LITERATURE CITED

Burrows, G. J., "The Rate of Hydrolysis of Methyl Acetate by Hydrochloric Acid in Water-Acetone Mixtures," *J. Chem. Soc.* (*London*), 109, 67 (1916).

Chen, J. W., and W. M. Kalback, "Effect of Ultrasound on Chemical Reaction Rates," *Ind. Eng. Chem. Fundamentals,* 6, 175 (1967).

Couppis, E. C., "An Experimental Study on the Effect of Ultrasonics on Liquid Phase Hydrolysis Reactions," *Ph.D. dissertation,* U. of Pittsburgh (1972).

Fogler, S., and D. Barnes, "Shift in the Optimal Power Input in an Ultrasonic Reaction," *Ind. Eng. Chem. Fundamentals,* 7, 222 (1968).

Fogler, S., "Reactor Design and Continuous Sampling Criteria for an Ultrasonic Reaction," *ibid.*, 387.

Frost, A., and R. Pearson, *Kinetics and Mechanisms,* pp. 123-159, Wiley, New York (1953).

Griffith, R. O., and W. C. M. Lewis, "Stoichiometric and Catalytic Effects Due to Progressive Displacement of One Reagent by Another in the Acid Hydrolysis of Methyl Acetate," *J. Chem. Soc.* (*London*), 109, 67 (1916).

Khoroshev, G. A., "Collapse of Vapor-Air Cavitation Bubbles," *Soviet Physics-Acoustics,* 9, 275 (1964).

Neppiras, E., and B. Noltingk, "Cavitation Produced by Ultrasonics," *Proc. Physical Soc.* (*London*), B63, 674 (1950).

Weissler, A., H. W. Cooper, and S. Snyder, "Chemical Effect of Ultrasonic Waves: Oxidation of Potassium Iodide Solution by Carbon Titrachloride," *J. Am. Chem. Soc.*, 72, 1769 (1950).

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Synthesis Strategies for Multicomponent Separation Systems with Energy Integration

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The problem of synthesizing an optimal multicomponent separation system which is energy integrated is solved by a combined decomposition and dynamic programming technique.

Dynamic programming is an optimization technique which allows the solution by decomposition of a multistage or serial optimization problem. Whenever the special serial structure is absent, again decomposition can be tried, but in this case it is by no means obvious how to decompose effectively the given problem into subproblems. In this paper the nonserial problem of synthesizing an energy integrated separation system is solved by decomposing the original problem so that a serial structure results.

SCOPE

In the synthesis of chemical processing systems two key subproblems are:

1. The selection of the basis and sequence of separation, and

2. The determination of a heat exchanger network for energy recovery.

The quality of solution of these subproblems can have a large effect on the overall efficiency of a chemical processing system. The separation problem is important in that a major part of the capital investment and utilities for a process are determined by the separator types and sequences. The recovery of energy in heat exchanger networks is also an important feature as energy integration reduces consumption of increasingly expensive energy resources.

Each of the subproblems has been solved separately. The separation problem has been solved by three basic techniques. Heuristic methods in which rules of thumb are used to limit the search to solutions which appear to be best have been developed by several workers including Thompson and King (1972). An embedding approach in which all possible separation sequences are embedded in a structure on which parameter optimization is performed has been advanced by Ichikawa and Fan (1973). In this method all possible separators considered for a given problem are interconnected and optimization is performed over stream split parameters.

A final approach is a dynamic programming method developed by Hendry and Hughes (1972). In their method, Hendry and Hughes systematically generate the separation subproblems which can occur in all possible separation sequences. They then use the principle of optimality to select the optimal separation sequence.

The heat exchanger network synthesis problem has been studied by modern methods since Hwa (1965) developed a separable programming method to determine the optimal network. Kesler and Parker (1969) developed a linear programming model and Masso and Rudd

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(1969) applied heuristic programming methods to the problem. Lee et al. (1970) developed a branch and bound technique for determining the optimal heat exchanger network.

These methods offer effective means for solving each of these synthesis subproblems separately. These subproblems interact strongly. The solution to the separation sequencing problem often depends on the cost of heating and cooling operations. The cost of heating and cooling depends on how much heat recovery occurs in the process. Hence, the separation problem depends on the solution of the heat exchanger network synthesis problem. The problem is further complicated by the fact that the heat exchanger network synthesis problem depends on what streams are available for energy exchange. The streams are not known until the separation sequence has been selected. Hence, both of the subproblems are strongly coupled.

In this paper, we develop a method for solving both of these subproblems at the same time.

The method is tested on a five-component distillation problem in which all columns operate at the same pressure. In addition, high recoveries (99%) are required for each distillation column. These two assumptions are used to reduce the size of the synthesis problem. With all columns at the same pressure the dew points and bubble points are fixed and many energy integrations are infeasible due to the second law of thermodynamics. By assuming high recoveries and constant pressures for the separation, the information flow is serial and dynamic programming can be used to select the optimal sequence.

Energy integration is considered only between reboiler and condenser streams. Energy integration with tower feeds and products are neglected as they are small energy sources or sinks when compared to the reboiler and condenser streams.

CONCLUSIONS AND SIGNIFICANCE

In previous work the overall process synthesis problem has been decomposed into small, hopefully independent and more easily solvable subproblems. The subproblems are reaction path synthesis, species allocation, separation sequencing, and energy integration. The solutions of these subproblems has been the focus of much of the research effort in process synthesis. In this paper we have shown how two of these subproblems can be solved simultaneously to overcome the interactions which occur between them.

Decomposition followed by dynamic programming is an effective strategy for the synthesis of optimal separation sequences which are energy integrated. The five exclusion rules for determining the feasibility of energy integration are very powerful within the limits of isobaric operation.

The computations required to find the optimal sequence are much less than those required for exhaustive search. Very seldom is it necessary to make multiple passes through the dynamic programming search.

Methods based on first solving the separation sequencing problem and then energy integrating that sequence give only a local optimum while this method gives the global optimum.

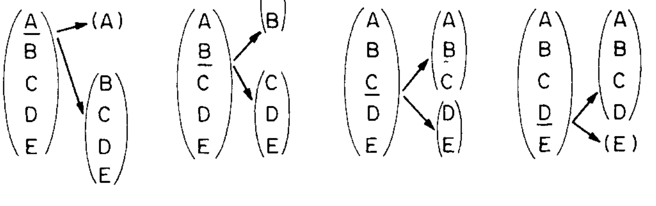
The assumptions of constant pressure and constant high recovery in all columns are restrictive. Relaxing the constant pressure constraint introduces more energy integrations and cyclic information flow which prevents the direct use of dynamic programming methods. If constant high recoveries are not assumed, the separation subproblems interact and again dynamic programming cannot be used.

Multicomponent separation problems are an important part of almost all chemical processing systems. The separation problems that occur in the synthesis of a chemical process arise from the allocation of chemical species from a single source stream to multiple destinations. The sources in most chemical systems are raw material inputs and reactors effluents. The destinations are reactor inputs, products, and waste streams. In order to achieve a given species allocation, it is necessary to determine the best sequence of separators to be used. The solution to a given separation problem is defined by giving the physical or chemical property difference exploited at each separator, the phases at each separator, the forces involved in each separator, and finally, the sequence in which the separations are to occur.

One convenient way to consider the selection of separation basis and sequence is to first rank the species in the mixture according to their physical or chemical properties. For example, the species in a solid-solid mixture could be ranked by their size—from largest to smallest; species in a liquid mixture might be ranked by the volatility—from most volatile to least volatile. The result of the ranking is an ordered list for each property which gives the species name and its property rank relative to the other species in the mixture. It is then possible to discuss separation as a list splitting operation in which species above a certain property value are separated from species below that value. The generation of a separation sequence then involves selecting the appropriate property list and the location within the list for separation. The separations possible for one property list of five components are shown in Figure 1.

Note that there are four possible separation points for the five-component mixtures and that nearly complete separation is assumed.

The sublists which result from a split of an ordered list are themselves ordered and can be further considered



(a) (b) (c) (d)

Fig. 1. The four possible ways of splitting a five-component ranked list ABCDE.

Table 1. All Possible Subgroups Resulting from the Splitting of the Ranked List ABCDE
Figure 2 illustrates how these subgroups are generated

5-component subgroups	4-component subgroups	3-component subgroups	2-component subgroups	1-component subgroups
(ABCDE)	(ABCD)	(ABC)	(AB)	(A)
	(BCDE)	(BCD)	(BC)	(B)
		(CDE)	(CD)	(C)
			(DE)	(D)
				(E)

for separation. Figure 2 illustrates the generation of separation subgroups for a five-component separation problem when only one property ranking is considered. The numbered arcs on Figure 2 denote possible separation subproblems. For example, subproblem 20 involves separating the mixture ABCDE into two mixtures, one containing ABCD and the other containing only E. Table 1 gives all the subgroups which can appear in this five-component problem. There are 20 separation subproblems involving these subgroups. From these subproblems and subgroups it is possible to generate 14 separation sequences. Each sequence completely separates the original five-component mixture. Three of the fourteen sequences are shown in Figure 3. Table 2 illustrates how the number of subgroups, subproblems, and sequences varies with the number of components in the mixture. Note that the number of sequences grows rapidly for mixtures containing more than six components. Fortunately, there are very few industrial separation problems which contain six different species each of which is required at a different destination.

Several techniques have been advanced to overcome the problems associated with the large number of solutions indicated in Table 2. Experienced engineers utilize heuristics or rules of thumb to guide their search for a satisfactory sequence. Thompson and King (1972) have used a heuristic approach to develop computer programs which aid a designer in selecting a satisfactory separation sequence. Since their approach uses heuristics, no direct mathematical claims for optimality can be made. Similar heuristic approaches have been used by Heaven (1969), King (1971), Maikov et al. (1972), Nishimura and Hiraizumi (1971), Petlyuk et al. (1965), and Rudd et al. (1973).

A separation sequencing method based on dynamic programming has been developed by Hendry and Hughes (1972). The method focuses on the separation subproblems which make up each possible separation sequence. The search for the optimal sequence is started at the binary separation subproblem and proceeds to ternary and

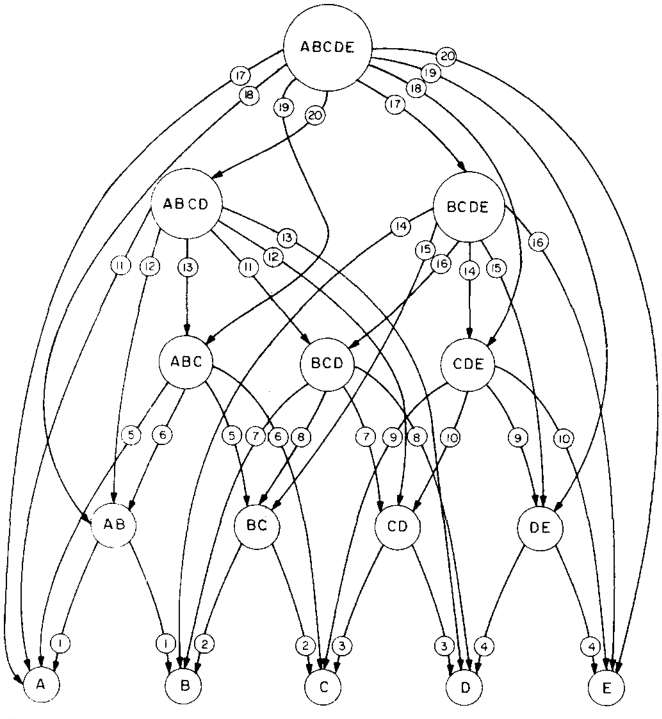


Fig. 2. The generation of subgroups from a ranked list ABCDE. Two arcs bearing the same number represent one separation operator. The subgroups at the ends of each arc are generated from the parent group.

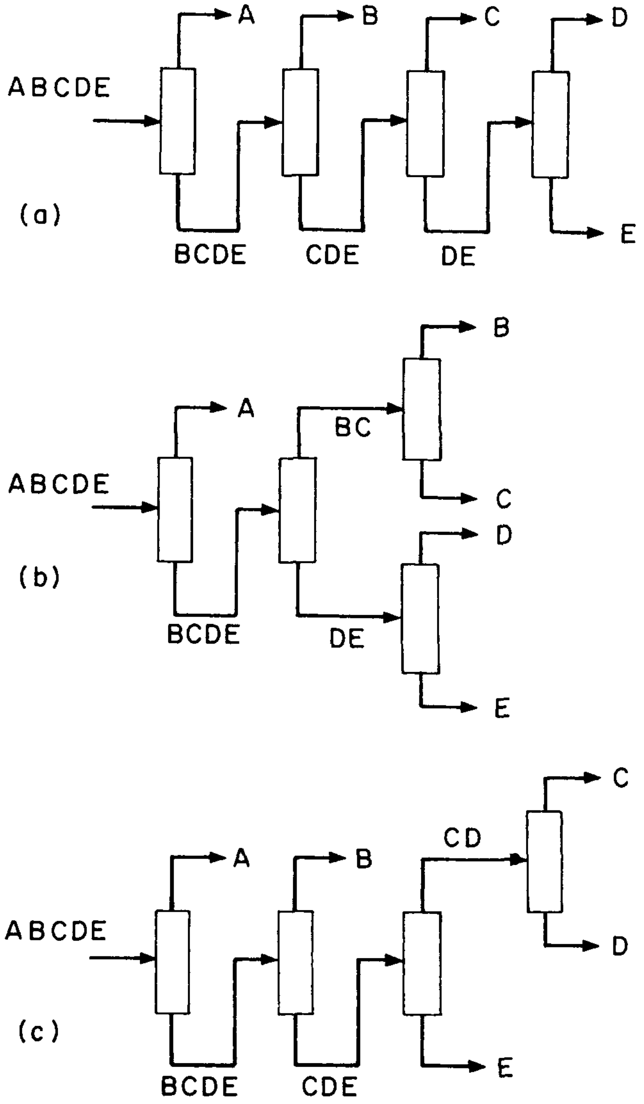


Fig. 3. Three out of fourteen possible sequences for separating the five-component mixture ABCDE using one property difference.

larger separations. The solutions to each subproblem are assembled using the principle of optimality (Bellman and Dreyfus, 1962). Table 3 illustrates this procedure. It is desired to separate the mixture ABCDE into pure A, B, C, D, and E streams. The binary separations are considered first and the optimal means for carrying out each one determined. The optimization is over type of separation, that is, distillation, extraction, crystallization, etc., and the conditions of the separation, that is, temperature, pressure, reflux ratio, number of stages, etc. Table 4 describes the mixture, and design and cost equations which are used to compute optimal cost of each separation operation.

The ternary separation subproblems are considered next. The optimal method for separating the ternary mixtures is to determine first the optimal costs for separating the ternary mixture into two streams (one containing one species, the other containing two). To these costs is added the previously determined optimal cost for separating the stream which contains two species. For example, the mixture ABC can be separated in two ways. One separation yields the streams A and BC, the other gives streams AB and C. The optimal means for separating a mixture ABC depends on the costs for separating A from ABC plus the costs for separating BC versus the costs for separating C from ABC plus the cost for separating AB. By systematically computing the optimal costs for each separation subproblem it is possible to build up the costs for all sequences in the process. The method has a mathematical guarantee of optimality. This method will be used later in this paper to determine the optimal distillation structure when energy integration is considered.

A key assumption in the use of dynamic programming search methods is that the information flow is serial. That is, there is no feedback of information in the system. The principle of optimality is based on the fact that optimal decisions preceding a decision can only be made if they do not depend on later decisions. (If the later decisions

TABLE 2. NUMBER OF SUBGROUPS, SEPARATION SUBPROBLEMS, AND SEPARATION SEQUENCES ASSOCIATED WITH SEPARATION OF A MULTICOMPONENT MIXTURE FOR ONE PROPERTY DIFFERENCE

Number of components $[N]$	Number of subgroups $[N(N+1)/2]$	Number of separation subproblems $[(N-1)(N)(N+1)/6]$	Number of sequences $\frac{[2(N-1)]!}{N!(N-1)!}$
2	3	1	1
3	6	4	2
4	10	10	5
5	15	20	14
6	21	35	42
7	28	56	132
8	36	84	429
9	45	120	1,430
10	55	165	4,862

TABLE 3. DYNAMIC PROGRAMMING SYNTHESIS OF THE OPTIMAL SEPARATION SEQUENCE FOR THE MIXTURE ABCDE DESCRIBED TABLE 4. COSTS ARE FOR CASE WHERE NO ENERGY INTEGRATION OCCURS

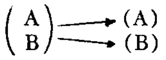
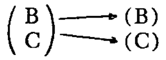
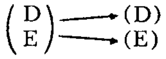
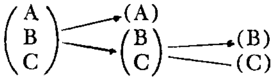
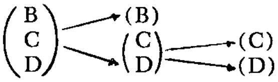
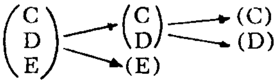
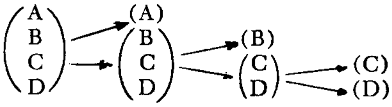
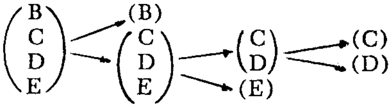
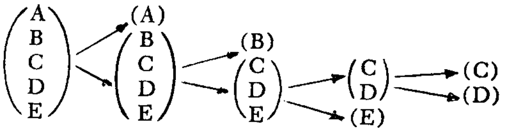
Subgroup	Separation	Minimum cost of separation, \$/yr.	Total cost including subsequent separations, \$/yr.	Minimum subgroup decomposition cost, \$/yr.	Optimal sequence
(AB)	A/B	0.5909×10^5	0.5909×10^5	0.5909×10^5	
(BC)	B/C	1.196×10^5	1.196×10^5	1.196×10^5	
(CD)	C/D	0.7198×10^5	0.7198×10^5	0.7198×10^5	
(DE)	D/E	3.272×10^5	3.272×10^5	3.272×10^5	
(ABC)	A/BC	0.9260×10^5	2.1220×10^5	2.1220×10^5	
	AB/C	3.881×10^5	4.4719×10^5		
(BCD)	B/CD	1.305×10^5	2.0248×10^5	2.0248×10^5	
	BC/D	0.9041×10^5	2.1001×10^5		
(CDE)	C/DE	0.9394×10^5	4.2034×10^5		
	CD/E	3.144×10^5	3.8638×10^5	3.8638×10^5	
(ABCD)	A/BCD	0.9935×10^5	3.0183×10^5	3.0183×10^5	
	AB/CD	4.208×10^5	5.5187×10^5		
	ABC/D	0.9806×10^5	3.1026×10^5		
(BCDE)	B/CDE	1.446×10^5	5.3098×10^5	5.3098×10^5	
	BC/DE	1.100×10^5	5.5680×10^5		
	BCD/E	3.314×10^5	5.3388×10^5		
(ABCDE)	A/BCDE	1.149×10^5	6.4588×10^5	6.4588×10^5	
	AB/CDE	4.615×10^5	9.0697×10^5		
	ABC/DE	1.171×10^5	6.5650×10^5		
	ABCD/E	3.449×10^5	6.4673×10^5		

TABLE 4. DESCRIPTION OF THE MIXTURE ABCDE AND THE DESIGN AND COST EQUATIONS USED FOR THE EVALUATION OF SEPARATION SUBPROBLEMS. COSTS IN TABLES 3, 6, AND 7, ARE BASED ON DATA IN THIS TABLE

Mixture Components: Propane (A), i-butane (B), n-butane (C), i-pentane (D), n-pentane (E)

Feed Rate: 907.2 kg mol/hr

Composition:

Component	Mole Fraction
A	0.05
B	0.15
C	0.25
D	0.20
E	0.35

Separator type: distillation column

Design and cost equations

Minimum number of stages (Fenske, 1932):

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

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

Minimum reflux ratio (Underwood, 1948)

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

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

Number of stages (Gilliland, 1940; Van Winkle and Todd, 1971):

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

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 (Heaven, 1969):

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

where:

$$V = .761 \left(\frac{1}{P}\right)^{1/2}$$

Height of the column (Heaven, 1969):

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

Cost basis of optimization:

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

Column cost (Guthrie, 1969):

$$\text{Installed cost of the column} = 4.34 \left[762\, D_c \left(\frac{H_c}{12.2}\right)^{.68}\right]$$

TABLE 4. (Continued)

If the column pressure is more than 3.4 atm a correction factor of $[1+00147\,(P-3.4)]$ is applied.

Tray cost (Guthrie, 1969):

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 (Guthrie, 1969):

2 % of the total installed cost of the column

Heat exchanger cost (Guthrie, 1969)

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

If the pressure is more than 10.2 atm a correction factor of $[1+0.0147\,(P-10.2)]$ is applied.

Heat exchanger operating cost = 8500 ($C_U Q$) + 2 % of the total installed cost.

Material of construction: Carbon steel

Cost of Utilities (Guthrie, 1969):

Utility	Cost ($/million kcal)
Steam (28.23 atm)	4.29
Steam (11.22 atm)	3.24
Steam (4.08 atm)	2.40
Steam (1.70 atm)	1.75
Cooling water (32.2 °C)	0.28
Ammonia (1 °C)	6.91
Ammonia (-17.78 °C)	12.43
Ammonia (-21.67 °C)	16.59

Physical Properties:

K-values liquid and vapor enthalpies are estimated from the poly correlations of experimental data (API, 1953).

Assumed values:

η = 80 % in all the columns

P = 6.8 atm, all columns

R = optimal value with respect to the total annual cost

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

depend on present decisions, a recycle or feedback of information exists.) In the separation problem described in Table 1 no recycle of information existed. Interactions between separation subproblems can occur if material, energy, or momentum are passed between separators along their connecting streams. The flow rate and species concentration entering a separator depends on the performance of previous separators. The feed temperature and phase depend on the conditions in the previous separators if no precooler or preheater is used. The pressure of a separation depends on the pressure of previous separators if no valves or pumps are used to change the feed stream pressure. In addition, if a separation requires that an agent be added to the system, the subsequent separations will depend on the amount of the agent and where it is subsequently removed from the separator product. Similarly, when energy integration is considered, a strong recycle of information exists. The optimal means for separating a mixture often depends on the costs of utilities used to drive the separation.

In distillation the costs associated with supplying and removing energy are very important. In many distillations the energy cost can account for up to 70% of the total cost of the separation (King, 1971). Hence, the cost of energy can have a large effect on the size and sequence of distillation columns used to solve a multicomponent separation problem. The energy costs of other separations such as crystallization, extractive distillation, and absorption can also be significant (King, 1971; Treybal, 1968).

The cost of energy to drive a given separation depends on the following two factors:

1. The cost of utilities that could be used to supply and remove energy from the separator. The utilities include steam at various pressures, cooling water, and various temperature levels of refrigerant. Table 4 illustrates typical costs for utilities of this type.

2. The availability of streams within the processing system that could be used for heat exchange. These are streams which must be heated or cooled as they pass between units in the process.

The cost of performing a separation with energy supplied from a stream already within the process will be much less than if utilities are used. The energy from the process stream is essentially free. Since energy costs are very important in designing distillation columns one might expect that the recovery of energy would be important in determining the sequence of separators used to solve multicomponent distillation problems. The main idea here is to use energy sources or sinks available in other process streams to condense vapor in the overhead of a column or to boil liquid in the reboiler of a column. These other process streams might be reboiler or condenser streams in the same separation sequence. One possible integration of this type is shown in Figure 4. In order to determine how to match the system energy sources and sinks within the possible separation sequences, it is necessary to solve an energy integration problem. The next section gives a brief review of energy integration strategies.

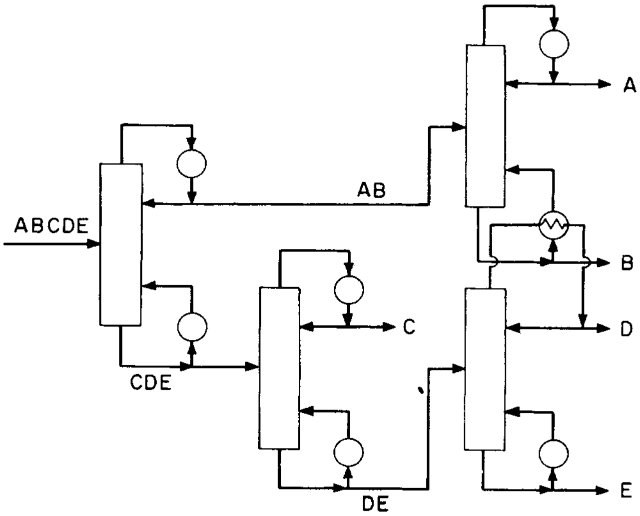


Fig. 4. One possible sequence illustrating energy integration.

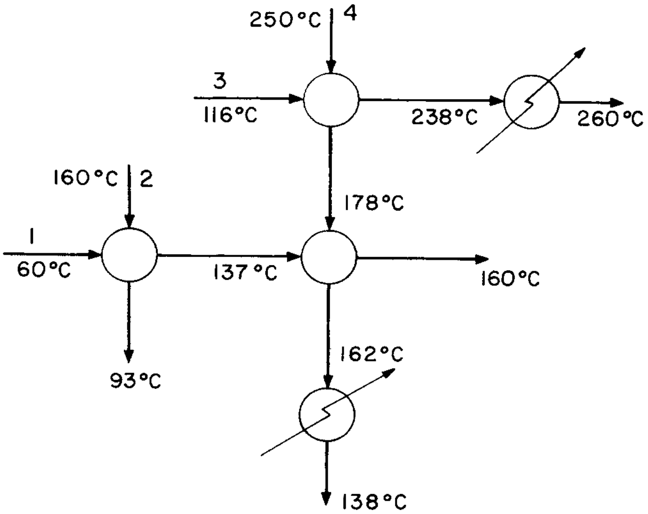


Fig. 5. One possible heat exchange network for a four stream energy integration problem (Lee et al., 1970).

OPTIMAL HEAT EXCHANGER NETWORK SYNTHESIS

The problem of synthesizing an optimal heat exchanger network has been studied by several workers over the past decade. The problem can be stated simply:

> Given *n* streams to be heated and *m* streams to be cooled, find the heat exchanger network which will carry out the desired temperature changes with the minimal cost.

The cost is made up of two factors: (1) The cost of heat exchangers to carry out the energy transfers, and (2) the cost of utilities which might be required to process each stream to its required final conditions (temperature).

The optimal solution to this problem usually involves an integration of the hot and cold streams in heat exchangers to reduce the need for outside energy sources and sinks (utilities). For even simple problems, there exists a large number of ways the hot and cold streams can exchange energy with each other. Figure 5 illustrates one of over 200 possible solutions to a four-stream energy integration problem (Lee et al., 1970). Those who have worked on the heat exchange network synthesis problem have concentrated on means for overcoming the combinatorial aspects of the problem.

Hwa (1965) proposed a separable programming approach to solve the problem. Kesler and Parker (1969) formulated the energy integration as a linear programming problem. Masso and Rudd (1969) used heuristics to determine the proper energy matches which would lead to efficient heat exchanger networks. Ichikawa and Fan (1973) have proposed a search method based on the maximum principle. Lee et al. (1970) solved the problem using a branch and bound technique. This technique is explained here in more detail since it will be used later.

Branch and bound methods (Lawler and Wood, 1966; Mitten, 1970) are schemes for searching for optimal solutions. The power of the methods derives from the fact that, for certain problems, only a small fraction of the possible solutions need actually be enumerated. The remaining solutions are eliminated from consideration through the application of bounds that establish that such solutions can not be optimal. These methods involve two basic steps:

1. Branching, which consists of dividing sets of solutions into subsets.

2. Bounding, which consists of establishing bounds on the value of the objective function over subsets of the solutions.

The basic strategy is to generate sets of subproblems by decomposing the original problem. Bounds (both lower and upper) are then formulated for the system. Each set of subproblems is checked to see if it possesses solutions within the bounds. If the solutions to a given subset of problems are outside the bounds (in the proper sense), then that subset is no longer considered. Hence, by bounding the problem certain sets of problems need not be investigated.

More formally, let S be a given set whose elements are feasible solutions to a given problem. Also, $f\colon S \rightarrow R$ be a specified real-valued function and let

$$\sup_{x \in S} f(x) = f^*$$

The objective is then to find the set of optimal feasible solutions

$$S^* = \{x^* | x^* \in S \quad \text{and} \quad f(x^*) = f^*\}$$

To facilitate the bounding and branching steps, the representation of the original problem is frequently changed. The original problem is commonly embedded in a larger problem involving less restrictive assumptions or constraints. For this purpose a nonempty superset T with $S \subset T$ is introduced along with a bounded extension $g\colon T \rightarrow R$ of the function f with the requirements that $g(x) = f(x)$ whenever $x \in S$ and that there exists an $x \in T$ such that $g(x) = f^*$. A good bit of the art of applying branch and bound methods consists of choosing T and g so as to yield a small search space.

A bounding problem for the heat exchanger network can be created by relaxing one condition of network feasibility—namely, that a stream can be used in more than one place at the same time. If this condition is allowed the optimal solution is less costly than the optimal solution of the original problem. However, if in solving this new and physically unrealistic problem, the simultaneous multiple use of streams does not occur, the original problem is satisfied and optimal solution is found. The advantage is that the larger problem is easier to solve. If the optimal solution to the larger problem contains infeasibilities, that is, simultaneous multiple use of one or more streams, it is necessary to branch to a new problem which avoids that particular infeasibility. The branching, of course, must be to a problem that still maintains a lower bound on the solution. The details of the methods are explained in the original paper of Lee et al. (1970). In general the method involves enumerating and evaluating all the possible means for processing each stream from its source to its destination. Multiple simultaneous use of streams is allowed in determining the processing sequence and evaluation. The best ways for processing each stream are then collected and checked for feasibility. If the set of stream processings contains no multiple simultaneous usages the optimal solution is obtained. If a simultaneous usage is found, the next best set of stream processings is checked for feasibility. This procedure is repeated until the first feasible solution, which is guaranteed to be optimal due to the lower bound, is found. Menzies and Johnson (1972) have extended this branch and bound technique to more general energy integration systems which include compressors, turbo-expanders, etc. They also applied heuristics to the branch and bound procedure to further reduce the size of the search.

In summary, the branch and bound method is a simple method for efficiently searching for solutions to the heat exchanger network synthesis problem. In the following section, we discuss the application of this method when separation sequencing is simultaneously considered.

SEPARATION SEQUENCING WITH ENERGY INTEGRATION

In the previous sections solution methods for the separation sequencing and energy integration problems were discussed separately. The dynamic programming method for selecting optimal separation sequence was shown to be a feasible technique when no feedback of information exists. Unfortunately, when energy integration is considered feedback is introduced. The total cost of performing a given separation depends on the cost of utilities required for the separation. However, the cost of the utilities is not known until the complete separation sequence is synthesized and its energy sources and sinks integrated.

The integration of energy for the complete system is also coupled with the solution of the separation sequencing problem. An energy integration problem is specified by listing the sources and sinks of the energy to be matched. However, all the sources and sinks are not known until the optimal sequence is synthesized. Without knowing which streams will appear in the system it is not possible to solve the energy integration problem. Hence, these two problems are very tightly coupled. The separation sequencing depends on energy costs determined by the solution to the energy integration problem; but the energy integration problem can not be solved until the streams in the separation sequence are known.

In this section we describe a strategy for solving these two subproblems simultaneously. Figure 6 presents the logic for the solution procedure based on a branch and bound method. The first step is to determine which streams elsewhere in the process are available for energy integration. For example, reactor effluents may be used to drive the separations. The mixture to be separated is then considered. All the streams (subgroups) which could arise in the separation of the given mixture are then generated using the list splitting technique described earlier. Table 1 lists all such streams for the ordered list ABCDE. For each property considered for the separation, all the species are placed in an ordered list. The species order in the lists can be different, of course, for different properties. All the streams which result from splitting these lists are considered for potential energy integration. This set of streams represents all the streams which could occur in any separation sequence. For a given sequence only a fraction of all the streams in the feasible stream set will occur. The energy integration character of a stream can also change depending on the separation sequence. For example, in Figure 3 the stream containing nearly pure C occurs in each of the three sequences. However, in sequences (a) and (c) stream C is taken as an overhead product while in sequence (b) it occurs as a bottom product. Thus stream C could be either a source or a sink of energy depending on how it occurs in the separation sequence.

It is possible to reject certain stream matches for energy integration based on the second law of thermodynamics and the structure of the property lists. The following rules have been developed for isobaric sequences of high recovery distillation columns (volatility property ordering). Similar rules can be developed for other types of property orders and for nonisobaric conditions.

Rule 1. The most volatile member in an i-component (for $i < N$) subset of the feasible stream set must go overhead in any subsequent distillation. For example, streams containing subgroups ABCD, ABC, AB and A of the Table 1 can occur as column overheads only. All such streams will always be energy sources (must be condensed). Furthermore, since all streams of this type are

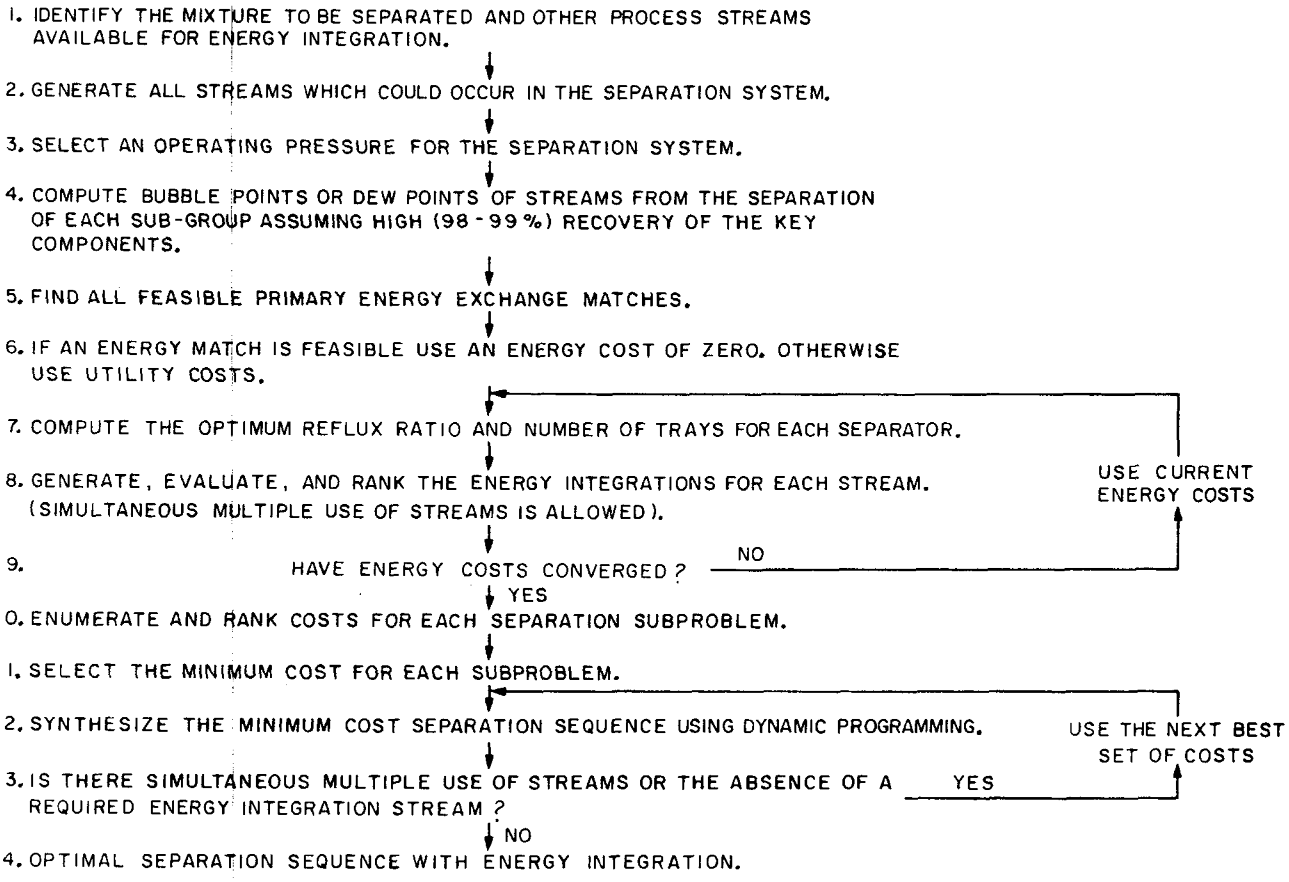


Fig. 6. Strategy for optimal synthesis of isobaric multicomponent separation systems with energy integration.

sources of energy no matches for energy integration can occur between these streams—a source must always match with a sink.

Rule 2. The least volatile member in an i-component (for $i < N$) subset of the feasible stream set must go to the bottom in any subsequent distillation. For example, streams containing subgroups BCDE, CDE, DE, and E can occur as column bottoms only. All such streams will always be energy sinks (must be vaporized). Furthermore, since all streams of this type are sinks of energy, no matches for energy integration can occur between these streams.

Rule 3. A member of an i-component subset can not exchange energy with the $i - 1$ consecutive members of the ordered list in the same subset. Such groups can not occur together in the same sequence. For example, streams AB and BC cannot occur simultaneously since B must go completely with one stream (high recovery).

Rule 4. Feasible energy matches must be consistent with sequential list splitting. For example, an energy match between streams B and BC is thermodynamically feasible when B is an energy sink (bottom of a column) and BC is a source (top of a column). However, list structure dictates that when stream BC occurs in a sequence the stream B will always be source of energy (goes out the top of the following column). These list structure infeasibilities occur in matches between streams containing common species.

Rule 5. Any given energy source stream (top of a column) can only exchange energy with more volatile sinks (bottoms of columns). Similarly, any given sink of energy (bottom of a column) can only exchange energy with less volatile sources (tops of columns). This rule is based on the second law of thermodynamics for isobaric sequences of distillation columns.

It should be noticed that these rules do not apply to matches involving external streams or matches with column inputs or effluents. The only matches considered in this problem are those between condensers and reboilers in the system. The heat loads for vaporization and condensation are almost always much larger than the sensible heat loads for changing stream conditions entering or leaving the columns. For the isobaric case the feed and products are assumed to be saturated liquids and no heating or cooling is required between columns.

During condensation and vaporization the temperature of the stream does not change. The incomplete matching of a source and sink of energy results in a portion of the unmatched stream still being available for further matching at its original temperature. This unmatched portion is then considered for further matches with other sources (or sinks) within the system. The important feature is that the temperatures of the streams do not change when a match is made. This assumes no subcooling or superheating during phase change. Figure 7 illustrates the use of these rules for the mixture ABCDE (volatility decreases from A to E). The match matrix in Figure 7 gives all the possible energy matches. An F appearing as the matrix element for a given match means the match is feasible. If the match is infeasible, a number corresponding to the rule(s) which indicated its infeasibility is placed in the element space. In this matrix only matches within the separation sequence are considered. When external sources and sinks are also considered the number of possible energy matches becomes very large and the solution of the optimal sequence and energy integration becomes combinatorially more difficult.

The primary matches given in Figure 7 indicate which streams may be incorporated in the energy integration. Unfortunately, in order to perform the energy integration it is necessary to know not only that the match is feasible with respect to the second law and the list structure, but also the amount of energy available at each source and the amount required at each sink. The amount of energy depends on the operating conditions of the separators. For distillation it depends on the reflux ratio and feed rate for the column. However, the optimum reflux ratio for each column is determined in part by the cost of the energy. The cost of energy is dependent on how much energy integration is possible. Hence, it is not possible to determine the amounts of energy at the sources and sinks until the cost of energy is fixed, but the cost depends on the amount of energy. The scheme illustrated in Figure 6 is used to uncouple this problem. The method is based on finding repeated lower bounds on energy costs until a feasible energy integration which yields that cost is found.

HOT STREAMS / COLD STREAMS	A	B	C	D	AB	BC	CD	ABC	BCD	ABCD	ABCDE
B	5	4,5	F	F	5	4	F	F	4	F	F
C	5	5	4,5	F	5	5	4	5	F	F	F
D	5	5	5	4,5	5	5	5	5	5	5	F
E	5	5	5	5	5	5	5	5	5	5	F
BC	5	5	4,5	F	3,5	4,5	3,5	5	4,5	5	F
CD	5	5	5	4	5	3,5	4,5	4,5	5	5	F
DE	5	5	5	5	5	5	3,5	5	4,5	4,5	F
BCD	5	5	F	4	4,5	5	4,5	4,5	4,5	5	F
CDE	5	5	5	F	5	4,5	5	4,5	4,5	4,5	F
BCDE	5	5	F	F	4,5	5	F	4,5	5	3,5	F
ABCDE	F	F	F	F	F	F	F	F	F	F	5

Fig. 7. Primary feasible energy exchange matches for isobaric distillation sequences corresponding to the mixture ABCDE.

TABLE 5. TEMPERATURES AND HEAT LOADS IN REBOILERS AND CONDENSERS FOR ALL THE SEPARATION SUBPROBLEMS CORRESPONDING TO RANKED LIST ABCDE. THE HEAT DUTIES CORRESPOND TO THE OPTIMAL REFLUX RATIOS WHEN UTILITIES ARE USED TO DRIVE THE SEPARATIONS IN TABLE 4

	Distillate		Bottoms	
Separation	Temp., °C	Condenser duty, kcal/hr.	Temp., °C	Reboiler duty, kcal/hr.
A/BCDE	14.28	1.271×10^6	79.00	1.438×10^6
AB/CDE	37.51	5.622×10^6	86.65	5.853×10^6
ABC/DE	49.52	4.073×10^6	101.65	4.443×10^6
ABCD/E	59.49	12.08×10^6	104.98	12.29×10^6
A/BCD	14.27	1.102×10^6	68.01	1.203×10^6
AB/CD	37.51	5.173×10^6	75.49	5.272×10^6
ABC/D	49.52	3.513×10^6	95.98	3.657×10^6
B/CDE	49.89	5.644×10^6	86.65	5.735×10^6
BC/DE	56.90	3.892×10^6	101.65	4.143×10^6
BCD/E	66.29	11.75×10^6	104.98	11.88×10^6
A/BC	14.27	1.028×10^6	58.11	1.085×10^6
AB/C	37.51	4.781×10^6	62.61	4.803×10^6
B/CD	49.89	5.164×10^6	75.49	5.191×10^6
BC/D	56.90	3.272×10^6	95.98	3.367×10^6
C/DE	61.88	3.347×10^6	101.65	3.501×10^6
CD/E	73.32	11.25×10^6	104.98	11.31×10^6
A/B	14.27	0.635×10^6	50.27	0.669×10^6
B/C	49.89	4.738×10^6	62.61	4.735×10^6
C/D	61.83	2.567×10^6	95.98	2.627×10^6
D/E	93.46	11.86×10^6	104.98	11.83×10^6

Table 5 presents the temperatures and heat duties in condensers and reboilers corresponding to all the separation subproblems for the mixture ABCDE. These values correspond to the optimum costs for the separations listed in Table 3. In Table 3 utilities are used to drive the separations. Once the exact temperatures in the condensers and reboilers are known, some matches which were shown to be feasible in Figure 7 may be discarded based on the second law of thermodynamics and minimum allowable temperature approach of 8.5°C.

Table 6 enumerates the optimal costs of each separation subproblem for all possible combinations of energy matches. The optimization is over the total cost for both columns involved in the energy match. Utility costs are used for the energy cost for the ends of the column not involved in the match. Utilities are used for the unmatched portion resulting from a match if no other matches can be found for that part. The total cost includes both capital and operating costs as described in Table 4. The multiple simultaneous use of streams has been allowed for energy integration. The values are ranked from lowest to highest, and only matches within the separation se-

TABLE 6. RANKED LIST OF COSTS FOR EACH SEPARATION SUBPROBLEM WHEN ALL POSSIBLE ENERGY INTEGRATIONS ARE CONSIDERED

Separation subproblem	cost, \$/yr.	Energy match
A/BCDE	0.9320×10^5	BCDE:D(DE)
	1.1490×10^5	None
AB/CDE	4.6150×10^5	None
ABC/DE	1.1710×10^5	None
ABCD/E	3.3880×10^5	ABCD:B(AB)
	3.4490×10^5	None
A/BCD	0.9935×10^5	None
AB/CD	4.2080×10^5	None
ABC/D	0.9805×10^5	None
B/CDE	1.4460×10^5	None
BC/DE	1.100×10^5	None
BCD/E	3.314×10^5	None
A/BC	0.7573×10^5	BC:D(DE)
	0.9260×10^5	None
AB/C	3.150×10^5	C:D(DE)
	3.881×10^5	None
B/CD	1.305×10^5	None
BC/D	0.9041×10^5	None
C/DE	0.8794×10^5	C:B(AB)
	0.9394×10^5	None
CD/E	3.077×10^5	CD:B(AB)
	3.144×10^5	None
A/B	0.4862×10^5	B:D(DE)
	0.5841×10^5	B:ABCD(ABCDE)
	0.5841×10^5	B:CD(CDE)
	0.5841×10^5	B:C(CD)
	0.5841×10^5	B:C(CDE)
	0.5909×10^5	None
B/C	0.4405×10^5	B:D(DE)
	1.196×10^5	None
C/D	0.6771×10^5	C:B(AB)
	0.7198×10^5	None
D/E	3.083×10^5	D:BC(ABC) and C(BC)
	3.088×10^5	D:BCDE(ABCDE) and C(BC)
	3.099×10^5	D:C(ABC) and B(AB)
	3.169×10^5	D:BCDE(ABCDE)
	3.192×10^5	D:B(AB)
	3.272×10^5	None

BCDE: D(DE) means that stream BCDE from separation A/BCDE is matched with stream D from subgroup DE.

quences are considered. A match "BCDE: D(DE)" means stream BCDE available from the separation A/BCDE matches with the stream D which is derived from the separation of the subgroup DE. It was found for this problem that the optimum reflux ratio for a particular separation subproblem increases when an energy match is available to drive that separation. The increase in most cases was found to be small (<10%). Hence, it seldom took more than 3 to 4 integrations to find the optimal cost of a separation with energy integration.

For one separation subproblem in an isobaric system three types of energy matches can occur. First, the condenser of the column could be matched with the reboiler of another column [that is, in the previous example the condenser of the D/E column (the D stream) is matched with the reboiler of the A/BCDE column (the BCDE stream)]. Second, the reboiler of a column can match with the condenser of another column. This is just the inverse of the first case. Third, both the condenser and the reboiler of a single column could be matched with other sources or sinks of energy. For isobaric systems with matches only with other column reboilers and condensers, no such single columns of this type exist. This is due to the preservation of property ordering at each separation.

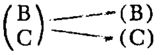
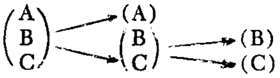
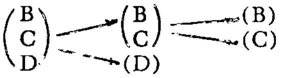
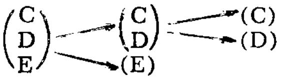
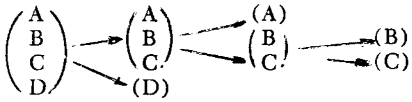
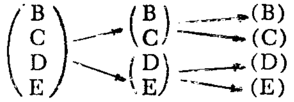
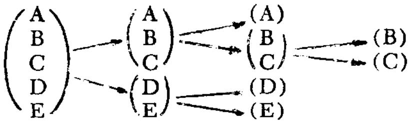
It is possible that parts of one source (or sink) of energy could be simultaneously matched with several other sinks (or sources). In this case it is necessary to evaluate the optimal costs for all possible combinations of the matches. For example the match D:BC(ABC) and (CBC) involves the optimization of three columns simultaneously. The three columns can be decomposed so that three single-column optimizations will solve the original problem. Such combinations do not occur very often in distillation systems.

In the next step, lowest costs for each separation subproblem are used to construct a dynamic programming table, and a first minimum cost separation sequence is synthesized. Serial information flow exists in this problem since high recoveries are assumed (99%) and the columns are all at the same pressure. Table 7 illustrates this procedure for the mixture ABCDE described in Table 4. The lowest cost for each separation subproblem is taken from Table 6. Fortunately, in this case the energy matches occurring in the minimum cost sequence are all feasible. Therefore, this is also the optimal separation sequence. It should be noticed that the optimal separation sequence synthesized in Table 7 is different from the one synthesized in Table 3, and the new optimal separation sequence offers 15.5% savings in the total annual cost for the same separation problem. The energy matches occurring in the new optimal separation sequence are illustrated in Figure 8.

This example demonstrates the strong dependence of the separation sequencing problem on energy integration and shows that significant cost reductions can be obtained using this approach.

Since the rules 1 to 5 described previously are systematically used in conjunction with the second law of the thermodynamics to discard several energy matches

Table 7. Dynamic Programming Synthesis of Optimal Separation Sequence for the Mixture ABCDE (See Table 4). Costs Correspond to Minimum Cost Listed for Each Separation Subproblem in Table 6

Subgroup	Separation	Cost of separation, \$/yr.	Total cost including separations, \$/yr.	Minimum subgroup decomposition cost, \$/yr.	Optimal sequence
(AB)	A/B	0.4862×10^5	0.4862×10^5	0.4862×10^5	
(BC)	B/C	0.4405×10^5	0.4405×10^5	0.4405×10^5	
(CD)	C/D	0.6771×10^5	0.6771×10^5	0.6771×10^5	
(DE)	D/E	3.083×10^5	3.083×10^5	3.083×10^5	
(ABC)	A/BC	0.7573×10^5	1.1978×10^5	1.1978×10^5	
	AB/C	3.1530×10^5	3.6392×10^5		
(BCD)	B/CD	1.305×10^5	1.9821×10^5		
	BC/D	0.9041×10^5	1.3446×10^5	1.3446×10^5	
(CDE)	C/DE	0.8794×10^5	3.9624×10^5		
	CD/E	3.077×10^5	3.7541×10^5	3.7541×10^5	
(ABCD)	A/BCD	0.9935×10^5	2.3381×10^5		
	AB/CD	4.2080×10^5	5.3713×10^5		
	ABC/D	0.9805×10^5	2.1778×10^5	2.1778×10^5	
(BCDE)	B/CDE	1.446×10^5	5.2001×10^5		
	BC/DE	1.100×10^5	4.6235×10^5	4.6235×10^5	
	BCD/E	3.314×10^5	4.6586×10^5		
(ABCDE)	A/BCDE	0.9320×10^5	5.5555×10^5		
	AB/CDE	4.6150×10^5	8.8553×10^5		
	ABC/DE	1.1710×10^5	5.4518×10^5	5.4518×10^5	
	ABCD/E	3.3880×10^5	5.5658×10^5		

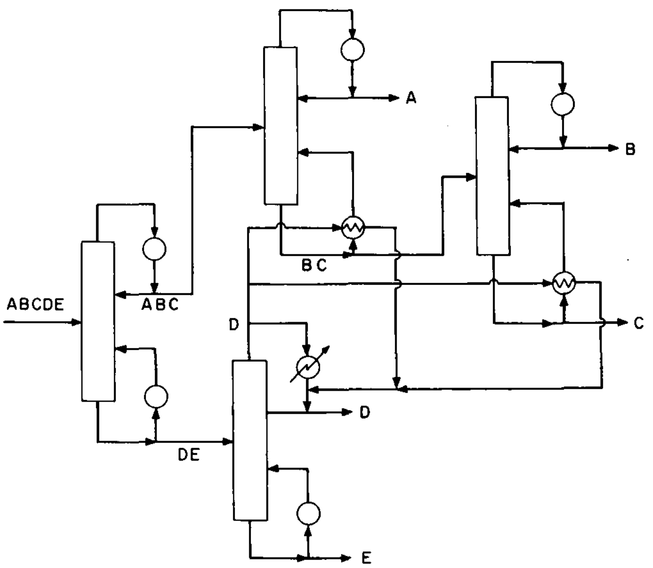


Fig. 8. Optimal separation sequence with energy integration for the mixture described in Table 4.

before Table 6 is computed, there is a very high probability of obtaining the optimal separation sequence by only one application of the dynamic programming search. However, if the energy matches occurring in the first minimum cost separation sequence are infeasible, the next combination of separation costs is selected such that the sum of the costs for all separation subproblems increases monotonically as the number of iterations increases. (Note that the infeasibilities can occur due to simultaneous multiple use of streams and/or to the use of matches between streams which did not occur in the minimum cost sequence.) It can be proved that the cost of the optimal separation sequence synthesized in each iteration also increases monotonically as the number of iterations increases. Therefore, the first feasible separation sequence synthesized this way is also optimal. The efficiency of this search method lies in the fact that very few iterations are normally necessary to find the optimal solution.

If one desires to generate other competitive separation sequences, the iterative search can be continued until sufficient number of feasible solutions are found.

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NOTATION

A = area of heat exchanger, m^2
C_U = cost of utilities, \$/million kcal.
D = flow rate of distillate, kg mol/hr.
D_C = diameter of the column, m
H_C = height of the column, m
N = number of components in the feed mixture
P = column pressure, atm
Q = heat duty, million kcal/hr.
R = reflux ratio
R_m = minimum reflux ratio
S = number of stages
S_m = minimum number of stages
T_{DV} = dewpoint of the vapors at the column top, °K
V = average velocity of the vapors in the column, m/s
$X_{i,D}$ = mole fraction of component i in the distillate
$Z_{i,F}$ = mole fraction of component i in the feed

Greek Letters

α_i = relative volatility of component i with respect to the heavy key component
$\alpha_{i\text{-}r}$ = relative volatility of component i with respect to component r
η = average tray efficiency, fraction
θ = a constant that satisfies the Underwood equation and lies between the values of relative volatilities of light and heavy keys
ϕ = fraction of liquid in column feed
$\subset$ ≡ contained in
ϵ ≡ an element of

LITERATURE CITED

API, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbon and Related Compounds," Am. Petrol. Inst. Project No. 44, Washington, D.C. (1953).

Bellman, R., and S. E. Dreyfus, *Applied Dynamic Programming*, Princeton Univ. Press, N. J. (1962).

Fenske, M. R., *Ind. Eng. Chem.*, **24**, 482 (1932).

Gilliland, E. R., *ibid.*, **32**, 1220 (1940).

Guthrie, K. M., "Capital Cost Estimating," *Chem. Eng.*, 114 (March 24, 1969).

Heaven, D. L., "Optimum Sequencing of Distillation Columns in Multicomponent Fractionation," M.S. thesis, Univ. Calif., Berkeley (1969).

Hendry, J. E., and R. R. Hughes, "Generating Separation Process Flowsheets," *Chem. Eng. Progr.*, 68(6), 71 (1972).

Hwa, C. S., "Mathematical Formulation and Optimization of Exchanger Networks using Separable Programming," AIChE-IChE Joint Meeting, London (1965).

Ichikawa, A., and L. T. Fan, "Optimal Synthesis of Process Systems," *Chem. Eng. Sci.*, **28**, 157 (1973).

Kesler, M. G., and R. O. Parker, "Optimal Networks of Heat Exchange," *Chem. Eng. Progr. Symp. Ser. No.* 92, 111 (1969).

King, C. J., *Separation Processes*, McGraw-Hill, New York (1971).

Lawler, E. L., and D. E. Wood, "Branch and Bound Methods: A Survey," *Operations Research*, **14**, 699 (1966).

Lee, K. F., A. H. Masso, and D. F. Rudd, "Branch and Bound Synthesis of Integrated Designs," *Ind. Eng. Chem. Fundamentals*, **9**, 48 (1970).

Maikov, V. P., G. G. Vilkov, and A. V. Galtsov, "Optimum Design of Multi-component Fractionating Plants from the Thermodynamic Standpoint," *Intern. Chem. Eng.*, **12**, 426 (1972).

Masso, A. H., and D. F. Rudd, "The Synthesis of System Designs II: Heuristic Structuring," *AIChE J.*, **15**, 10 (1969).

Menzies, M. A., and A. I. Johnson, "Synthesis of Optimal Energy Recovery Networks Using Discrete Methods," *Can. J. Chem. Eng.*, **50**, 290 (1972).

Mitten, L. G., "Branch and Bound Methods: General Formulation and Properties," *Operations Research*, **18**, 24 (1970).

Nishimura, N., and Y. Hiraizumi, "Optimum System Pattern for Multi-component Distillation System," *Intern. Chem. Eng.*, **11**, 188 (1971).

Petlyuk, F. B., V. M. Platonov, and D. M. Slavinskii, "Thermodynamically Optimal Method for Separating Multi-component Mixtures," *ibid.*, **5**, 555 (1965).

Rudd, D. F., G. J. Powers, and J. J. Siirola, *Process Synthesis*, Prentice-Hall, N. J. (1973).

Thompson, R. W., and C. J. King, "Systematic Synthesis of Separation Schemes," *AIChE J.*, **18**, 941 (1972).

Treybal, R. E., *Mass Transfer Operation*, 2nd edit., McGraw-Hill, New York (1968).

Underwood, A. J. V., *Chem. Eng. Progr.*, **44**, 603 (1948).

Van Winkle, M., and W. A. Todd, "Optimum Fractionation Design by Simple Graphical Methods," *Chem. Eng.*, 136 (Sept. 20, 1971).

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