Subscripts

A = acetone
Abs = absorption (swelling)
Ads = adsorption (chemisorption or hydrogen bonding)
MCH = methylcyclohexane
P = phenol
W = water

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Manuscript received January 25, 1974; revision received May 16 and accepted May 17, 1974.

Synthesis of Distillation Systems with Energy Integration

A formal method is described for the synthesis of multicomponent distillation systems when energy integration is considered between streams both within the separation sequence and in other parts of the process. The pressure in each column is considered as an optimization variable for both the energy integration and column sizing computations. Four rules are used to enumerate all feasible energy matches between the streams associated with the distillation columns. A bounding strategy which uses both upper and lower bounds is combined with dynamic programming to synthesize the optimal distillation sequence with energy integration. A five-component separation problem demonstrates the effectiveness of the methods.

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Distillation systems are widely used in the manufacture of petroleum and petrochemical products. These systems consume large amounts of energy to achieve separation. In view of increasing energy costs, it is important to design distillation systems which consume less energy.

Several authors have described intuitive schemes for minimizing energy consumption in multicomponent distillation processes, for example, King (1971), Petlyuk et al.

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(1965), Stupin and Lockhart (1972). In a recent paper, Rathore et al. (1974) described a strategy for synthesizing optimal separation systems with energy integration. The major drawback of this strategy is that it does not allow pressure variations in the separation subproblems to achieve energy integration. It is found that many more energy matches become possible when pressure variation is allowed. More specifically, for distillation systems, pressure is an important operating and design parameter that determines both the ease of separation and the level of energy integration.

In this paper, a method is described for synthesizing optimal energy integrated distillation systems in which the pressures in the distillation columns need not all be the same. Using this method the savings from energy integration can then be compared to the costs associated with having a more complicated system, additional start-up equipment, and potential control problems.

CONCLUSIONS AND SIGNIFICANCE

This work is significant in that a systematic strategy for the synthesis of optimal energy integrated distillation systems has been developed and tested on an industrially significant separation problem. Four rules, based on the second law of thermodynamics and the volatility order of the species in the mixture to be separated, are offered to rapidly identify all feasible energy integrations. It is found that there are a large number of possible integrations even for simple systems. An upper bound based on utility costs and a lower bound based on optimal single energy matches greatly reduces the computational effort to establish the optimal energy integrated distillation system.

If the distillation system requires the removal of energy from the condensing streams below ambient temperatures, the amount of economic energy recovery will depend very strongly on how quickly the utility costs rise with decreasing temperature. An example shows that decreasing the rate of rise of utility costs with temperature by 50% increases the number of profitable energy integrations. The utility costs will depend on the rest of the processing environment in each plant. The example also illustrates that the separation sequence associated with the optimal energy integrated distillation system can often be different from the separation sequence corresponding to the optimal distillation system when energy integrations are not allowed.

Systems of distillation columns are found in widespread use in the petroleum and petrochemical industries. These columns consume a large amount of energy. The sources and sinks of energy for the columns can be utilities such as cooling water, refrigerants, and steam, or other streams within the process. The use of energy integration can give large savings in utility costs. In a previous paper, Rathore et al. (1974) described a methodology for synthesizing separation sequences when energy integration is considered.

Briefly, the strategy is to identify all possible separation subproblems which could occur in the system. All the feasible energy matches between these separation subproblems are then identified. The optimal conditions are computed for each column-energy match combination. The best possible energy matches computed in this way are used in a dynamic programming scheme to select the optimal separation sequence. A key assumption in this approach is that all the columns operate at the same pressure. This assumption is made to simplify the identification of feasible energy matches. When isobaric operation is assumed, the dew points and bubble points of the mixtures involved define the temperatures at which the energy exchanges take place. If the pressures are allowed to vary between energy integrated columns, these temperatures will change, thus affecting the extent of energy exchange. In addition, pressure levels will affect the heat duties for the columns. At higher pressures the differences in relative volatilities become smaller and reflux ratios increase. Equipment costs also depend on pressure. A number of industrial distillation schemes utilize these facts to select column pressures which result in low cost processing. For example, it is common practice to increase the pressure of a column so that the overhead can be condensed with cooling water rather than a more expensive refrigerant. Hence, the pressure in the individual columns is an important parameter which should be considered during column design and energy integration. What is needed is an efficient way for determining column pressures, energy integration, and separation sequence so that the savings in energy and capital are greater than the extra expenses associated with more complex operations.

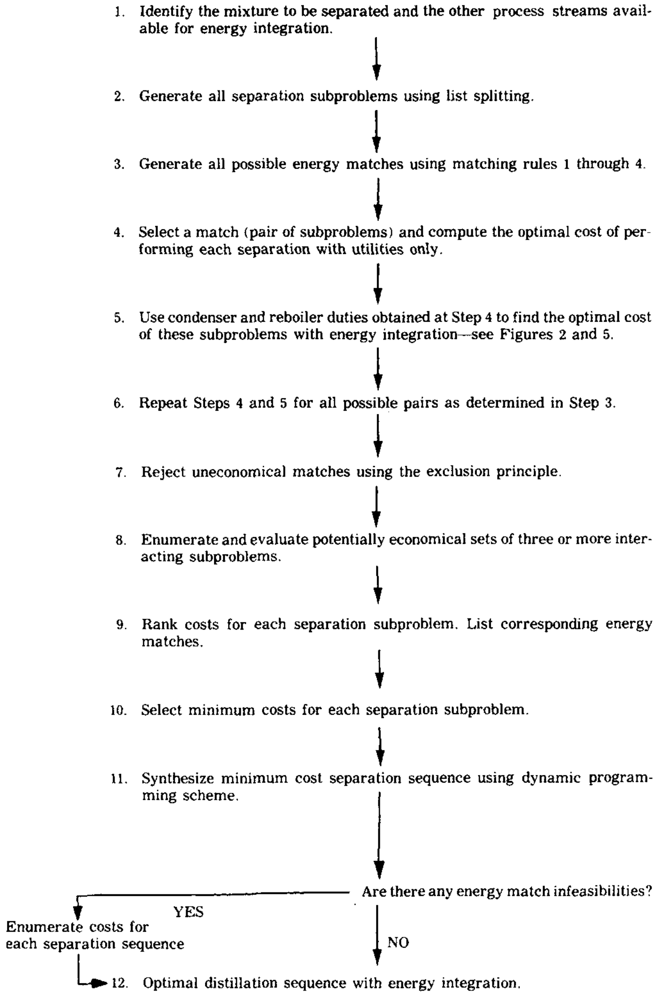
In the following sections the isobaric system strategy is generalized to handle the nonisobaric distillation system problem. A detailed introduction to this problem is given in Rathore et al. (1974).

SYNTHESIS STRATEGY

The problem is the separation of a multicomponent mixture by distillation. The goal is to find a distillation system which solves the separation problem at the minimum total cost. In this paper it is assumed that:

1. Each column operates at high recovery.
2. The volatility order does not change with changes in pressure.
3. The cost of changing the temperature and pressure of streams as they pass between columns is negligible compared to column capital and energy costs.
4. Energy matches occur only between boiling and condensing streams.
5. No matches occur with streams outside of the distillation system.
6. No vapor recompression is used.
7. A continuous function is used for utility costs.
8. Saturated liquid feed and products are present in each column. Assumptions 1, 2, and 3 are fundamental to the method. The remainder have been used to simplify the example problem.

The general strategy is to decompose the original multicomponent separation problem into a number of subprob-



1. Identify the mixture to be separated and the other process streams available for energy integration.
2. Generate all separation subproblems using list splitting.
3. Generate all possible energy matches using matching rules 1 through 4.
4. Select a match (pair of subproblems) and compute the optimal cost of performing each separation with utilities only.
5. Use condenser and reboiler duties obtained at Step 4 to find the optimal cost of these subproblems with energy integration—see Figures 2 and 5.
6. Repeat Steps 4 and 5 for all possible pairs as determined in Step 3.
7. Reject uneconomical matches using the exclusion principle.
8. Enumerate and evaluate potentially economical sets of three or more interacting subproblems.
9. Rank costs for each separation subproblem. List corresponding energy matches.
10. Select minimum costs for each separation subproblem.
11. Synthesize minimum cost separation sequence using dynamic programming scheme.

Are there any energy match infeasibilities?

YES

Enumerate costs for each separation sequence

NO

12. Optimal distillation sequence with energy integration.

Fig. 1. The synthesis strategy for distillation systems with energy integration.

lems each of which involves one separation. The decomposition is done in such a way that feasible combinations of the optimal solutions of the subproblems constitute a bound on the optimal solution of the multicomponent separation problem. The bounding nature of the decomposition is what guarantees the optimality of the systems synthesized by this scheme. A more rigorous statement of this principle is given in our previous paper (Rathore et al., 1974).

The basic steps of the synthesis strategy are given in Figure 1. The first step is to identify the mixture to be separated along with the utilities and other process streams which are available and could be used for energy sources or sinks.

Once the components of the mixture are known, their relative volatilities are used to create an ordered list corresponding to that mixture. For example, a mixture containing species A, B, C, D, and E may be represented by the ordered list ABCDE if the relative volatilities of the species decrease from A to E. This list can then be split into ordered sublists which represent streams which could be present in the separation system. High recoveries (99%) are assumed so that the effect of trace components from an incomplete separation can be neglected. The details of the list splitting procedure are described elsewhere (Hendry and Hughes, 1972; Rathore et al., 1974).

The subgroups which result from splitting the ABCDE mixture are ABCDE, ABCD, BCDE, ABC, BCD, CDE, AB, BC, CD, DE, A, B, C, D, and E. The generation of subgroups in this way corresponds to the separations which could occur in the separation system. For example, the splitting of the list ABCDE into subgroups AB and CDE corresponds to the separation subproblem AB/CDE. In general, there are $N - 1$ separation subproblems associated with a subgroup containing N components. In addition, there are $N(N + 1)/2$ feasible subgroups and $(N - 1)(N)(N + 1)/6$ separation subproblems for an N component mixture. Out of these, only $2N - 1$ subgroups and $N - 1$ separation subproblems occur in a particular solution. Hence there are $([2(N - 1)]!)/N!(N - 1)!$ different solutions to an N component separation problem.[*]

The third step in the solution procedure is to generate all feasible energy matches which could occur for the subproblems generated by the list splitting procedure. Figure 2 illustrates a typical energy match which could occur in a distillation system for separating the mixture ABCDE. Stream D, which is the overhead of a column separating the mixture DE, is matched with stream B, which is the bottom stream of a column separating the mixture AB. An energy match means that the reboiler and condenser heat loads are matched. Other matches could occur between streams passing between columns. The heat load associated with the sensible heat change for these streams is usually much smaller than that required in the column condensers and reboilers. Only reboiler-condenser energy matches are considered in the following sections.

Each separation subproblem could generate energy matches between its condenser and reboiler and all other potential sources and sinks of energy in the process. Many

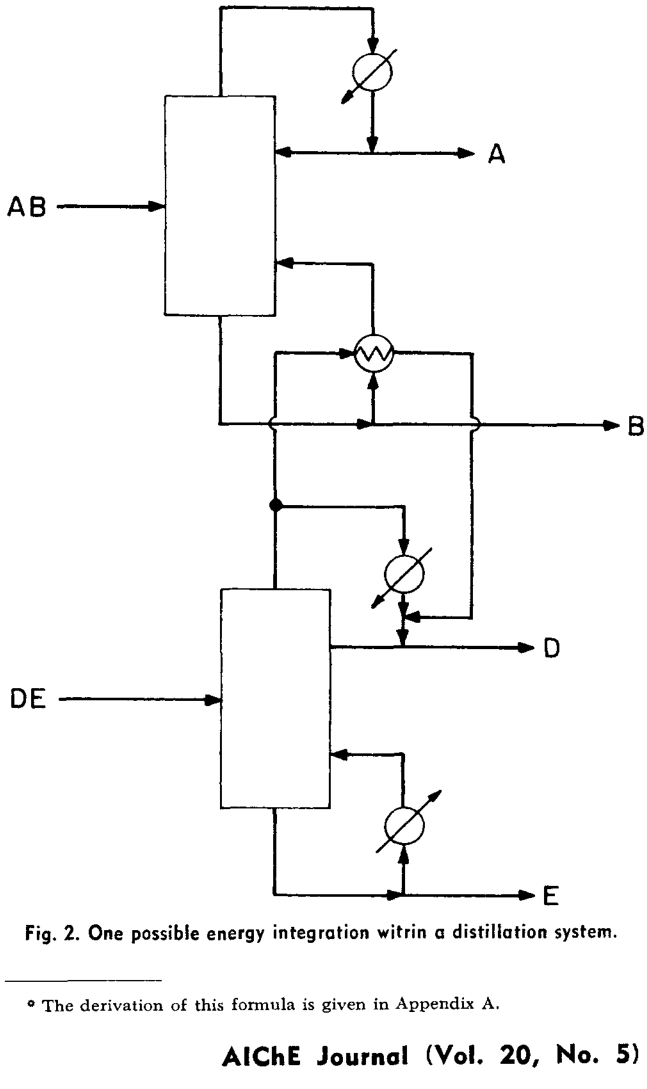


Fig. 2. One possible energy integration witrin a distillation system.

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[*] The derivation of this formula is given in Appendix A.

COLD STREAMS \ HOT STREAMS	A	B	C	D	AB	BC	CD	ABC	BCD	ABCD
B	VR	4	F	F	F	4	F	F	4	F
C	F	VR	4	F	VR	F	4	F	F	F
D	F	F	VR	4	F	VR	F	VR	F	F
E	F	F	F	VR	F	F	VR	F	VR	VR
B C	VR	F	4	F	3	4	3	F	4	F
C D	F	VR	F	4	VR	3	4	4	F	F
D E	F	F	VR	F	F	VR	3	VR	4	4
B C D	VR	F	F	4	4	F	4	4	4	F
C D E	F	VR	F	F	VR	4	F	4	4	4
B C D E	VR	F	F	F	4	F	F	4	F	3

Fig. 3. The energy match matrix for a five component mixture. F means the match is feasible. VR indicates that vapor recompression is required for the match to be feasible. A number denotes the rule which indicated the match was infeasible.

of these matches will be infeasible for a number of reasons. The following four rules have been developed to detect infeasible energy matches between reboilers and condensers within the separation system. These rules are based on the simple facts that:

1. Sources of energy must be matched with sinks, and
2. The co-existence of streams must obey the property order and high recovery constraints.

Rule 1. The most volatile member of an *i*-component subgroup must go overhead in any subsequent distillation. Hence, all of these streams will be sources (condenser streams) of energy and no energy matches can occur between them. For example, mixtures containing subgroups ABCD, ABC, AB, and A can only occur as column overheads. Hence, an energy match between ABCD and AB is infeasible. They are both sources of energy and an energy match requires both a source and a sink.

Rule 2. The least volatile member of an *i*-component subgroup must go to the bottom in any subsequent distillation. Hence, all of these streams will be sources of energy and no energy matches can occur between these streams. For example, energy matches cannot occur between BCDE, CDE, DE, and E.

Rule 3. A member of an *i*-component subgroup cannot exchange energy with the $i - 1$ consecutive members of the ordered list in the same subgroup. Such groups cannot occur together in the same distillation sequence due to the high recovery assumption. For example, streams AB and BC cannot occur simultaneously. The component B must go completely with one stream.

Rule 4. Feasible energy matches must be consistent with the energy source and sink relations implied by the list order and the list splitting constraint of high recovery. For example, an energy match between streams B and BC is feasible if B is an energy sink (bottoms stream) and BC is a source (overhead stream). However, the volatility order dictates that when stream BC occurs in a separation sequence the stream B will always be a source of energy.

An additional rule (Rule 5), based on the second law of thermodynamics was used in previous work (Rathore et al., 1974) for isobaric systems. With this rule if the temperature of a source of energy was lower than the temperature of a sink, the match was rejected as infeasible. When the pressures of the columns are variable, these temperatures are not defined and it is not possible to reject energy matches on this basis. The inapplicability of this rule allows many more matches to occur.

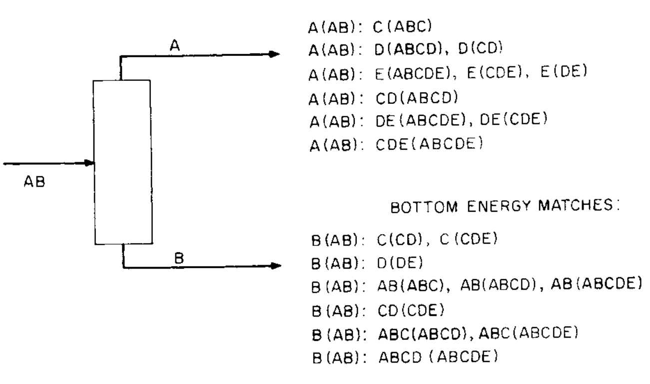
Figure 3 illustrates a matrix of all possible matches which could occur in a system separating the mixture ABCDE. An F appearing as an element in the match matrix means that the match corresponding to that row and column is feasible. A VR appearing as an element means that vapor recompression is required for the energy match to be feasible. The two streams making up the VR matches must come from the same column. Hence both streams are assumed to be at the column pressure. The dew points and bubble points of the mixtures prevent the energy match from occurring unless the vapor is recompressed. The cost of vapor compression is usually quite high and it will not be used in the following example. However, there are a few cases where vapor recompression is economical (King, 1971). If a match is infeasible, a number corresponding to the rule which indicated its infeasibility is placed in the matrix element. The matrix in Figure 3 does not include matches with external streams which may be numerous in an industrial problem.

Figure 4 illustrates all feasible energy matches (excluding vapor recompression) for the condenser and reboiler streams of separation subproblem A/B. The match "A(AB):C(ABC)" is read as: "stream A obtained from the separation of subgroup AB matches with stream C obtained from the separation of subgroup ABC."

The pressure range in each column over which an energy match is feasible depends on the dew point and bubble point of the streams being matched, the minimum temperature approach for heat exchange, and the upper and lower bounds on column operating pressure. In this study an approach temperature of 8.5°C is used. An upper bound of 34 atm. and a lower bound of 1.0 atm. are used for column pressures. If an energy match requires pressures outside of this range, it is considered infeasible.

Subproblem Optimization Strategies

The overall synthesis strategy, as described earlier, is to decompose the synthesis problem into subproblems. The subproblems are optimized and these subproblem solutions are used to solve the original problem so that the resulting solution bounds the optimal solution. The objective function is the total venture cost for the system. It includes the capital costs associated with the column and associated heat exchangers and instruments and the operating costs associated with utilities and maintenance. The cost functions are given in Table 1.



TOP ENERGY MATCHES:

A(AB): C(ABC)
A(AB): D(ABCD), D(CD)
A(AB): E(ABCDE), E(CDE), E(DE)
A(AB): CD(ABCD)
A(AB): DE(ABCDE), DE(CDE)
A(AB): CDE(ABCDE)

BOTTOM ENERGY MATCHES:

B(AB): C(CD), C(CDE)
B(AB): D(DE)
B(AB): AB(ABC), AB(ABCD), AB(ABCDE)
B(AB): CD(CDE)
B(AB): ABC(ABCD), ABC(ABCDE)
B(AB): ABCD(ABCDE)

Fig. 4. All feasible energy matches for the separation subproblem A/B which occurs in a five component separation problem.

TABLE 1. DESIGN AND COST EQUATIONS USED FOR THE DISTILLATION CALCULATIONS

Minimum number of stages

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

$\alpha_{i\text{-}r}$ value is geometric mean of the values at the column top and bottom.

Minimum reflux ratio

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

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

Number of stages

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

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

$$- 0.1738 \left[\frac{(R - R_m)}{(R+1)}\right]^3$$

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

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

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:

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

If the column pressure is more than 3.4 atm. a correction factor

$[1 + 0.0147\,(P - 3.4)]$ is applied.

Cost of trays

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

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:

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

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

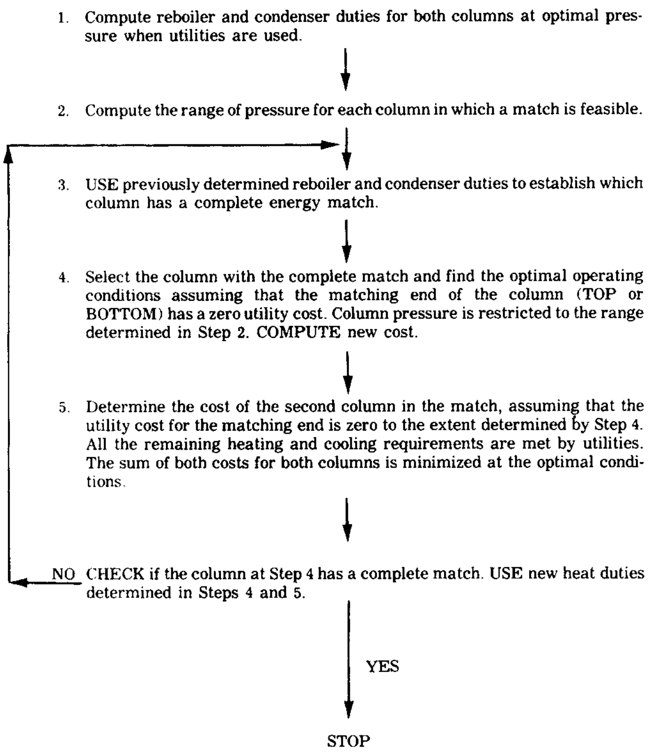
Physical properties

K-valued liquid and vapor enthalpies are estimated from a polynominal correlations of experimental data (API, 1953).

Assumed values:

η = 80% in all the columns
P = optimal value
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



1. Compute reboiler and condenser duties for both columns at optimal pressure when utilities are used.
2. Compute the range of pressure for each column in which a match is feasible.
3. USE previously determined reboiler and condenser duties to establish which column has a complete energy match.
4. Select the column with the complete match and find the optimal operating conditions assuming that the matching end of the column (TOP or BOTTOM) has a zero utility cost. Column pressure is restricted to the range determined in Step 2. COMPUTE new cost.
5. Determine the cost of the second column in the match, assuming that the utility cost for the matching end is zero to the extent determined by Step 4. All the remaining heating and cooling requirements are met by utilities. The sum of both costs for both columns is minimized at the optimal conditions.

NO CHECK if the column at Step 4 has a complete match. USE new heat duties determined in Steps 4 and 5.

Fig. 5. The strategy for computing the optimum conditions for each energy match.

Figure 5 illustrates the overall approach used in subproblem optimization. The cost of performing a separation depends strongly on the extent of energy integration. In a single energy match two distillation columns are involved. It is necessary to determine the optimal reflux ratio, number of trays and pressure in each of these columns when the energy integration is considered. The procedure in Figure 5 avoids iterative calculations in most cases by properly ordering the column calculations. Since both columns must be present in a system for the energy match to be feasible, the sum of the venture costs for both columns is minimized.

The cost of utilities was assumed to be given by

$$C_U = \begin{cases} 8.0 - 0.26\,T \text{ for cooling in the range} & \\ \qquad\qquad -50^\circ\text{C} \leq T \leq 30^\circ\text{C} & \\ 0.2 \qquad\qquad\qquad T > 30^\circ\text{C} & \\ -0.4 + 0.02\,T \text{ for heating in the range} & \\ \qquad\qquad 30^\circ\text{C} \leq T \leq 300^\circ\text{C} & \\ 0.2 \qquad\qquad\qquad T < 30^\circ\text{C} & \end{cases} \qquad (1)$$

With these costs a utility is selected with the minimum cost such that the minimum allowable temperature approach is satisfied.

EXCLUSION PRINCIPLE

If an upper bound on the cost of the solution of a set of interacting subproblems can be established, then an alternative solution of these subproblems with a higher cost than this upper bound can be excluded.

In an energy match of the type shown in Figure 2, two separation subproblems interact through the energy match, that is, the distillation columns are coupled. If the energy match is not allowed (that is, only utilities are used to achieve separation) the subproblems do not interact. Let us assume that the optimal costs of solving the participating subproblems when no match is allowed are C_1^* and C_2^*, respectively. Then the sum of these two costs ($C_1^* + C_2^*$) constitutes the upper bound on the cost of solving these two subproblems. This means that a match with a cost higher than the optimal cost using only utilities is excluded. Let C_{1m}^* and C_{2m}^* be the optimal cost of solving these subproblems with energy matching. One can now define the profit associated with an energy match m as

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

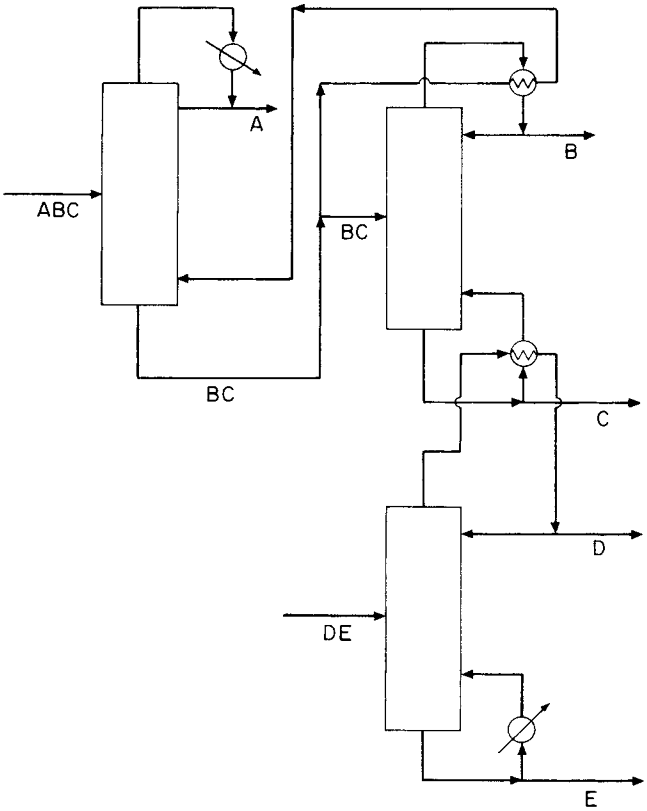


Fig. 6a. An example of an higher order energy match in which both the condenser stream and reboiler stream of a single column are matched.

If P_m is negative, the exclusion principle applies and the match can be discarded. It will be shown later that this bound is very useful and drastically reduces computation effort in the synthesis step. A match with a positive profit P_m is defined as an economical match.

Enumeration of Higher Sets of Interacting Subproblems

It is sometimes possible to have interaction between three or more separation subproblems through energy matches. Interaction between three separation subproblems can occur in two different ways:

1. When both overhead and bottom streams associated with a separation subproblem can match with the other streams in a sequence. Figure 6a illustrates a possible combination of this type.
2. When an overhead or a bottom stream associated with a separation subproblem is large enough to exchange energy with more than one stream in a sequence. Figure 6b illustrates a possible combination of this type.

Feasibility of such combinations depends strongly on the pressure ranges associated with the energy matches causing the interaction. Consider the case where R_{1j} is the range of pressure for subproblem j in the match m_1 between the streams obtained from the separation subproblems i and j, and where R_{2j} is the range of pressure for subproblem j in the match m_2 between the streams obtained from the separation subproblems j and k. Then a

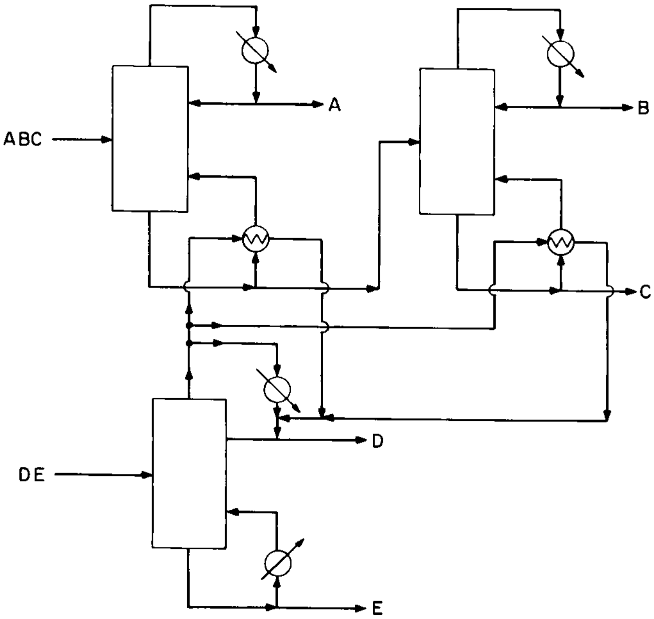


Fig. 6b. An higher order match in which the condenser stream of a single column is matched with two other reboiler streams.

three subproblem interaction will be feasible only if the intersection of ranges R_{1j} and R_{2j} ($R_{1j} \cap R_{2j}$) is not empty. In addition, all the streams participating in the matches m_1 and m_2 must obey rules 1 through 4 and the feasibility constraints described earlier for two subproblems.

These feasibility constraints invalidate most of the possible combinations of three interacting subproblems. Further it is possible to avoid evaluation of a large number of combinations by use of the exclusion principle. Let $P_{m1}(R_{1j})$ be the profit associated with the match m_1 when only two subproblems interact (say i and j), and $P_{m1}(R_{1j} \cap R_{2j})$ be the profit associated with the same match when three subproblems interact (say i, j, and k). Then, it is clear that

$$P_{m1}(R_{1j}) \geq P_{m1}(R_{1j} \cap R_{2j}) \qquad (3)$$

because $R_{1j} \supseteq R_{1j} \cap R_{2j}$. From condition (3) one can show that the maximum possible profit associated with the matches m_1 and m_2 corresponding to a set of three interacting subproblems is

$$P_{m1}(R_{1j} \cap R_{2j}) + P_{m2}(R_{1j} \cap R_{2j}) \leq P_{m1}(R_{1j}) + P_{m2}(R_{2j}) \qquad (4)$$

Therefore, the cases for which $[P_{m1}(R_{1j}) + P_{m2}(R_{2j})]$ is negative can be discarded as they will be uneconomical. Notice that the values of $P_{m1}(R_{1j})$ and $P_{m2}(R_{2j})$ have already been obtained in the evaluation of the set of two interacting subproblems. Hence, the application of conditions (3) and (4) results in a considerable reduction in computational effort.

The cases, when $[P_{m1}(R_{1j}) + P_{m2}(R_{2j})]$ is positive, are potentially economical and their evaluation is necessary. A generalization of the procedure shown in Figure 5 is used to compute the optimal costs and the operating conditions in such cases. Once the evaluation of these cases is complete, it is further possible to discard several of them by use of exclusion principle.

The other higher order sets of interacting subproblems can be similarly generated and evaluated.

With assumption 4, the only energy exchanges occurring in the distillation system involve condensing and boiling streams. Hence the temperatures of the matching streams do not change (only latent heats are exchanged) and the residual streams from a match are at the same temperature as their parents. For this special case, it is possible to split the energy available in a stream and send it to several different matches. The subproblem optimization considers all such possible matches with residuals. For example, the stream D from the separation subproblem DE could be energy integrated with B from AB, or C from ABC, or C from BC. The amount of D to be matched with each of the other streams depends on the energy change required in D and in each of the other streams. The residual energy content in D from each match is matched with the remaining streams until all possible matches have been considered. This is the approach used by Lee et al. (1970). The enumeration of the matches is much simpler in this case since the temperatures of the streams do not change during energy exchange.

Once the evaluation of all the possible sets of interacting subproblems is complete, the costs are ranked for each subproblem. At this point only the costs associated with the economical matches and the cost with no match (utilities only), need be considered. What remains is to combine the solutions of these subproblems to solve the original multicomponent distillation problem. This procedure is described in the next section.

SEPARATOR SEQUENCING BY DYNAMIC PROGRAMMING AND ENUMERATION

Once all of the single column subproblems and interacting sets of subproblems have been optimized, it is necessary to assemble them into the proper optimal solution for the complete separation problem. For the assumption given earlier the interaction between subproblems is small. This means that the streams leaving a column do not interact with other separators except through energy matching which was accounted for in the subproblem optimization. The high recovery assumption removes interactions between columns since, for example, the flow rate and concentrations in the stream BC (which will be separated into B and C) do not depend on the column from which BC came. The costs of changing the pressure and temperature of streams as they enter the downstream distillation column are considered negligible when compared to the column capital and utility costs. For liquid streams passing between columns the pressure change costs are those associated with pumping a liquid. If partial condensers are used, the higher costs of vapor compression will be encountered and the subproblems will interact more strongly. Saturated liquid products and feeds are assumed for the following examples. The heat loads for changing a saturated liquid product at one pressure into a saturated liquid feed to another column operating at another pressure is assumed negligible when compared to reboiler and condenser heat duties.

With these assumptions the interactions between subproblems can be neglected. It is then necessary to select the minimal cost subset of subproblem solutions, that solves the original problem, from the set of all subproblem solutions. The cost for the solution is the sum of the costs for the subproblem solutions. A dynamic programming approach has been advanced by Hendry and Hughes (1972) for this problem. The lowest costs for each of the optimal subproblem solutions are used to construct a dynamic programming tableau. The search of the tableau reveals the first minimum cost separation sequence. This sequence is checked for two types of energy integration infeasibilities: (1) a stream is used more than once for the same purpose (that is, it exchanges more energy than it has available), and (2) a stream that is required for energy integration is not in the separation sequence. If these infeasibilities are not detected the minimum cost sequence is optimal and the solution of the original problem is complete.

If infeasibilities are detected, the separation subproblems for each of the separation sequences are grouped together and the total cost for each sequence computed for each possible energy integration. No additional column calculations are required. It is necessary to simply add the subproblem costs together for a number of different combinations. The minimum cost combination revealed by this enumeration is the optimal solution to the original problem.

Limited experience with this method shows that it is often not necessary to carry out the enumeration as the minimal cost separation sequence synthesized by the first dynamic programming search is often feasible and hence optimal.

SEPARATION OF LIGHT PARAFFINS—AN EXAMPLE

Consider the separation of the components of the following feed stream containing five components. The feed rate is 907.2 kg mol/hr. and all the products are desired as pure components.

Component	Feed mole 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

TABLE 2. ENERGY MATCH COSTS FOR THE SUBPROBLEM *A/B*

Energy match	First separation subproblem	Optimal cost without match $/yr.	Optimal pressure without match, atm.	Optimal cost with match $/yr.	Optimal pressure with match	Second separation subproblem	Optimal cost without match	Optimal pressure without match, atm.	Optimal cost with match, $/yr.	Optimal pressure match, atm.	Match profit, $/yr.
A (AB): C (ABC)	A/B	0.2613×10^5	15.1	0.2014×10^5	14.3	AB/C	1.1980×10^5	8.5	6.4500×10^5	1.0	-5.1911×10^5
A (AB): D (ABCD)	A/B	0.2613×10^5	15.1	0.2060×10^5	15.1	ABC/D	0.9445×10^5	6.3	4.8690×10^5	1.0	-3.8692×10^5
A (AB): D (CD)	A/B	0.2613×10^5	15.1	0.2060×10^5	15.1	C/D	0.5927×10^5	4.5	2.8980×10^5	1.0	-2.2500×10^5
A (AB): E (ABCDE)	A/B	0.2613×10^5	15.1	0.2223×10^5	18.0	ABCD/E	2.6600×10^5	4.9	12.1100×10^5	1.0	-9.2110×10^5
A (AB): E (CDE)	A/B	0.2613×10^5	15.1	0.2233×10^5	18.0	CD/E	1.8530×10^5	3.3	8.6820×10^5	1.0	-6.7910×10^5
A (AB): E (DE)	A/B	0.2613×10^5	15.1	0.2233×10^5	18.0	D/E	1.6920×10^5	2.0	4.7260×10^5	1.0	-2.9963×10^5
A (AB): CD (ABCD)	A/B	0.2613×10^5	15.1	0.1769×10^5	10.5	AB/CD	1.4050×10^5	8.5	6.6810×10^5	1.0	-5.1916×10^5
A (AB): DE (ABCDE)	A/B	0.2613×10^5	15.1	0.2156×10^5	16.8	ABC/DE	1.1490×10^5	6.3	5.4580×10^5	1.0	-4.2633×10^5
A (AB): DE (CDE)	A/B	0.2613×10^5	15.1	0.2156×10^5	16.8	C/DE	0.7817×10^5	4.5	3.5200×10^5	1.0	-2.6926×10^5
A (AB): CDE (ABCDE)	A/B	0.2613×10^5	15.1	0.2376×10^5	21.1	AB/CDE	1.6500×10^5	8.5	7.2810×10^5	1.0	-5.6073×10^5

TABLE 3. COSTS FOR THE SELECTION OF THE OPTIMAL SEPARATION SEQUENCE

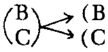
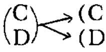
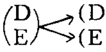
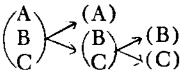
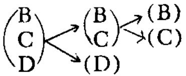
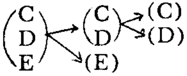
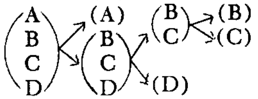
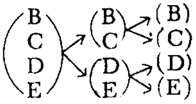
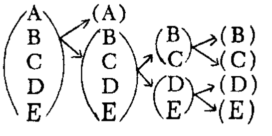
Subgroup	Separation	Optimal pressure	Cost of separation, $/yr.	Total cost including subsequent separations, $/yr.	Minimum subgroup decomposition cost, $/yr.	Optimal sequence
(AB)	A/B	15.1	0.2613×10^5	0.2613×10^5	0.2613×10^5	
(BC)	B/C	6.3	0.9493×10^5	0.9493×10^5	0.9493×10^5	
(CD)	C/D	4.5	0.5927×10^5	0.5927×10^5	0.5927×10^5	
(DE)	D/E	2.0	1.6920×10^5	1.6920×10^5	1.6920×10^5	
(ABC)	A/BC	15.1	0.3953×10^5	1.3446×10^5	1.3446×10^5	
	AB/C	8.5	1.1980×10^5	1.4593×10^5		
(BCD)	B/CD	6.3	1.1260×10^5	1.7187×10^5		
	BC/D	5.1	0.7675×10^5	1.7168×10^5	1.7168×10^5	
(CDE)	C/DE	4.5	0.7817×10^5	2.4737×10^5		
	CD/E	3.3	1.8530×10^5	2.4457×10^5	2.4457×10^5	
(ABCD)	A/BCD	15.1	0.4707×10^5	2.1875×10^5	2.1875×10^5	
	AB/CD	8.5	1.4050×10^5	2.2590×10^5		
	ABC/D	6.3	0.9445×10^5	2.2891×10^5		
(BCDE)	B/CDE	6.3	1.3340×10^5	3.7797×10^5		
	BC/DE	5.1	0.9443×10^5	3.5856×10^5	3.5856×10^5	
	BCD/E	4.1	2.4180×10^5	4.1358×10^5		
(ABCDE)	A/BCDE	15.1	0.5715×10^5	4.1571×10^5	4.1571×10^5	
	AB/CDE	8.5	1.6500×10^5	4.3570×10^5		
	ABC/DE	6.3	1.1490×10^5	4.1856×10^5		
	ABCD/E	4.9	2.6600×10^5	4.8475×10^5		

Table 4. Economical Matches and Costs of Participating Separation Subproblem when the Utility Cost Function Given in Equation (5) is Used

Energy match	First separation subproblem	Optimal cost without match, \$/yr	Optimal pressure without match, atm.	Optimal cost with match, \$/yr.	Optimal pressure with match, atm.	Second separation subproblem	Cost without match, \$/yr.	Optimal pressure without match, atm.	Cost with match, \$/yr.	Optimal pressure with match, atm.	Match profit \$/yr.
C (CD): B (AB)	C/D	0.5487×10^5	7.79	0.6291×10^5	15.72	A/B	0.2141×10^5	15.16	0.1171×10^5	15.05	0.0166×10^5
D (DE): C (BC)	D/E	1.5730×10^5	2.81	1.9030×10^5	6.72	B/C	0.8427×10^5	9.16	0.3721×10^5	9.10	0.1406×10^5
D (DE): CDE (BCDE)	D/E	1.5730×10^5	2.81	2.1910×10^5	10.31	B/CDE	1.1000×10^5	8.78	0.4239×10^5	8.97	0.0581×10^5
BC (BCD): BCD (ABCD)	BC/D	0.6887×10^5	8.36	0.8343×10^5	25.96	A/BCD	0.3598×10^5	15.16	0.1630×10^5	15.05	0.0513×10^5
BCD (BCDE): C (BC)	BCD/E	1.9620×10^5	5.76	2.2560×10^5	12.39	B/C	0.8427×10^5	9.16	0.3709×10^5	9.11	0.1778×10^5

Table 5. Costs of Separation Subproblems That do not Participate in Economical Matches

Separation subproblem	Cost, \$/yr.	Optimal pressure, atm.
A/BC	0.3110×10^5	15.16
AB/C	0.8661×10^5	8.36
B/CD	0.9602×10^5	8.93
C/DE	0.7117×10^5	6.97
CD/E	1.7870×10^5	4.77
AB/CD	0.9857×10^5	8.36
ABC/D	0.7559×10^5	9.92
BC/DE	0.8328×10^5	7.99
A/BCDE	0.4238×10^5	15.16
AB/CDE	1.1280×10^5	8.36
ABC/DE	0.9045×10^5	9.54
ABCD/E	2.1050×10^5	6.71

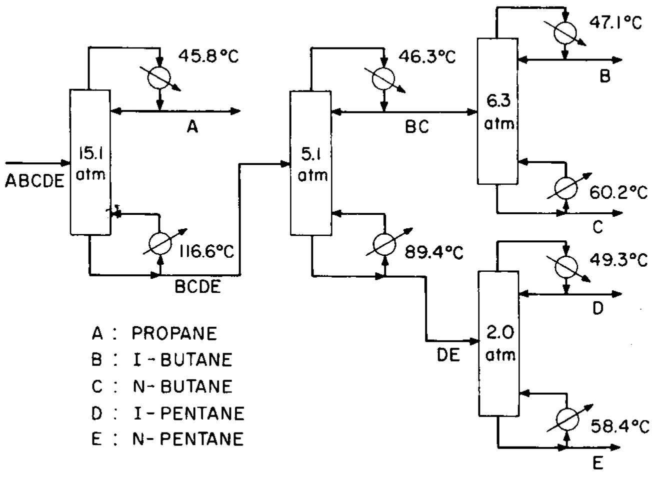


Fig. 7. The optimal separation sequence for a five-component separation problem involving light paraffins.

This example was used by Rathore et al. (1974) to illustrate a strategy for the synthesis of isobaric distillation systems. Table 1 summarizes the design equations and the cost basis for optimization. These equations are the same as those used in the previous paper.

This problem has 20 separation subproblems and there are 126 different matches (sets of two interacting subproblems). Figure 4 lists 20 of these matches. All the 126 matches were evaluated using the calculation procedure shown in Figure 5. Approximately 26 min. of CPU time were required to evaluate all these matches on a PDP-10 computer. Table 2 presents some typical costs associated with the first ten matches listed in Figure 4. For the utility costs given in Equation (1) none of the 126 possible energy matches is economical for this problem. This result is due to the fact that as the pressure in a column is changed to create an energy match, for example, with its reboiler the other end of the column (condenser) is requiring a more expensive utility. For sharply increasing utility costs with deviations from ambient temperatures the optimal pressure for solving a separation subproblem almost always corresponds to low cost utilities, that is, cooling water or low pressure steam. However, when an energy match is allowed the pressure is constrained to be in a limited range. For this problem the optimal pressures corresponding to separation subproblems when an energy match is allowed are significantly different from the optimal pressure when no energy match is allowed (see Table 2). This results in the use of more expensive utilities to meet the heating or cooling requirements at the other end of the column. There are no economical three-column matches for this problem. Thus the reduction in the amount of utilities by the energy match is more than offset by the increased cost of utilities. For matches with utilities only the costs given in Table 3 are used to synthesize the optimal separation sequence shown in Figure 7. This system costs 24% less than the previously reported separation sequence for the same problem under the isobaric assumption (Rathore et al., 1974).

The cost data used to formulate Equation (1) are particularly severe with respect to the change in utility costs with deviation from ambient conditions. For many in-plant situations the cost equation given below is more realistic.

$$C_U = \begin{cases} 4.36 - 0.131T \text{ for cooling in the range} \\ \qquad -50°\text{C} \leq T \leq 32°\text{C} \\ 0.2 \qquad T > 32°\text{C} \\ -0.12 + 0.01T \text{ for heating in the range} \\ \qquad 32°\text{C} \leq T \leq 300°\text{C} \\ 0.2 \qquad T < 32°\text{C} \end{cases} \tag{5}$$

The example problem was solved using Equation (5) for the utility costs and the 5 energy matches given in Table 4 proved economical.

Table 5 lists costs of separation subproblems that do not participate in the economical matches.

The separation subproblems A/B, B/C, C/D, D/E, BC/D, A/BCD, B/CDE, and BCD/E have more than one cost figure associated with them (a consequence of economical matches). The cost figures for these separation subproblems are first ranked. The minimum cost separation sequence is synthesized by dynamic programming using the minimum cost for each separation subproblem. For this case, it is found that the minimum cost separation sequence is infeasible.

For example, the separation D/E has the minimum cost for the case where no energy match is considered. Hence the no match cost, 1.5730×10^5 \$/year (from Table 4), is used in the dynamic programming tableau. The separation subproblem B/C has a minimum cost when an energy match is made with stream D from separation D/E. But this energy match was not considered for the cost used with the D/E separation. Hence the first minimum cost

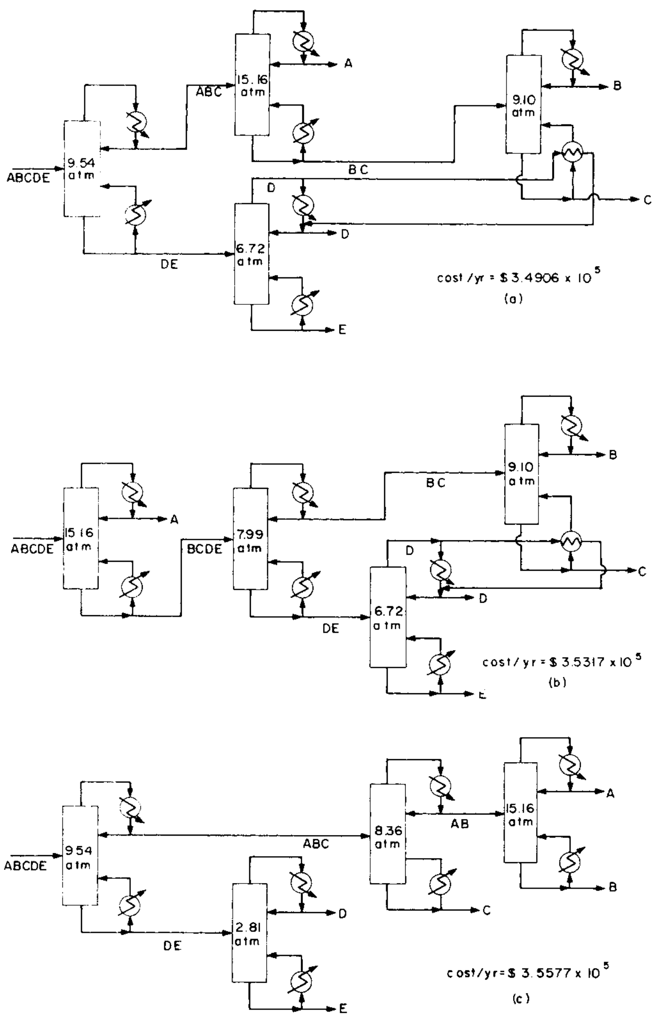


Fig. 8. The three best separation sequences for the example when the utility cost function given in Equation (5) is used.

sequence developed by the dynamic programming scheme is not correct. Therefore, it is necessary to enumerate all separation sequences that can include the energy matches and the remaining separation sequences (if any) that do not include the economical energy matches.

For this problem one finds that at least one out of the five economical matches listed in Table 4 can occur in 7 out of 14 possible separation sequences for the 5-component mixture. Therefore 14 enumerations lead to a determination of the optimal distillation system with energy integration. Figure 8 shows the three best solutions for the example problem.

A few observations about these solutions are in order. The optimal system contains an energy match between the condenser of the D/E column and the reboiler of the B/C column. The difference in cost between the optimal structure and the third best system (which does not include integration) is 2%. For this example, this small decrease in cost would probably not justify the added complexity and potential control problems associated with energy integration.

For other feed streams, in different economic environments this strategy could be used to measure the potential benefits of energy integration.

ACKNOWLEDGMENTS

Dr. J. J. Siirola made several valuable suggestions during the course of this work. Ram Rathore received financial support from Tufts University.

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 = temperature of utility, °C
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
α_{i-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

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APPENDIX A. COMBINATORIAL ASPECTS OF SEPARATION SEQUENCING

Enumeration of Subgroups

Let us consider an ordered list 1 2 3 4 5 . . . . N, in which each digit represents a chemical species corresponding to a mixture containing N components. By sequential splitting of this list one can obtain:

1 N-component subgroup (no splitting);
2 $(N-1)$-component subgroups;
3 $(N-2)$-component subgroups;
.
.
.
$(N+1-j)$ j-component subgroups:
.
.
.
$(N-1)$ 2-component subgroups;
N 1-component subgroups.

Therefore, the total number of different subgroups that may be obtained by splitting the original list equals

$$\sum_{j=1}^{N} j = N(N+1)/2$$

In separation sequencing problem these subgroups define the compositions of all the feasible streams that may occur in any separation sequence. The collection of these feasible streams is called the *feasible stream set.*

Enumeration of Separation Subproblems

Any list containing j digits can be split in $j - 1$ different ways. Therefore,

the number of separation subproblems associated with subgroups containing j digits $= (j-1) \times (N+1-j)$.

[Notice $(N+1-j)$ j-component subgroups can be obtained from an N-digit list.]

Hence the total number of separation subproblems equals

$$\sum_{j=1}^{N} (j-1)(N+1-j)$$

$$= N \sum_{j=1}^{N} (j-1) - \sum_{j=1}^{N} (j-1)^2$$

$$= N \sum_{j=1}^{N-1} j - \sum_{j=1}^{N-1} j^2$$

$$= (N-1)(N)(N+1)/6$$

Enumeration of Separation Sequences

For continuous separation of all components of an N-component mixture it is necessary to use $N - 1$ separators. Each of these separators has two output streams. Thus, there are $[2(N-1)]$ output streams in a separation sequence. Out of these $[2(N-1)]$ output streams, $(N-2)$ streams interconnect the separators.

$$\text{Number of possible ways for obtaining such connections} = \frac{[2(N-1)]!}{(2N-2-N+2)!\,(N-2)!} = \frac{[2(N-1)]!}{N!\,(N-2)!}$$

This number also includes the cases when an output stream from a particular separator is connected to the same separator. Such connections are not allowed in real separation sequences. The number of all possible connections that do not include such connections can be obtained simply by dividing the above expression by $(N-1)$. Each of these connections corresponds then to a separation sequence. Therefore,

$$\text{Numer of separation sequences} = \frac{[2(N-1)]!}{N!\,(N-2)!\,(N-1)} = \frac{[2(N-1)]!}{N!\,(N-1)!}$$

Manuscript received January 10, 1974; revision received May 10 and accepted May 20, 1974.

Mechanisms of Secondary Nucleation in Agitated Crystallizers

Experiments were designed to identify the mechanism of the secondary nucleation of ice in a vigorously agitated crystallizer. It has been shown that the nucleation rate is proportional to the product of two factors, one characterizing crystal morphology and the other the rate of removal of potential nuclei from the surfaces of the existing crystals. Consequently, the nucleation rate attributable to different mechanisms is additive and the rate is proportional to the number of collisions per crystal. The contribution to the secondary nucleation of ice, by collisions of crystals with the impeller, baffles, and other crystals in an agitated crystallizer have been identified by measurements in a batch crystallizer in which each of the different collision mechanisms could be suppressed.

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SCOPE

Crystal size distribution and the production rate per unit volume are parameters of major importance in the design of industrial crystallizers. However, although the crystal size distribution in continuous crystallizers is controlled by the rates of secondary nucleation and growth of the crystals, little is known about the mechanisms and rates of secondary nucleation.

Previous studies of the secondary nucleation of ice have correlated the nucleation rate N with the nth moments of the crystal size distribution:

$$\dot{N} = a_n \, \mu_n$$

where the moment μ_n is proportional to crystal concentration for $n = 0$, to perimeter for $n = 1$, area for $n = 2$, etc.

The value of n has not been well established and the factors controlling the value of the proportionally constant μ_n have not been adequately understood. Furthermore, the

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