.

Column	Pressure (10^6 Pa)	Heat Load (10^9 J/h)	Optimal Cost ($/yr)
D/E-(ABC/DE, B/C); A/BC			*279380*
D/E	0.21	48.98	
ABC/DE	1.17	21.10	
B/C	1.16	27.84	
A/BC	1.95	5.23	
D/E-(ABC/DE, AB/C), A/B			*280860*
D/E	0.22	49.27	
ABC/DE	1.22	21.22	
AB/C	1.57	28.00	
A/B	1.96	3.35	
D/E-(BC/DE, B/C), A/BCDE			*282780*
D/E	0.20	48.60	
BC/DE	1.00	20.47	
B/C	1.16	27.67	
A/BCDE	1.69	6.49	

It is only necessary to estimate the multipliers for the different structures using the simple formulas Eqs. (25) and (26).

The subsystems are strongly coupled and zero multipliers lead to meaningless lower bounds. While for higher order matches the computational optimization task can become quite involved without decomposition techniques (~ three independent variables per column) only single column optimizations are required for our method. Aris et al. (1964) suggest as a rule of thumb that for problems with more than four independent variables decomposition techniques are to be preferred.

The heuristic for guessing the optimum operating conditions of the coupled columns provides some valuable insight about the relative importance of the variables which did not become apparent in the *brute force* optimization of all the possible flowsheets. The key variable appears to be the average temperature difference in the intercolumn heat exchangers. The operating conditions in the column with the auxiliary heat exchanger are hardly influenced at all by the availability of a heat source (sink) in the form of another process stream. On the other hand for columns with intercolumn heat exchangers an increase in the ratio of the operating reflux ratio to the minimum reflux ratio was always observed. It should be emphasized that the heuristics serve only as an aid to improve the efficiency of our algorithmic synthesis technique but that the optimal flowsheet found is completely independent of their accuracy.

Clearly the choice of the upper bound will strongly influence the efficiency of our technique. Because the optimal sequence without heat integration can be easily found, it is logical to propose some heat exchanger network for this sequence and to use the costs of the resulting flowsheet as an upper bound. Indeed in the presented example the optimal heat exchanger network for the optimal unmatched sequence would have resulted in the optimal flowsheet for Case 2 and in a flowsheet close to optimal for Case 1. This is quite an exceptional coincidence, however.

In a case study, Freshwater and Ziogou (1976) found that the optimal sequence changed in more than 50% of the cases when heat integration was allowed. Each change resulted in energy savings of 10% or more. In their paper the pressure was fixed. In our study, the pressure is a variable which should yield even more drastic savings. Siirola (1978), who has carried out many industrial case studies, states that this heuristic often leads to flowsheets whose cost can exceed the optimal costs by as much as 25%.

One reviewer noted that the allowed heat integration might be constrained by operability considerations and the risk of product contamination through leaks in the heat exchangers. For the type of integration discussed here, the control problems will not be different from those for separate columns because of the presence of auxiliary heat exchangers. Operability problems for more *exotic* types of integrations will be discussed by one of the authors (MM) in a forthcoming publication. If product contamination is to be avoided, heat itegration between certain columns has to be prohibited. This can be included in our method simply by restricting the set K^m in Eq. (4) appropriately.

Relaxation of the Assumptions

Though very simple techniques for the column design were used in our example calculations, these approximations can be discarded of and almost all assumptions presented in the introduction can be relaxed without effecting the main features of the synthesis scheme. Most of the time a relaxation will not be warranted, however, because the improvements in accuracy are of the same order of magnitude as the modelling errors.

A1. Each column operates at high recovery. Major modifications would be required to allow nonsharp splits. As long as the splits are sharp the purities of the streams can be considered as additional optimization variables and can be treated through additional multipliers. We learned, however, that stream impurities form only weak couplings (Westerberg and Stephanopoulos, 1975) and the increased effort is unlikely to be justified by the improved accuracy.

A3. Only heat matches of the type shown in Figure 1a and 1c are considered; that is, condenser/reboiler matching is allowed exclusively and a column must not be matched at both ends, Figure 1b.

As discussed in the introduction these types of three-column matches are rarely economical. We attempted to apply our synthesis method to these more complicated structures but found our heuristics to yield poor Theorem 2—dual bonds and thus destroying one of the key advantages of the method. If Theorem 1 is employed, a stepwise improvement of the bounds is possible using well-known gradient techniques for the dual problem. If a good heuristic can be found nothing will stand in the way of an effective application of our method.

A4. Only cooling water, no refrigerant is used.

A5. The steam costs are approximated by a continuous function dependent on pressure. No modifications are needed for A4 and A5.

A6. The costs of changing the temperature and pressure of streams as they pass between columns are negligible.

A8. Feeds and products are saturated liquids. Those assumptions can be relaxed by introducing additional multipliers and additional independent variables for the subsystems. Increased computational effort has to be balanced against increased accuracy.

A7. Vapor recompression is not used. The local nature of vapor recompression does not require the definition of additional interconnection multipliers. The simplest approach would be to optimize each distinct separator once with vapor recompression and to include these figures in the calculation of the lower and upper bounds.

A9. Only total condensers and reboilers are employed. This assumption is conservative. Coolants for partial condensation can be *warmer* than coolants for total condensation; the operating costs are almost certain to decrease and more networks will be feasible. For two column matches the present method can be applied without modifications. If more than two columns are involved in a match, additional multipliers will have to be defined.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research. Parts of this work were presented at the 12th Symposium on Computer Applications in Chemical Engineering (European Federation of Chemical Engineering, 214th Event) in Montreux, Switzerland, April 8 to 11, 1979. The authors are grateful to B. Linnhoff, J. J. Siirola, and R. N. S. Rathore for their detailed and helpful reviews.

APPENDIX: DESIGN AND COST EQUATIONS USED FOR THE DISTILLATION CALCULATIONS

Minimum number of stages:

$$\left(\frac{\text{kg mol of component } i \text{ in distillate}}{\text{kg mol of component } i \text{ in bottoms}}\right) = (\alpha_{i-r})S_m$$

$$\left(\frac{\text{kg mol of component } r \text{ in distillate}}{\text{kg mol of component } r \text{ in bottoms}}\right)$$

α_{i-r} value is geometric mean of the values at the column top and bottom.

Minimum reflux ratio:

$$\sum_{I=1} \frac{\alpha_i Z_{i,F}}{\alpha_i - \theta} = 1 - \phi$$

$$R_m = \sum_{I=1} \frac{\alpha_i X_{i,D}}{\alpha_i - \theta} - 1$$

Number of stages:

$$\text{For } \left[\frac{(R - R_m)}{(R + 1)}\right] < 0.125;\ \left[\frac{(S - S_m)}{(S + 1)}\right] = 0.5039 - 0.5968\left[\frac{(R - R_m)}{(R + 1)}\right] - 0.0908 \log\left[\frac{(R - R_m)}{(R + 1)}\right]$$

$$\text{and for } \left[\frac{(R - R_m)}{(R + 1)}\right] > 0.125;\ \left[\frac{(S - S_m)}{(S + 1)}\right] = 0.6257 - 0.9868\left[\frac{(R - R_m)}{(R + 1)}\right] + 0.5160\left[\frac{(R - R_m)}{(R + 1)}\right]^2 - 0.1738\left[\frac{(R - R_m)}{(R + 1)}\right]^3$$

Diameter of the column:

$$D_c = \left[\left(\frac{4}{\pi V}\right)(D)(r+1)(22.2)\left(\frac{T_{DV}}{273}\right)\left(\frac{1}{P}\right)\left(\frac{1}{3600}\right)\right]^{1/2}$$

where

$$V = 0.761\left(\frac{1}{P}\right)^{1/2}$$

Height of the column:

$$H_c = 0.61\left(\frac{S}{\eta}\right) + 4.27$$

Cost basis of optimization:

$$\text{Total annual cost} = \text{annual operating cost} + \frac{\text{total installed equipment cost}}{\text{Project life}}$$

Column cost:
Installed cost of the column

$$= 4.34\left[762\, D_c\left(\frac{H_c}{12.2}\right)^{0.68}\right]$$

If the column pressure is more than 3.4 atm, a correction factor [1 + 0.0147(P − 3.4)] is applied.

Cost of trays:
Installed cost of trays $= 70\left(\frac{S}{\eta}\right)\left(\frac{D_c}{1.22}\right)^{1.9}$

Instrumentation cost:
column instrumentation cost = 4,000.00

Maintenance cost of the column:
2% of the total installed cost of the column.

Heat exchanger cost:
Total installed cost $= 3.39\left[9000\left(\frac{A}{92.1}\right)^{.65}\right]$

Auxiliary heat exchanger cost:
Total installed cost = 9.5 A + 40000
where A = area of heat exchanger, m².

If the pressure is more than 10.2 atm, a correction factor of [1 + 0.0147 (P − 10.2)] is applied. Heat exchanger operation cost = 8500 ($C_u Q$) + 2% of the total installed cost.

Material of construction: carbon steel

Physical properties: Vapor pressures used to compute relative volatilities are calculated from Harlacher-Braun vapor pressure coefficient (Reid, et al., 1977).

Utility costs:
Cooling water at 305 K
C_u = 0.0478 \$/10⁹J.
Steam, 305 K ≤ T ≤ 573 K
C_u = −0.0287 + 0.00239 (T − 273) \$/10⁹J.
Allowable pressure range: 1 x 10⁵ to 34 x 10⁵ Pa.
Column efficiency, η = 80% in all columns.
Key component recoveries = 98% for both keys in all columns.
Feed condition = saturated liquid feed for all columns.
Operating hours in a year = 8500.
Project life = 10 years.

LITERATURE CITED

Aris, R., G. L. Nemhauser, and D. J. Wilde, "Optimization of Multistage Cycling and Branching Systems by Serial Procedures," *AIChE J.*, **10**, 913 (1964).

Beveridge, G. S. G., and R. S. Schecter, *Optimization, Theory and Practice*, McGraw Hill (1970).

Doukas, N., and W. L. Luyben, "Economics of Alternative Distillation Configurations for the Separation of Ternary Mixtures," *Ind. Eng. Chem. Proc. Des. Dev.*, **17**, 272 (1978).

Faith III, D. C., "The Synthesis of Distillation Trains with Heat Integration," M.S. Thesis, Univ. of Wis. (1979).

Freshwater, D. C., and E. Ziogou, "Reducing Energy Requirements in Unit Operations," *Chem. Eng. J.*, **11**, 215 (1976).

Hendry, J. E., and R. R. Hughes, "Generating Separation Process Flowsheets," *Chem. Engr. Prog.*, **68**, 71 (June, 1972).

Hlaváček, V., Synthesis in the Design of Chemical Processes, *Comp. & Chem. Eng.*, **2**, 67 (1978).

Lasdon, L. S., *Optimization Theory for Large Systems*, McMillan, New York (1970).

Linnhoff, B., and J. R. Flower, "Synthesis of Heat Exchanger Networks," *AIChE J.*, **24**, 633 and 642 (1978).

Linnhoff, B., D. R. Mason, and I. Wardle, "Understanding Heat Exchanger Networks," Proc. of 12th Symp. on Computer Appl. in Chem. Eng., EFCE 214th event, Montreux, Switzerland (1979).

McGalliard, R. L., and A. W. Westerberg, "Structural Sensitivity Analysis in Design Synthesis," *Chem. Engr. J.*, **4**, 127 (1972).

Mix, T. J., J. S. Dweck, M. Weinberg, and R. C. Armstrong, "Energy Conservation in Distillation," *Chem. Engr. Progr.*, **74**, 49 (April, 1978).

Nath, R., and R. L. Motard, "Evolutionary Synthesis of Separation Processes," paper 50b presented at 85th Nat. AIChE Mtg., Philadelphia (1978).

Nishida, N. Y., A. Liu, and L. Lapidus, "Studies in Chemical Process Design and Synthesis: III. A Simple and Practical Approach to the Optimal Synthesis of Heat Exchanger Networks," *AIChE J.*, **23**, 77 (1977).

Perry, R. H., and C. H. Chilton (ed.), *Chemical Engineers' Handbook*, 5th ed., McGraw Hill (1973).

Petlyuk, F. B., Platonov, V. M., and D. M. Slavinskii, "Thermodynamically optimal method for separating multicomponent mixtures," *Int. Chem. Eng.*, **5**, 555 (1965).

Prengle, H. W., J. R. Crump, C. S. Fang, M. Frupa, Henly, and T. Wooley, "Potentials for Energy Conservation in Industrial Operations in Texas," Final Report on Project S/D-10 Gover-

nor's Energy Advisory Council, The State of Texas (1974).
Rathore, R. N. S., K. A. VanWormer, and G. J. Powers, "Synthesis Strategies for Multicomponent Seqparation Systems with Energy Integration," *AIChE J.*, **20**, 491 (1974a).
Rathore, R. N. S., K. A. VanWormer, and G. J. Powers, "Synthesis of Distillation Systems with Energy Integration," *AIChE J.* **20**, 940 (1974b).
Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of gases and liquids*, 3rd ed., McGraw Hill (1977).
Rodrigo, F. R., and J. D. Seader, "Synthesis of Separation Sequences by Ordered Branch Search," *AIChE J.*, **21**, 885 (1975).
Seader, J. C., and A. W. Westerberg, "A Combined Heuristic and Evolutionary Strategy for Synthesis of Simple Separation Sequences," *AIChE J.*, **23**, 951 (1977).
Siirola, J. J., "Progress toward the synthesis of heat integrated distillation schemes," paper 47a, 85th Nat. AIChE Mtg. Philadelphia (1978).
Siirola, J. J., G. J. Powers, and D. F. Rudd, "Synthesis of System Designs: III. Toward A Process Concept Generator," *AIChE J.*, **17**, 677 (1971).
Siirola, J. J., and D. F. Rudd, "Computer in Aided Synthesis of Chemical Process Designs; from Reaction Path Data to the Process Task Network," *Ind. Eng. Chem. Fundam.*, **10**, 353 (1971).
Sophos, A., G. Stephanopoulos, and M. Morari, "Synthesis of Optimum Distillation Sequences with Heat Integration Schemes," 71st Amn. AIChE Mtg., Miami (1978).
Stephanopoulos, G., and A. W. Westerberg, "Studies in Process Synthesis II; Evolutionary Synthesis of Optimal Process Flowsheets," *Chem. Eng. Sci.*, **31**, 195 (1976).
Stephanopoulos, G., and A. W. Westerberg, "The Use of Hestenes' Method of Multipliers to Resolve Dual Gaps in Engineering System Optimization," *J. Optim. Th. Appl.*, **15**, 285 (1975b).
Stupin, W. J., and F. J. Lockhart, "Thermally Coupled Distillation—A Case History," *Chem. Eng. Prog.*, **68**, 71 (Oct., 1972).
Tedder, D. W., and D. F. Rudd, "Parametric Studies in Industrial Distillation," *AIChE J.*, **24**, 303 (1978).
Umeda, T., K. Niida, and K. Shiroko, "A Thermodynamic Approach to Heat Integration in Distillation Systems," *AIChE J.*, **25**, 423 (1979).
Westerberg, A. W., "Decomposition Methods for Solving Steady State Process Design Problems," in *Decomposition of Large-Scale Problems*, D. M. Himmelblau, ed., North Holland (1973).
Westerberg, A. W., and G. Stephanopoulos, Letter to the Editors, *Chem. Eng. Sci.*, **31**, 325 (1976).
Westerberg, A. W., and G. Stephanopoulos, "Studies in Process Synthesis I; Branch and Bond Strategy with List Techniques for the Synthesis of Separation Schemes," *Chem. Eng. Sci.*, **30**, 963 (1975).
Wilde, D. J., and C. S. Beightler, *Foundations of Optimization*, Prentice Hall, Englewood Cliffs, N. J. (1967).

Manuscript received July 31, 1979; revision received November 28, and accepted January 25, 1980.

The Mixing of Granular Solids in a Rotary Cylinder

JACOB MU
and
D. D. PERLMUTTER
Department of Chemical
University of Pennsylvania
Philadelphia, Pennsylvania 19104

A model is derived for solids mixing and material transport in a continuous flow rotary dryer or reactor. Detailed analysis of the particle motions in the turnover process provides an opportunity to apply well-known reactor models to several subregions and to relate the overall results to different design geometries and operating conditions. The essential parameters of the model are the number of stages, the volume fractions of mixed flow and plug flow in each stage, the recycle ratio and the bypass ratio.

SCOPE

A new model is derived to describe in detail the particle movement patterns in various regions of a rotating cylinder such as find use as reactors, mixers and dryers. The solid feed rate, the speed of rotation and the effects of bed depth and cylinder geometry are included and accounted for. Tracer residence time distribution measurements and other bench scale experiments are suggested to estimate the parameters of the model.

CONCLUSIONS AND SIGNIFICANCE

A new model based on combinations of flow regimes in several subregions describes the isothermal mixing and the residence time distribution in a rotating cylinder. Comparisons are made with prior reports in the literature to emphasize the improvements expected and to demonstrate that the new model is applicable to a wide range of experimental conditions. This detailed phenomenological approach to the description of the mixing and transport processes uses sufficient details of the particle motions in each turnover step to be useful for the design of mixers, dryers and/or chemical reactors. Inclusion of appropriate thermal effects will be important, according to the purpose; this new model can also be extended to these applications.