n = order of dynamic system
q_i = denominator coefficient of transfer function
s = Laplace domain variable
τ_d = time delay

LITERATURE CITED

Bosley, M. J., and F. P. Lees, "A Survey of Simple Transfer Function Derivations from High-Order State-Variable Models," *Automatica*, 8, 765 (1972).

Chemical Rubber Publishing Company, *Handbook of Chemistry and Physics*, 42 ed. (1961).

Chen, C. F., and L. S. Shieh, "A Novel Approach to Linear Model Simplification," *Proc. JACC*, 454 (1968).

Edgar, T. F., "The Sensitivity of Time Domain Response to Frequency Domain Errors," *Int. J. Syst. Sci.*, 7, 691 (1976).

Friedly, J. C., *Dynamic Behavior of Processes*, Prentice-Hall, Englewood Cliffs, N.J. (1972).

Manuscript received March 4, and accepted March 16, 1977.

A Combined Heuristic and Evolutionary Strategy for Synthesis of Simple Separation Sequences

J. D. SEADER
Department of Chemical Engineering
University of Utah
Salt Lake City, Utah 84112

and

A. W. WESTERBERG
Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

This note presents a useful technique for merging two previously proposed strategies for synthesizing systems of simple separation sequences. The strategies are the use of heuristics (Lockhart, 1947; Rod and Marek, 1959; Nishimura and Hiraizumi, 1971; Thompson and King, 1972; Hendry and Hughes, 1972; Rudd, Powers, and Siirola, 1973; and King, 1971) and evolutionary methods. Two examples illustrate the apparent power of the approach over the use of the individual strategies alone.

Stephanopoulos and Westerberg (1976) outlined the view of evolutionary synthesis adopted here, that is, that four basic ideas are required: an initial flow sheet, rules to make systematic and small changes to the flow sheet creating what is termed a neighboring flow sheet, an effective strategy to apply these rules, and a means to compare the original flow sheet to any of its neighbors. At least fourteen heuristics have previously been proposed for synthesizing multicolumn separation sequences (Lockhart, 1976). In this note, we examine the use of the following set of six heuristics to aid in the first and third ideas above.

Heuristic 1: forbidden splits. In order to reduce the magnitude of the combinatorial problem, conduct a preliminary screening of separation methods based on an examination of various factors. While not rigorous, the graphical screening method of Souders (1964) is simple and convenient. It begins with an examination of the technical feasibility of ordinary distillation which, in principle, is applicable over the entire region of coexisting vapor and liquid phases. This region extends from the crystallization temperature to the convergence pressure, provided that species are thermally stable at the conditions employed. First, the column operating pressure is determined. If refrigeration is required for the overhead condenser, alternatives to ordinary distillation, such as absorption and reboiled absorption, might be considered. At the other extreme, if vacuum operation of ordinary distillation is indicated, liquid-liquid extraction with various solvents might be considered. In the wide intermediate region, ordinary distillation is generally not feasible economically when the relative volatility between key components is less than approximately 1.05. Even when this separation index is exceeded, extractive distillation and liquid-liquid extraction may be attractive alternatives, provided that relative separation indexes for these methods exceed those indicated by the curves plotted in Figure 3 of the Souders article or if an order of volatility (or other separation index) for these alternative methods is achieved that permits production of multicomponent products without blending. To develop these curves, Souders assumed a solvent concentration of 67 mole % and a liquid rate four times that used in ordinary distillation. In general, extractive distillation need not be considered when the relative volatility for ordinary distillation is greater than about two.

Heuristic 2: For each method, develop an ordered list of components according to volatility (or other separation index). Then, for each adjacent pair of components i and j, estimate their adjacent relative volatility $\alpha_{ij} = K_i/K_j > 1$. When the adjacent relative volatilities of the ordered components in the process feed vary widely, sequence the splits in the order of decreasing adjacent relative volatility. This heuristic is related to the heuristic, "separations where the relative volatility of the key components is close to unity should be performed in the absence of non-key components," as stated by King (1971).

Heuristic 3: Sequence the splits to remove components in the order of decreasing molar percentage in the process feed when that percentage varies widely but the rela-

TABLE 1. HENDRY-HUGHES PROBLEM SPECIFICATION

1) Species

A: Propane	C: *n*-butane	E: Cis-butene-2
B: Butene-1	D: Trans-butene-2	F: *n*-pentane

2) Feed specification
Component flows (kg mole/hr): 4.55, 45.5, 155.0, 48.2, 36.8, 18.2
Temperature, pressure: $T = 37.8°C$, $P = 10.3$ bars

3) Products desired (with high % recoveries):
a) A; b) BDE (butenes); c) *C*; d) *F*

4) Separation methods
I. Ordinary distillation
II. Extractive distillation with furfural

5) Component orderings
Method I: ABCDEF (A most volatile)
Method II: ACBDEF

6) Important adjacent relative volatilities (at 66°C)

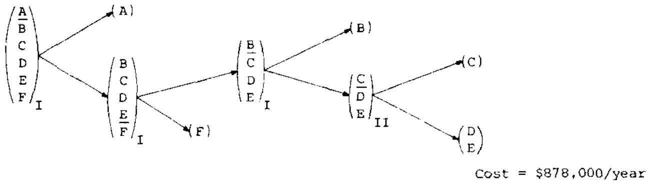
Method I:	$\alpha_{AB} \approx 2.45$,	$\alpha_{BC} \approx 1.18$,	$\alpha_{CD} \approx 1.03$,
	$\alpha_{EF} \approx 2.50$,	$\alpha_{AC} \approx 2.89$	
Method II:	$\alpha_{CB} \approx 1.17$,	$\alpha_{CD} \approx 1.70$	

tive volatility does not vary widely (Lockhart, 1947).

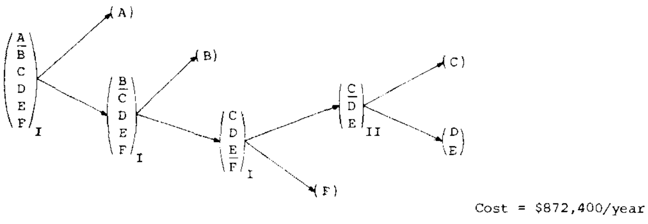
Heuristic 4: When neither relative volatility nor molar percentage in the feed varies widely, remove the components one by one as overhead products. The resulting structure is the so-called direct sequence, which is widely applied in practice. In this structure, when ordinary distillation is the separation method, pressure tends to be highest in the first separator and is reduced in each subsequent separator (Rudd, Powers, and Siirola, 1973).

Heuristic 5. When a mass separating agent is used, remove it in the separator immediately following the one into which it is introduced (Hendry and Hughes, 1972).

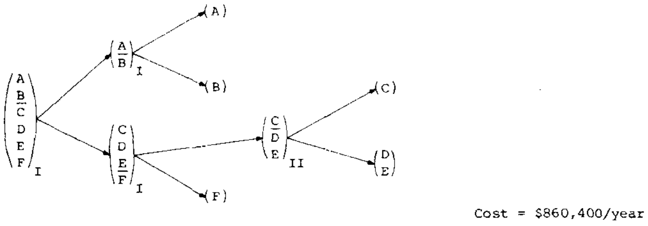
Heuristic 6. When multicomponent products are specified, favor sequences that produce those products directly or with a minimum of blending unless adjacent relative volatilities are appreciably lower than for a sequence that requires additional separators and blending (Thompson and King, 1972).



(a) Initial Sequence



(b) Result of First Interchange



(c) Result of Second and Final Interchange

Fig. 1. Development of flow sheet for example 1.

For the second idea above, the evolutionary rules to generate neighboring flow sheets are those of Stephanopoulos and Westerberg (1976): interchange the relative positions of two adjacent subproblems, and for a given separation subproblem using separation method α, substitute separation method β.

Finally, the technique for executing the four basic ideas stated above are contained in the following four steps:

1. Use the above six heuristics in the order stated to generate an initial flow sheet. Only if an heuristic does not apply should one following it be used. (Note, this ordering of the six heuristics is itself an heuristic.)

2. Consider the current flow sheet.
   A. Generate each possible neighbor.
   B. Keep the neighbor as a candidate only if
      i. it could have been generated by an heuristic if the heuristics ranked above it were relaxed somewhat in their meaning of the words "does not vary widely."
      ii. it is almost an equivalent choice using the same heuristic.
   C. List each neighbor retained in an order reflecting the heuristic responsible for its retention. For example, if we retained a flow sheet resulting from heuristic 2, list that flow sheet before all flow sheets resulting from heuristic 3 and after those resulting from heuristic 1.

3. Evaluate in order the neighboring flow sheets generated in step 2 until:
   A. A better flow sheet is found.
   B. No better flow sheet is found. If a better flow sheet is found, repeat from step 2; otherwise, go to step 4.

4. Before accepting the apparent best flow sheet, examine all remaining neighbors that might be somewhat less plausible, but possible, and which were ruled out in step 2B.

We now apply the combined heuristic and evolutionary strategy to two examples.

Example 1. The first example is the problem of Hendry and Hughes (1972) as specified in Table 1. For this example, we find that all ordinary distillation columns can be operated above atmospheric pressure and with cooling water condensers. Therefore, by heuristic 1, we consider only distillation for splits $(A/B\cdots)$, $(\cdot B/C\cdot\cdot)$,

TABLE 2. PROBLEM SPECIFICATION FOR EXAMPLE 2

1) Species

A: Ethane	C: Propane	E: *n*-butane
B: Propylene	D: 1-butene	F: *n*-pentane

2) Feed specification:
   Component flows (kg mole/hr): 9.1, 6.8, 9.1, 6.8, 6.8, 6.8,
   Temperature, pressure: $T = 37.8°C, P = 1.0$ bar

3) Products desired (with high % recoveries):
   a) *A*; b) *B*; c) *C*; d) *D*; e) *E*; f) *F*

4) Separation method
   Ordinary distillation only

5) Component ordering
   ABCDEF (A most volatile)

6) Important adjacent relative volatilities
   $\alpha_{AB} = 3.5$ $\alpha_{BC} = 1.20$ $\alpha_{CD} = 2.7$
   $\alpha_{DE} = 1.21$ $\alpha_{EF} = 3.0$

$(\cdots E/F)$, $(A/C\cdots)$ and forbid distillation for split $(\cdots C/D\cdot\cdot)$.

Splits $(A/B\cdots)_I$ and $(\cdots E/F)_I$ have the largest values of adjacent relative volatility. Because these values are almost identical, either split can be placed first in the sequence. We choose the former, noting that the small amounts of *A* and *F* in the feed render this decision of minor importance. Following removal of *A* and *F* by ordinary distillation, heuristic 5 can be applied by conducting the extractive distillation separation $(C/BDE)_{II}$ followed by the recovery of the MSA. The resulting sequence produces the multicomponent product *BDE* directly; however, the adjacent relative volatility of $(C/BD)_{II}$ is only 1.17. Alternatively, the split $(C/DE)_{II}$, with a much higher adjacent relative volatility of 1.70, preceded by the split $(B/CDE)_I$ to remove *B* and followed by removal of the *MSA* can be employed, with the product *BDE* formed by blending of *B* with *DE*. Because of the very strong effect of relative volatility on cost, this latter alternative, shown in Figure 1*a*, may be preferable despite the need for one additional ordinary distillation separation with a low relative volatility. The cost for this latter sequence is $878 000/yr.

The following exchanges are now possible by evolutionary rule 1: (a) $(A/B\cdots)_I$ with $(\cdots E/F)_I$, (b) $(\cdots E/F)_I$ with $(B/C\cdots)_I$, and (c) $(C/D\cdots)_{II}$ with $(B/C\cdots)_I$. Interchange (a) is not likely to cause any appreciable change in sequence cost when heuristics 1 and 2 are considered. The adjacent relative volatilities of the key components for the two splits are almost identical, and neither of the two compounds removed (*A* and *F*) are present in appreciable amounts. Therefore, we do not make this interchange.

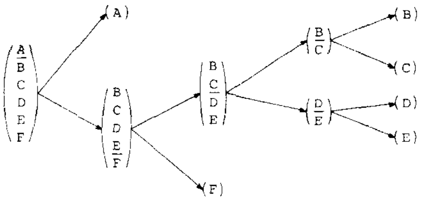
Interchange (b) may have merit. Table 1 indicates that the process feed contains a larger amount of *B* than *F*. According to heuristic 2, components present in larger quantities should be removed early in the sequence. However, heuristic 2 was ignored, and heuristic 1 was applied in developing the original sequence. By making this interchange, *B* can be removed earlier in the sequence.

Interchange (c) will result in the sequence that produces *BDE* directly. However, this sequence is likely to be more costly because of the small relative volatility for the extractive distillation separation $(C/BDE)_{II}$. Therefore, we make the second interchange only, with the result shown in Figure 1*b* at a lower cost of $872 400/yr.

If we now apply evolutionary rule 1 to this new sequence, the possible new interchanges are: (d) $(A/B\cdots)_I$ with $(\cdot\cdot B/C\cdot\cdot)_I$ and (e) $(\cdots E/F)_I$ with $(C/D\cdots)_{II}$. Interchange (*d*) opposes heuristic 1 and supports heuristic 2. The latter heuristic may dominate here because of the very small amount of *A* but larger amount of *B* present in the process feed. Interchange (e) would appear to offer less promise than interchange (d) because of the difficulty of the $(C/D\cdots)_{II}$ split. The result of making interchange (d) is shown in Figure 1*c* at a lower cost of $860 400/yr. No further interchanges are possible; the final sequence happens to be the optimum as found by Hendry and Hughes (1972).

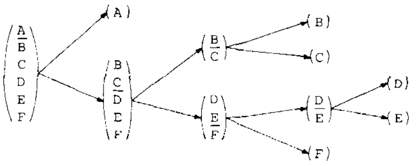
Hendry and Hughes prohibited the $(A/C\cdots)_{II}$ and $(\cdots E/F)_{II}$ splits and generated 64 *unique* separation subproblems and 227 separation system sequences. We have examined, to the extent of performing a cost analysis, only three separation sequences involving but eight separation subproblems.

Example 2. Consider the problem presented by Thompson



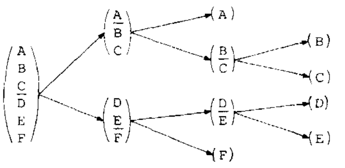
Cost = $1,234,000/year

(a) Initial Sequence



Cost = $1,213,000/year

(b) Result of First Interchange



Cost = $1,153,000/year

(c) Final Flowsheet

Fig. 2. Development of flow sheet for example 2.

and King (1972) as modified by Rodrigo and Seader (1975) and specified in Table 2.

With no forbidden splits, step 1 of the strategy generates the flow sheet in Figure 2*a*, where heuristic 2 has been applied throughout; thus, the large value of $\alpha_{AB} = 3.5$ dictates that split $(A/BCDEF)$ be made first in the sequence. Then, $\alpha_{EF} = 3.0$, the next largest adjacent relative volatility, dictates that split $(BCDE/F)$ be made next. Similarly, the last necessary decision is to perform split (BC/DE) followed by splits (B/C) and (D/E). The resulting initial flow sheet has a cost of \$1.234 × 10^6/yr.

We note that α_{AB}, α_{CD}, and α_{EF} are reasonably close in magnitude, which suggests that we consider interchanging the $(\cdot\cdot C/D \cdot\cdot)$ and $(\cdots E/F)$ subproblems giving a slightly decreased cost of \$1.213 × 10^6/yr, and consider interchanging the $(A/B\cdots)$ and $(\cdots E/F)$ subproblems, which, however, leads to a slightly increased cost of \$1.219 × 10^6/yr. The improved sequence is shown in Figure 2*b*.

A further improvement can be made to the sequence in Figure 2*b* by interchanging splits $(A/B\cdots)$ and $(\cdot C/D\cdot\cdot)$, which have reasonably close adjacent relative volatilities. This leads to the sequence shown in Figure 2*c* which has a decreased cost of \$1.153 × 10^6/yr. No further interchanges are suggested by the heuristics.

Unfortunately, the final sequence shown in Figure 2*c* is not the optimal solution, which has a cost of \$1.084 × 10^6/yr and is achieved by a further interchange between subproblems $(\cdot E/F)$ and (D/E). The failure to produce the optimal solution is due to the small, but important, effect of *n*-pentane on the relative volatility for 1-butene/*n*-butane. In Table 2, α_{DE} is taken as 1.21. However, as discussed by Gomez and Seader (1976), $\alpha_{DE} = 1.197$ when only D and E are present, but $\alpha_{DE} = 1.226$ in the presence of *n*-pentane. The result is that the cost of split (D/EF) is 15% less than the cost of split (D/E), and the total sequence cost is reduced by making split (D/EF) before split $(\cdot E/F)$. Nevertheless, we discovered a near optimal flow sheet by examining only four of forty-two flow sheets and eleven of thirty-five distinctly different separators.

Not included in the strategy discussed above is the consideration of energy integration. Especially when the lowest cost sequences are close in cost, energy integration may be the deciding factor among various alternative sequences. A method for synthesizing optimal distillation sequences, where condensers and reboilers are integrated, has been presented by Rathore, Van Wormer, and Powers (1974).

NOTATION

K_i = vapor-liquid phase equilibrium ratio for component i
P = pressure
T = temperature
α_{ij} = relative volatility of component i relative to component j

LITERATURE CITED

Gomez, A., and J. D. Seader, "Separation Sequence Synthesis by a Predictor Based Ordered Search," *AIChE J.*, **22**, 970 (1976).

Hendry, J. E., and R. R. Hughes, "Generating Separation Process Flowsheets," *Chem. Eng. Progr.*, **68**, No. 6, 71 (1972).

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

Lockhart, F. J., "Multi-Column Distillation of Natural Gasoline," *Petrol. Refiner*, **26**, No. 8, 14 (1947).

Lockhart, F. J., Private Communication (1976).

Nishimura, H., and Y. Hiraizumi, "Optimal System Pattern for Multicomponent Distillation Systems," *Intern. Chem. Eng.*, **11**, 188 (1971).

Rathore, R. N. S., K. A. Van Wormer, and G. J. Powers, "Synthesis of Distillation Systems with Energy Integration," *AIChE J.*, **20**, 940 (1974).

Rod, V., and J. Marek, "Separation Sequences in Multicomponent Rectification," *Coll. Czech. Chem. Comm.*, **24**, 3240 (1959).

Rodrigo, F. R., and J. D. Seader, "Synthesis of Separation Sequences by Ordered Branch Search," *AIChE J.*, **21**, 885 (1975).

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

Souders, M. "The Countercurrent Separation Process," *Chem. Eng. Progr.*, **60**, No. 2, 75 (1964).

Stephanopoulos, G., and A. W. Westerberg, "Studies in Process Synthesis—II: Evolutionary Synthesis of Optimal Process Flowsheets," *Chem. Eng. Sci.*, **31**, 195 (1976).

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

Manuscript received March 25, 1977; revision received August 1, and accepted August 8, 1977.

Nucleate Boiling in Thin Liquid Films

RUSSELL MESLER and GREGORY MAILEN

Department of Chemical and Petroleum Engineering
The University of Kansas
Lawrence, Kansas 66045

Nucleate boiling in thin liquid films requires low temperature differences for the same rate of heat transfer than is usual for nucleate boiling; this is supported by the research of Fletcher et al. (1974), Rychkov and Pospelov (1959), Parizhskiy et al. (1972), and Mesler (1976). Detergents in the film reduce the temperature differences even more (Nishikawa et al., 1967). These facts are rather surprising since they were not predicted. One