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Synthesis of Separation Sequences by Ordered Branch Search

An efficient and algorithmic procedure is developed for the synthesis of multicomponent separation sequences. The procedure involves list processing of the possible separation subproblems followed by an ordered branch search to find the optimal sequence with respect to system structure. The technique is conveniently represented by an and/or directed graph. The distribution of sequence costs for a separation problem is considered. When a wide distribution exists, only a minimum of separators need be analyzed to find the optimal sequence. Even when a narrow distribution of sequence costs exists, not all sequences must be developed. The importance of near optimal sequences is examined, and the search procedure is extended to find those sequences whose costs are within a specified factor of the cost of the optimal sequence.

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SCOPE

Chemical processes frequently involve separation of multicomponent mixtures into multiple products by a sequence of separators, each of which produces generally two, but sometimes more than two, product or intermediate streams. The products may consist of relatively pure species, or they may be multicomponent products that contain two or more major species. In general, the separations are effected by thermal, mechanical, or chemical means. The task of synthesizing the optimal separation sequence often represents a formidable combinatorial problem.

As reviewed by Ichikawa (1972) and Hendry et al. (1973), early research on the synthesis of separation sequences (primarily sequences involving only ordinary distillation) was directed towards the identification of useful heuristics. The application of heuristics permits the design engineer to quickly synthesize reasonable distillation sequences without performing design calculations. More recently, emphasis in synthesis research has shifted to the development of computerized search methods that require design calculations but allow consideration of a variety of separation techniques.

Thompson and King (1972b) used heuristic and algorithmic programming to search for separation sequences. Although their method does not guarantee an optimal

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solution, apparently it can produce near optimal sequences with very minimal computing requirements. Problems involving large numbers of product streams and candidate separator types are readily handled. Design calculations are minimized because the heuristics used greatly reduce the search space. Occasionally the procedure becomes unstable as it cycles between two sequences.

Hendry and Hughes (1972) combined list processing with dynamic programming to determine the optimal sequence. Although their method does not require that all sequences be examined, all separators must be designed, except for those that may be expressly forbidden. Thus, for large problems, computing requirements may become excessive. In addition, the usual restrictions on dynamic programming apply. For example, when separators involving mass separating agents are considered, the agent must be removed in the following separator to avoid a cyclic system. Rathore et al. (1974a,b) extended the method of Hendry and Hughes to include energy integration in distillation sequences.

The most recent strategy is that of Stephanopoulos (1974) and Westerberg. They used list processing with two-level decomposition in conjunction with a branch and bound strategy to find the optimal and near optimal sequences without having to search the entire space of separators. Compared to the method of Hendry and Hughes, the method of Stephanopoulos and Westerberg is more general, and computational requirements are somewhat less. However, the method is much more complex than previous methods, and if applied to large problems of the type considered by Thompson and King, computing requirements become excessive.

In this paper, a flexible, efficient, and simple search procedure is developed for determining optimal and near optimal separation sequences. List processing is used in conjunction with the branch-search procedure of Greenberg and Hegerich (1970). The search is ordered heuristically, and the search space is reduced by using a changing upper bound on the annual cost of the sequence. As with the method of Stephanopoulos and Westerberg, all sequences need not be examined, not all separators need be designed, and a mass-separating agent need not be recovered in the separator following the one to which it is added. As with the other three synthesis methods, certain separations may be forbidden when they are known to be infeasible or impractical. Several examples are presented to illustrate the application of the procedure.

CONCLUSIONS AND SIGNIFICANCE

The ordered branch-search procedure for finding optimal multicomponent separation sequences is found to be efficient with respect to computational time and memory requirements. By starting with the process feed and using backtracking as well as branching in the order of the cheapest first heuristic of Thompson and King (1972b), as applied at each junction in the sequence, the optimal sequence with respect to structure is rapidly developed. The procedure is readily extended with little additional computational requirements to obtain the near optimal sequences having costs within a specified factor of the cost of the optimal sequence.

The distribution of sequence costs is shown to be relatively narrow when only ordinary distillation is used. In this case, a relatively high percentage of all possible sequences may be near optimal, resulting in a search over most of the space of possible separations. When two or more different types of separators are involved, the distribution of sequence costs is most likely to be relatively wide, as shown in two examples here. Then, the optimal as well as near optimal sequence structures are found by searching only a fraction of the space of separation.

Two methods are successfully employed to reduce the search space. Multiplicate separators are identified and analyzed no more than once. They are conveniently indicated on an and/or directed graph of all possible sequence paths. Recognition of multiplicate separators is particularly important in problems involving large numbers of products. By specifying certain forbidden separations, other subsequent separations are frequently eliminated from consideration, resulting in a further reduction in search space that is often substantial. It is particularly important to forbid obviously impractical separations.

No attempt is made to optimize sequences with respect to the multiplicity of operating conditions because of the relatively small sensitivity of sequence cost to operating conditions within reasonable ranges of values. Even the effect of the flow rate of the mass separating agent on sequence cost is shown to be quite small in one example.

The search procedure presented here can be used to develop rapidly the several best separation sequence structures even for industrial problems of considerable magnitude. The structures can then be subjected to more rigorous analysis and optimization from both design and operational viewpoints in order to make a final selection.

PROBLEM FORMULATION

The general problem of synthesis of separation sequences may be stated in terms of process specifications. For a given process feed of known conditions (that is, composition, flow rate, temperature, and pressure); for specified products, product conditions, and overall recoveries of each species; and for selected types of separators to be considered (including designation of any required mass-separating agents), find the optimal separation sequence as well as the near optimal sequences that are within a specified percentage of the cost of the optimal sequence. The cost is a combination of capital and operating expenses.

As an example of a separation problem, consider the following process specifications for a case (Example 1) based on a more complex example presented by Thompson and King (1972a). The feed to a separation process consists of 56.7 kg mole/hr. each of *n*-hexane (*A*), benzene (*B*), and cyclohexane (*C*) at a temperature of 37.8°C and a pressure of 101,353 N/m^2 (14.7 lb/sq.in.abs). The process is to produce each species in a relatively pure form. Ordinary distillation may be considered as one possible type of separator (*I*). However, binary vapor-liquid equilibrium data of Richards and Hargreaves (1944) indicate that it may be impossible to separate benzene from cyclohexane by ordinary distillation. Therefore, a second type of separator (*II*) is to be considered, namely extractive distillation with phenol (*D*) as the mass separating agent. As shown by Dunn et al. (1945), the presence of relatively polar phenol

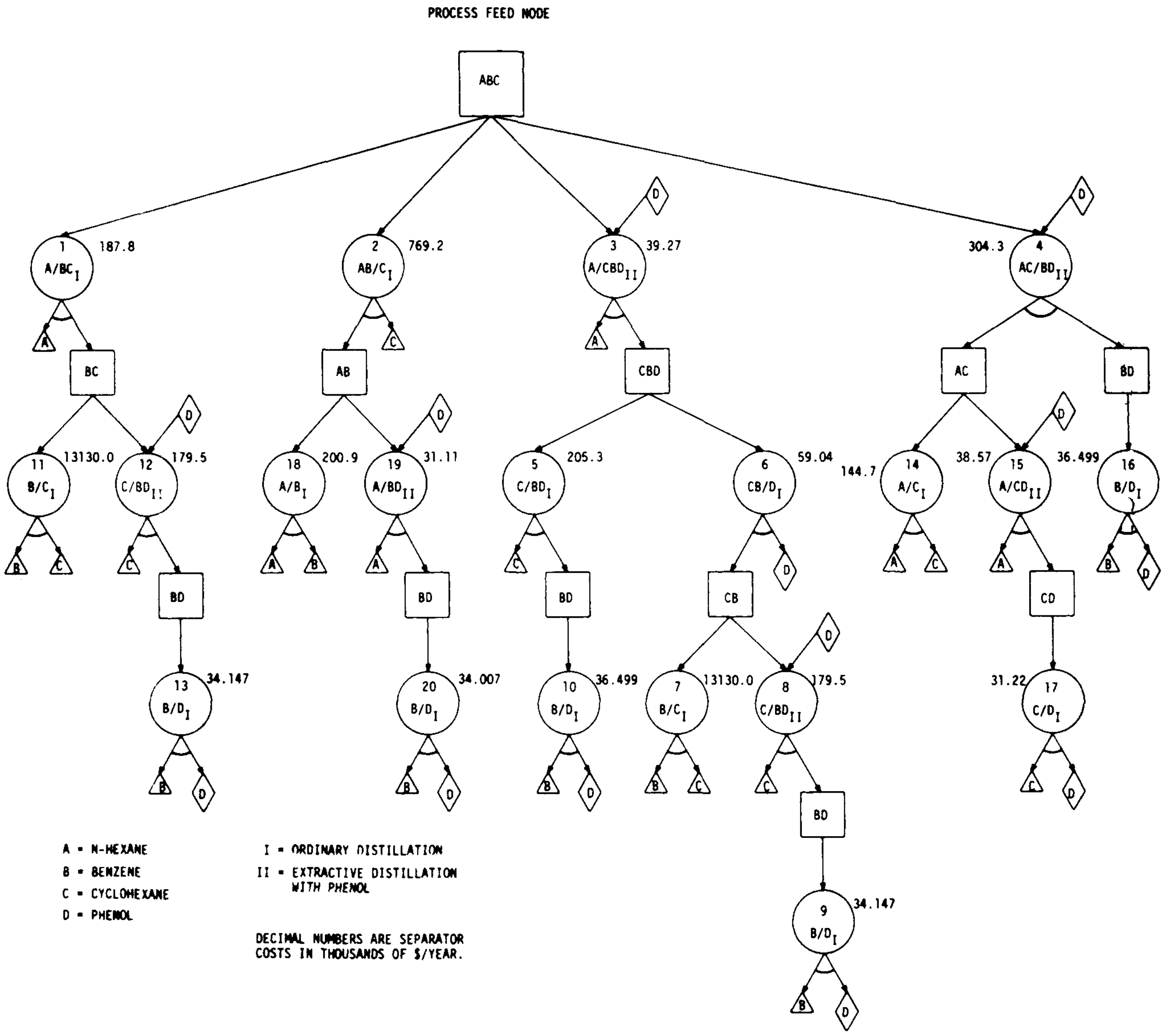


Fig. 1. Search space for example 1.

causes a large increase in the liquid phase activity coefficient of cyclohexane relative to benzene.

With the types of separators chosen, it is convenient to use list processing techniques, as shown by Hendry and Hughes (1972), to determine all possible separation subproblems. The modification of Stephanopoulos (1974) and Westerberg is used here, wherein mass separating agents are included in the list processing because the agents are not necessarily recovered in the separator following the one into which they are introduced.

Ranked lists of individual chemical species are first established. In these lists, species are ranked in order of decreasing values of an appropriate separation factor that is evaluated at some average or reference condition. For ordinary and extractive distillation, the separation factor is the vapor-liquid equilibrium constant. With the physical property subroutines of Thompson and King (1972a) used, the ranked lists for Example 1 are *ABC* in the absence of species *D*, and *ACBD* when D is present.

If species ranking in all ranked lists remains unchanged with respect to changes in temperature, pressure, and composition, a list splitting operation can be performed, starting with the process feed, to successively generate ranked separation *subproblems* (for example, AC/BD_{II}, where the slash and subscript indicate the separation point and the separator type, respectively) and species subgroups (for example, *AB*) until the desired products are obtained. The subgroups are intermediate streams that leave one separator and are fed to another.

The entire space of separation subproblems, subgroups, products, and process feed(s) may be represented by an and/or directed graph of the type described by Nilsson (1971). The graph for Example 1 is shown in Figure 1, where square nodes designate the process feed and subgroups, numbered circular nodes represent separation subproblems, triangular nodes signify products, and diamond shaped nodes are used for mass separating agents at locations of introduction or recovery. A separation sequence involving two or more separation subproblems can be determined by starting at the process feed node and making path decisions at each square node until all products are produced. From each square (or) node, only one path is selected. Both paths leading from a circular (and) node must be taken.

In Figure 1, there are twenty separation subproblems. Associated with each subproblem is an annual cost for the separator, including any preheating, or pressurization facilities needed to prepare the inlet stream(s) for that particular subproblem. Nine different separation sequences can be traced in Figure 1. The sum of the costs for each separation subproblem in a given separation sequence is the cost of the sequence.

PROBLEM SIMPLIFICATION

The global solution to synthesis of optimal separation sequences requires optimization with respect to system structure variables and separation subproblem decision variables. Structure variables are those involving path options from the square nodes for the process feed and subgroups in the directed graph as in Figure 1. Two types of choices are necessary. One involves the selection of separator type and leads to a ranked sublist (for example, *CBD*). The second choice involves the selection of the separation point within the ranked sublist (for example, C/BD). Both choices are required to determine a path to the next separation subproblem.

Separation subproblem decision variables are numerous, depend upon the type of separator, and may be constrained in a complex manner by process specifications. For ordinary distillation, the decision variables include: separator pressure, reflux rate and temperature, extent of preheating or precooling of the feed, distribution between distillate and bottoms of two key components, feed stage location, choice of equipment (for example, type of tray), choice of utilities (for example, pressure of heating steam), type of condenser operation (partial, total, or mixed), extent of approach to flooding, and approach temperatures in condenser and other heat exchangers. For extractive distillation, additional decision variables include inlet flow rate of solvent, extent of preheating or precooling of solvent, and solvent inlet stage location. The influence on cost of some of these variables was studied by Heaven (1969). Often, as shown by Heaven and discussed further by King (1971), the minimization of cost is not particularly sensitive to these variables over reasonable ranges of their values. Accordingly, near optimal values may be selected by heuristics.

Even after a set of values for separation subproblem decision variables is selected, further choices must be made with respect to the following sets of design equations to be used for analysis of the separation subproblems: physical properties, equipment sizing, cost estimation, and cost or profitability criteria. For example, determination of stage requirements for sizing of equipment may be made by empirical correlations (shortcut methods), approximate group methods, or rigorous stage-to-stage methods as discussed by King (1971). Computational requirements can vary by orders of magnitude between shortcut and rigorous methods. The latter methods are generally considered necessary for final design. A similar latitude of choice exists with respect to physical properties. Approximate procedures may utilize composition-independent separation factors and neglect heats of mixing and possibly sensible heat effects. For final designs, the use of accurate composition-dependent physical properties and rigorous heat balances appears to be widely employed.

In previous strategies for synthesizing separation sequences, none have utilized rigorous or accurate design equations. With respect to separator subproblem decision variables, Thompson and King (1972b) elected to make selections based on heuristics; Hendry and Hughes (1972), Rathore et al. (1974b), and Stephanopoulos (1974) and Westerberg optimized separator pressure, reflux rate, and some feed variables simultaneously with system structure variables. However, in the latter studies, values for all other decision variables were selected by heuristics. Thompson and King (1972b) did not optimize with respect to structure variables, while the other investigators did.

In this study, optimization is performed only with respect to system structure variables to determine the several best separation sequences. Separation subproblem decision variables are selected by the heuristics of Thompson and King (1972a). Also, except where noted, the design equations of Thompson and King are utilized with some modifications as noted in the Appendix. For the search strategy described in the next section, computational time is somewhat greater than that required for the procedure of Thompson and King, but it is substantially less than that for the methods of Hendry and Hughes (1972) and Stephanopoulos (1974) and Westerberg. The viewpoint taken here is that optimization with respect to separation subproblem decision variables should not be restricted arbitrarily to just certain design variables, and such optimization is, perhaps, best left to final design studies with rigorous design equations used for analyzing the several best sequences found by optimizing system structure only. It may be noted that Lee et al. (1970) and Pho and Lapidus (1973) only optimized with respect to system structure variables in synthesizing optimal heat exchanger networks.

Two further simplifications to the separation problem involve species material balances. Generally, process specifications dictate the overall recovery of each species in order to satisfy product purity requirements. For instance, suppose the specifications for Example 1 are 99% recovery of each of the three species in the process feed and 99.5% recovery of phenol. If a species is a key component for only one of the separation subproblems in the sequence, then the specified recovery for that species can be applied at that node in the sequence. However, the species may be a key component for more than one separation subproblem. For example, in Figure 1, cyclohexane is the heavy-key component in subproblem 3 and the light-key component in subproblem 8 of the same sequence. A choice is required as to how the overall loss of 1% of cyclohexane should be divided between the two separation subproblems. This choice may be avoided by employing one of the assumptions of Hendry and Hughes (1972), namely that the presence of relatively small quantities of nonkey components has only a slight effect on the cost of a separation subproblem. This assumption simplifies the determination of the composition of a feed to a separation subproblem, wherein (except for solvents) a species is either present at the same flow rate as in the process feed or is not present at all. If the species is a key component for that particular subproblem, the recovery for design purposes is taken as the overall process recovery. After the design calculation for the subproblem, the split for each species is reallocated on the basis of a perfect separation. As an example, consider separation subproblem 7 in Figure 1. The feed to this subproblem consists of 56.7 kg moles/hr. each of *B* and *C*. For design purposes, the split of *B* is 56.133 kg moles/hr. of distillate (99% recovery) and 0.567 kg moles/hr. of bottoms, while the split of *C* just happens to be the inverse of *B*. Upon the completion of the cost calculation for subproblem 7, the material balance is recomputed to send all *B* to the distillate and all *C* to the bottoms.

The simplication to subproblem material balance calculations leads to the possibility of multiplicate separation subproblems whenever the species present, the separator type, and the separation point are identical. In Figure 1, subproblems 7, 8, and 9, respectively, are identical to subproblems 11, 12, and 13, respectively. However, even though subproblems 10, 16, and 20 appear to be identical, only the pair 10, 16 are duplicates because of identical flow rates for the solvent D. The flow rate of D is established at the separator to which it is introduced as a solvent. In Example 1, the solvent rate is taken as three times that of the feed to the separator. In Figure 1, the flow rate of D in the feed to subproblem 20 is established at a value of 340.2 kg moles/hr. by subproblem 19. The flow rate of D in the feed to subproblem 10 is established at a value of 510.3 kg moles/hr. by subproblem 3.

When multiplicate separation subproblems are identified, computational requirements are reduced. As discussed by Hendry and Hughes (1972), this multiplication can be of great importance in problems involving large numbers of products because multiplicate sets of subproblems may abound. For example, for a process feed consisting of six species that is to be separated by ordinary distillation into six products, forty-two different separation sequences exist with a total of 210 separators. However, only thirty-five of the separators are unique. Multiplicates of separation subproblems need not be shown on and/or directed graphs. For instance, in Figure 1 the arc leading from subproblem 1 to the square node for subgroup BC may be redirected as a dashed arc to the subgroup CB that follows subproblem 6. The nodes for subproblems 11 and 12, as well as the descendant node of subproblem 12 (that is, subproblem 13), may then be eliminated.

SYNTHESIS BY ORDERED BRANCH SEARCH

A popular combinatorial synthesis problem is the so-called *knapsack problem* that arises in cargo loading operations. From a finite collection of N indivisible objects of differing weights w_i and differing values v_i, it is desired to form a loading of a subcollection of the objects such that

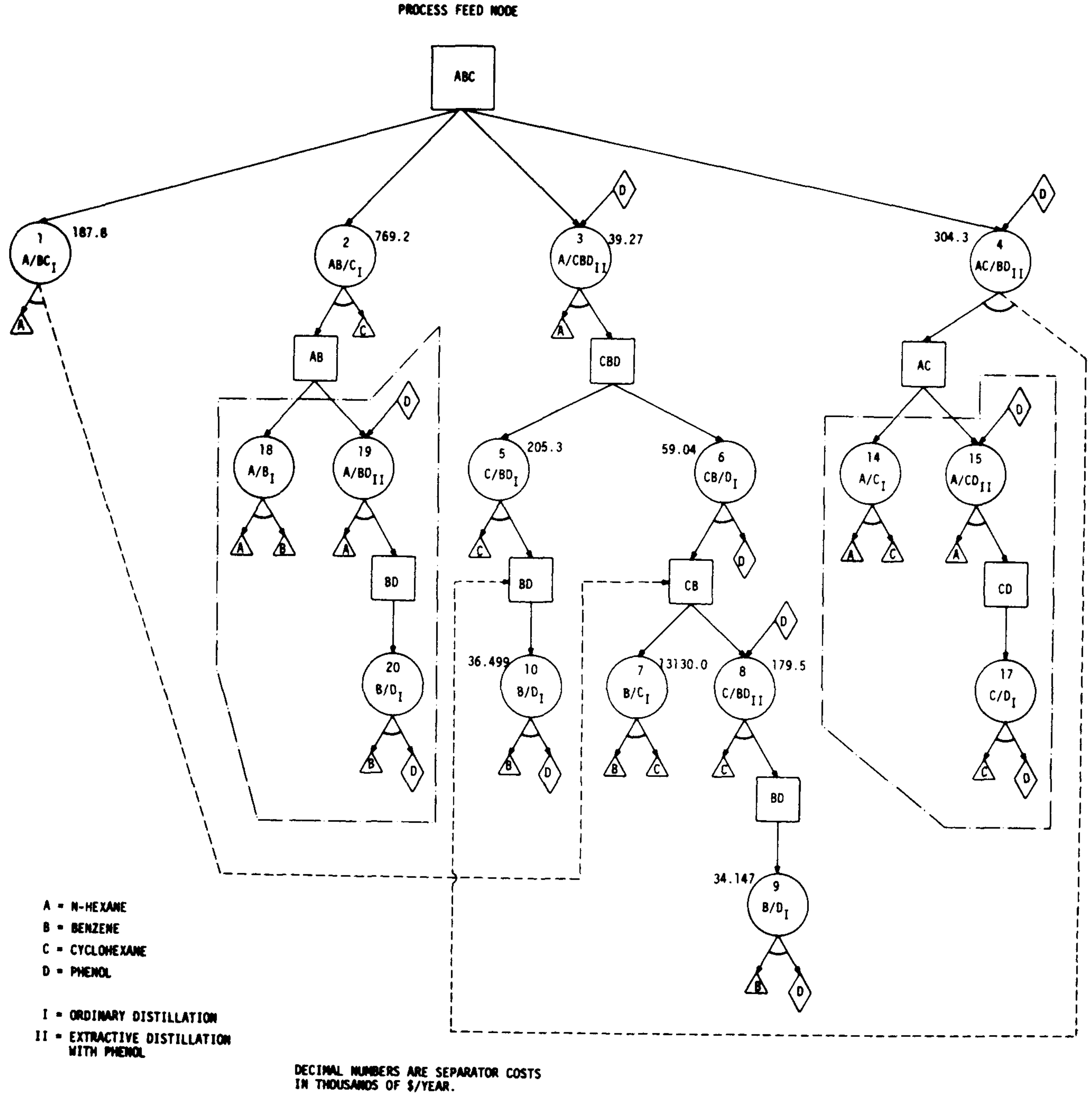


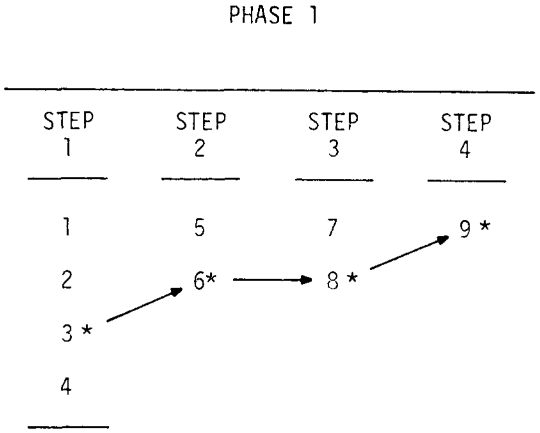
Fig. 2. Reduced and/or directed graph for example 1.

(1) the total weight of the subcollection W_T is less than a maximum permissible weight W_P (where $W_P < \sum_N w_i$) and (2) the total value of the subcollection is maximized. As discussed by Kolesar (1967) and by Greenberg and Hegerich (1970), the knapsack problem has been solved by a number of techniques including dynamic programming, branch and bound algorithms, and by a branch search procedure. Greenberg and Hegerich found that the relatively simple branch search procedure was particularly efficient with respect to computer memory and time requirements, particularly for large problems. The branch search procedure is applied here to the synthesis of separation sequences.

Consider Example 1. A reduced and/or directed graph for this example is shown in Figure 2, wherein only unique separation subproblems are included. By branch search, it is desired to find the separation sequence with the minimum cost. Although the cost associated with each separation subproblem is shown in Figure 1, these costs are only computed from the design equations as the search proceeds. Certain of the subproblems need not be analyzed and costed at all if the search terminates with the optimal solution before all separation subproblems are analyzed.

The search begins by expanding the process feed node to the first generation of separation subproblems. In Figure 2, subproblems 1, 2, 3, and 4 are generated. It is desirable to order expansion of process feed or subgroup nodes to alternative subproblems and to select one of these alternatives for subsequent splitting according to heuristics. From the work of Heaven (1969) and Thompson and King (1972b), the following heuristics were considered: (1) generate or select the subproblem where the first species in the ranked list is separated from the remaining species, (2) generate or select the subproblem where the split of species between the distillate and bottoms is most nearly equimolal, and (3) generate or select the subproblem having the lowest cost (cheapest first). For simplicity, the first heuristic is used here to determine the order of branching to alternative separation subproblems. Ordinary distillation is treated first followed by separators, with mass separating agents used in the order of agent input to the program. After analysis of the alternative subproblems, one branch must be selected as the path for the sequence being generated, and the corresponding subproblem must be split into subgroup and/or product nodes. Because of the apparent success of the third heuristic in the study of Thompson and King, it is applied here to make the path selection. The use of heuristics (1) and (3) is repeated as each subgroup in the path is expanded to alternative subproblems. When a separation subproblem produces two intermediate streams (subgroups), expansion of the distillate (or overhead) subgroup to the next set of subproblems is completed before the bottoms subgroup is expanded.

The ordered branch search consists of first and subsequent phases. In the first phase, the search in the graph proceeds as described above by branching until all products are produced, thus completing development of an initial separation sequence. In the case of multicomponent products, it is permissible to produce them by blending. Although this initial sequence may not be the optimal sequence, frequently it is a near optimal sequence. The total cost of the initial sequence is obtained during its development by accumulating costs of subproblems contained in the sequence as the subproblems are analyzed and selected. This total cost is referred to as the initial upper bound. In Figure 2, the initial sequence is obtained by analyzing separation subproblems in the vertical order (top first) shown at each step in Figure 3, where the asterisks indicate the lowest cost subproblems, and the arrows indicate the selected path. The initial separation sequence is 3-6-8-9, with a total cost (initial upper bound) of $311,957/yr.



*INDICATES LOWEST COST SUBPROBLEM FOR THE STEP.

Fig. 3. Development of the initial sequence for example 1.

The second and subsequent phases of the ordered branch search involve back tracking and then branching to seek subsequent and perhaps lower cost sequences. If a lower cost sequence is found, it becomes the new or current upper bound. In these phases, branching does not necessarily continue until a separation sequence is completed. Branching is discontinued and a new phase is begun by back tracking whenever the cost of a partially completed sequence exceeds the current upper bound. In this manner, for many separation problems, all sequences need not be developed, and not all unique separation subproblems need be analyzed.

The back tracking procedure begins at the node corresponding to the last separation subproblem of a completed or partially completed and discontinued sequence. A move is made backwards to the previous subgroup node. If alternative separation subproblems are generated from that subgroup node, the subproblems become parts of alternative sequences and are now considered for branching in the order of the third heuristic. When all alternative separation subproblems generated from a given subgroup node have been considered as parts of a sequence and judged against the current upper bound, backtracking is extended one more step. The entire back tracking and branching procedure is repeated again and again until no further sequences remain to be developed. In this manner, the ordered branch search is basically a modified depth-first method (Nilsson, 1971).

In Figure 2, phase 2 begins with back tracking in two steps from subproblem 9 to subgroup *CB* that represents the overhead product from subproblem 6. Branching to subproblem 7 completes a second separation sequence (3-6-7) with a total cost of $13,228,310/yr. This cost is far in excess of the initial upper bound. Phase 3 involves back tracking to subgroup *CBD*, the bottoms product from subproblem 3. Branching then develops the sequence 3-5-10 with a new upper bound of $281,069/yr. Subsequent search phases, with sequences or partial sequences

Table 1. Sequences Examined for Example 1

Phase	Subproblems of sequence (or partial sequence)	Total cost (or partial cost) \$/yr.	Comments
1	3-6-8-9	311,957	Initial upper bound
2	3-6-7	13,228,310	
3	3-5-10	281,069	New upper bound
4	(1-8)	(367,300)	
5	1-7	13,317,800	
6	(4)	(304,300)	
7	(2)	(769,200)	

as listed in Table 1, do not result in lower cost separation sequences. Thus, in order to obtain the optimal sequence, only four of nine possible sequences are developed. Only ten of twenty separation subproblems (sixteen of which are unique) are analyzed. In Figure 2, unique separation subproblems enclosed within the dash-dot border are not analyzed.

In order to assess the effectiveness of the ordered branch search strategy, it is convenient to define the following search factors:

Sequence search factor

$$= F_s = N_{sd}/N_s \qquad (1)$$

Subproblem search factor

$$= F_{sp} = N_{spa}/N_{sp} \qquad (2)$$

Unique subproblem search factor

$$= F_{usp} = N_{uspa}/N_{usp} \qquad (3)$$

Computational efficiency depends strongly on F_{usp}, but F_s is also important. The higher the F value, the less efficient the search. Search factors corresponding to Equations (1), (2), and (3) are 44.4, 50, and 62.5%, respectively, for Example 1.

FORBIDDEN SPLITS

Hendry and Hughes (1972) discussed the importance of prohibiting consideration of certain impractical separation subproblems (forbidden splits) prior to list processing so as to reduce the size of the combinatorial problem. In addition, it is useful to prohibit difficult or impossible subproblems that might not be detected as such by approximate design equations.

In Example 1, no splits were forbidden. However, it would seem advisable to prohibit the binary separation of benzene from cyclohexane by ordinary distillation. Actually, the design calculations detected the difficulty of this split (subproblem 7) quite well. A relative volatility of 1.024 is computed at feed conditions resulting in very large reflux and stage requirements at a cost of \$13,130,000/yr. Also, it might be anticipated for subproblem 5 involving the ordinary distillation of cyclohexane from benzene in the presence of phenol, that the separation would become impractical in the upper portion of the rectifier section of the distillation column because little phenol would be present. However, the shortcut design equations with a relative volatility based on the feed or on an average between the distillate and bottoms products fail to detect the difficulty. Separation subproblem 5 appears in the optimum sequence shown in Table 1.

In Example 1, suppose all separations between benzene and cyclohexane by ordinary distillation, including those where n-hexane and phenol are present, are forbidden (subproblems 2, 5, 7, and 11). This causes the elimination of other separation subproblems. For example, as seen in Figure 1, with subproblem 2 forbidden, subproblems 18, 19, and 20 are also eliminated because the path to them uniquely passes through subproblem 2. The separation problem is now reduced to one involving only twelve subproblems (ten of which are unique) and only four separation sequences. The optimal sequence is now 3-6-8-9 at a cost of \$311,957/yr. that is less than the cost of the simpler sequence 1-8-9 at a cost of \$401,447/yr. Alternatively, sequence 3-5-10 might be modified by adding additional solvent to subproblem 5 to convert it to extractive distillation. The current version of the computer program used in this study does not permit a second solvent or an additional portion of the same solvent already present to be added before the first solvent is recovered. This restriction does not exist in the Thompson and King method (1972a).

DISTRIBUTION OF SEQUENCE COSTS

The values obtained for the search factors defined by Equations (1), (2), and (3) are strongly dependent on the distribution of separation sequence costs. For sequences involving only ordinary distillation, a relatively narrow range of sequence costs may exist. For example, Heaven (1969) computed costs of all ordinary distillation sequences for forty-two cases involving three products (two separators) and for one case involving five products (four separators). The highest cost sequence was no more than 17% greater in cost than the lowest cost sequence. Analysis of the five-product case of Heaven was repeated by Rathore et al. (1974b) who used different design equations in conjunction with a dynamic programming technique. This case is referred to here as Example 2. The distribution of costs for all fourteen sequences of Example 2 is shown in Figure 4 in terms of sequence costs relative to the lowest cost sequence. The costs of six of the sequences are within 6% of the cost of the optimal sequence. The highest cost sequence is 22% greater in cost than the lowest cost sequence. Example 2 was solved by

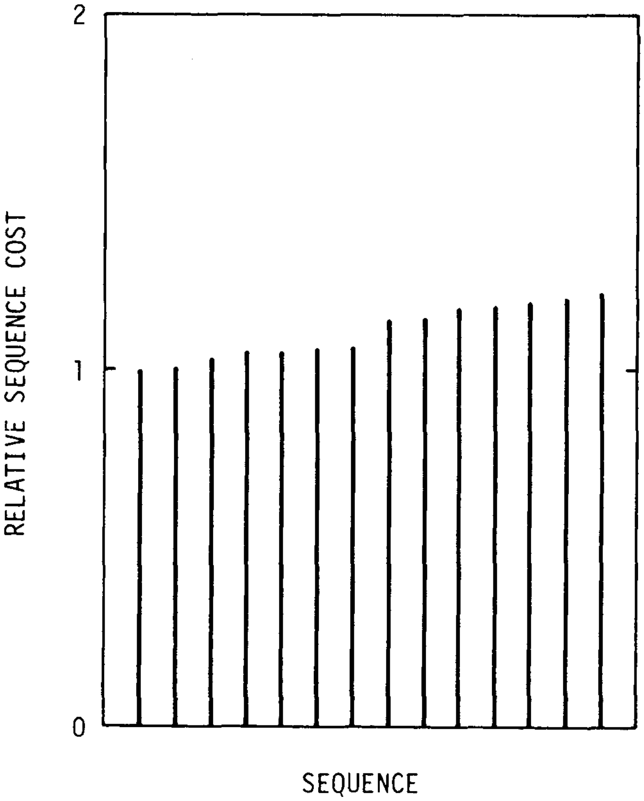


Fig. 4. Distribution of sequence costs for example 2.

the ordered branch search method by using the subproblem costs of Rathore et al. (1974b) to obtain sequence costs identical to theirs. The resulting search factors were $F_s = 78.6\%$, $F_{sp} = 92.5\%$ (based on forty subproblems), and $F_{usp} = 100\%$ (based on twenty unique subproblems).

As a further case (Example 3) involving a larger number of possible sequences, the six-component problem of Thompson and King (1972b) was solved by the ordered branch search method after the problem was modified to specify six (rather than four) relatively pure products to be obtained by ordinary distillation only. For the forty-two possible sequences, the ratio of the cost of the highest cost sequence to the cost of the optimal sequence was 1.357. Again, with a relatively narrow range of sequence costs, F_{usp} was 100%. However, F_s was only 42.9%. Accordingly, for cases where the distribution of sequence costs is suspected to be relatively narrow, it may be worthwhile to obtain costs for all sequences. For Example 3, the CPU time (on a Univac 1108 digital computer) required to obtain costs of all sequences (by a procedure described below) was 12.10 s compared with 7.26 s to seek the optimal sequence by the ordered branch search method.

When the cost of certain ordinary distillation subproblems is impractically high (for example, when the average relative volatility between the key components is less than 1.05) and other more practical separator types are considered, a wide distribution of sequence costs is likely to exist. Such is the case in Example 1. Consider also a modification of the example presented by Hendry and Hughes (1972) involving the separation of propane, *n*-butane, butene-1, trans-butene-2, cis-butene-2, and pentane into four products (including one multicomponent product consisting of the three butene isomers) by a combination of ordinary distillation and extractive distillation with 96 wt % aqueous furfural. In addition to forbidden splits cited by Hendry and Hughes involving the use of extractive distillation to remove propane and pentane, it is worthwhile to reduce further the size of the separation problem by prohibiting separations where both the light and heavy keys are butene isomers, because such separations are difficult and all three isomers must eventually appear in one of the products. In this manner, the number of possible separation sequences is further reduced from 227 to 33, and the number of unique subproblems is further reduced from 64 to 30. The resulting separation problem is referred to here as Example 4. This example was solved by the ordered branch search method by using subproblem costs derived from the tabulations of Hendry (1972). The optimal sequence obtained was the same as that of Hendry and Hughes. A value of 42.4% was obtained for F_s, and a value of 76.7% was obtained for F_{usp}.

The distribution of costs for the thirty-three sequences of Example 4 is shown in Figure 5. Relative sequence costs are almost as high as six. Twelve of the sequences are relatively low in cost, while the remaining twenty-one sequences are much greater in cost. The seven best sequences differ in cost by no more than 5%.

NEAR OPTIMAL SEQUENCES

Figure 5 shows the importance of seeking near optimal sequences as well as the optimal sequence. The ordered branch search method is easily modified to obtain near optimal sequences within a selected percentage of the optimal sequence. The modification involves the discontinuance of branching and a switch to back tracking whenever the cost of a partially completed sequence exceeds a modified current upper bound equal to the current upper bound multiplied by a near optimal sequence factor F_{no}, say 1.15. Normally, if a reasonable value for this factor is selected, the additional computing requirements are small. For instance, in Example 4, with a value of F_{no} equal to 1.15, only one additional subproblem must be analyzed, and one additional sequence must be developed to obtain seven near optimal sequences. With F_{no} equal to 1.30, only three additional subproblems must be analyzed, and two additional sequences must be developed to obtain ten near optimal sequences. If all sequences are desired, a large value of F_{no} is specified.

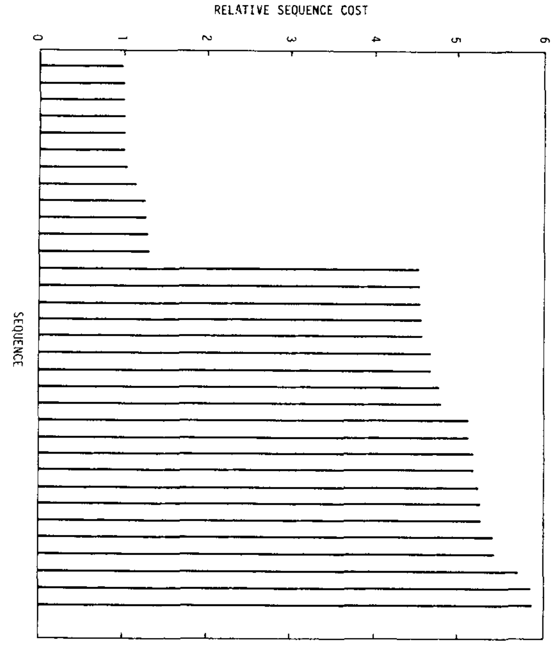


Fig. 5. Distribution of sequence costs for example 4.

COMPARISON WITH THOMPSON AND KING (T-K) METHOD

As mentioned above, the ordered branch search method was implemented on a digital computer by using the design equations of Thompson and King (1972a). Other similarities, as well as differences, between the two methods are as follows:

1. In cases where multicomponent products are specified, the T-K method solves the separation problem for a computer determined feasible product set. For each product set, feasible separation subproblems are determined by a product separability matrix, indexing all products and potential mass separating agents. In this work, all product sets are considered sequentially, and separation subproblems are generated by list processing.
2. Both methods begin by expanding the process feed node and order the descendant nodes by the cheapest first heuristic. Unless the T-K β factors are not updated, the cost of a separation subproblem in the T-K method may be an estimated cost based on the number of equilibrium stages. In this work, the cost is always the actual cost.
3. The T-K method carries along the actual material balance during the development of a sequence and, therefore, does not recognize multiplicate separation subproblems.
4. The T-K method develops only one sequence from each node that is a descendant of the process feed node unless β weighting factors are used to update costs. Then the synthesis may be repeated from the beginning. In that case, each separation subproblem selected is reanalyzed. Back tracking is not utilized in the T-K method.

Therefore, the T-K method cannot guarantee development of the optimal sequence.

5. The ordered branch search method can readily generate near optimal sequences.

The distinction noted in item 4 above is most important. Although few sequences are ordinarily developed by Thompson and King, they claim to achieve good answers. Their claim has merit. In Example 2, with only one product set, application of the T-K technique without updating of β factors leads to the optimal sequence by analyzing only nine of the forty separation subproblems. In Example 3, application of the T-K method without updating of β factors leads to the fourth best sequence, which is 8.6% greater in cost than the optimal sequence. This is achieved by analyzing only thirteen of thirty-five unique separation subproblems. For Example 4, the fourth best sequence, which is only 2.0% greater in cost than the optimal sequence, is developed by analyzing only ten of thirty unique subproblems. If desired, the ordered branch search procedure can be terminated upon development of the initial sequence to obtain these same results. However, the T-K method may give different results when different product sets are possible and updating of β factors is used.

A comparison of computing times for the T-K and ordered branch search methods was made by using a modification of the example presented by Thompson and King (1972b), wherein only ordinary distillation and extractive distillation with tetrahydrofuran (THF) were considered. In this case, Example 5, a β weighting factor of 80% was used in the T-K method. Both strategies achieved the optimal solution with the T-K method requiring 26 s of CPU time compared to 36 s for the method of this study.

Because of the above discussion of the distribution of sequence costs, item 5 above is also important. For instance, in Example 5, costs of fifteen sequences are within 15% of the cost of the optimal sequence. These near optimal sequences were developed by the method of this study by the additional expenditure of only 11 CPU s.

EFFECT OF FLOW RATE OF MASS SEPARATING AGENT

In Example 5, the optimal sequence does not involve extractive distillation with THF. However, six of the fifteen near optimal sequences do include one extractive distillation unit. The cost of the best of these six sequences is within 8% of the cost of the optimal sequence. In the design equations of Thompson and King, the ratio of the solvent flow rate to the feed flow rate for an extractive distillation column is fixed at 2.0. A brief study was made to determine the effect of this ratio on sequence cost. A lower solvent-to-feed ratio of 1.0 was found to be insufficient to cause the desired change in the ranked list of species. Higher ratios of 3.0 and 4.0 cause the affected sequence costs to rise almost linearly with the solvent-to-feed ratio. At the highest ratio of 4.0, however, the sequence costs are no more than 3% higher than the costs at a ratio of 2.0; for five affected sequences, the difference amounted to only approximately 1%.

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NOTATION

F_{no} = near optimal sequence factor
F_s = sequence search factor
F_{sp} = subproblem search factor
F_{usp} = unique subproblem search factor
N_s = number of possible sequences
N_{sd} = number of sequences developed
N_{sp} = number of subproblems
N_{spa} = number of subproblems analyzed
N_{usp} = number of unique subproblems
N_{uspa} = number of unique subproblems analyzed
β = quantity used by Thompson and King equal to separator cost per stage

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APPENDIX: MODIFICATIONS MADE TO DESIGN EQUATIONS OF THOMPSON AND KING

Subroutine distl: A change involving the calculation of reboiler heat duty was made. In the original subroutine, the reboiler duty was computed on the basis of a saturated liquid feed to the column. The modification retained the assumption of constant molal overflow but allowed for any feed condition.

Subroutine pump: The equations for calculating the horsepower requirement and the annual operating cost were modified to

$$HP = 0.0015607\, F\, T \ln(P_{out}/P_{in})$$

and

$$OP = 63\, HP$$

where:

HP = brake horsepower
F = feed flow rate, lb moles/hr.
T = feed temperature, °R
P_{out} = discharge pressure, lb./sq.in.abs.
P_{in} = suction pressure, lb/sq.in.abs.
OP = annual operating cost, \$/yr.

This subroutine was used not only to compute pumping costs for intermediate process streams but also for the feed stream to the initial separator in the sequence. Thompson and King did not attach a pumping cost to the process feed stream.

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A Deborah Number for Diffusion in Polymer-Solvent Systems

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A Deborah number is introduced as a means of characterizing diffusional transport in amorphous polymer-solvent systems. Two types of temperature-penetrant concentration diagrams are constructed, and the various regions on these figures are identified by their Deborah number values. The utility of the diffusion Deborah number is demonstrated by using this dimensionless group to anticipate conditions under which thickness anomalies can be expected in sorption experiments for the atactic polystyrene-pentane system.

SCOPE

Investigations of diffusion phenomena in amorphous polymer-solvent systems have shown that it is possible to observe widely differing behavior by traversing a large enough range of temperature, concentration, and polymer molecular weight. It is convenient to depict the different types of diffusional transport of penetrants in high polymers by utilizing a temperature-penetrant concentration diagram. The various regions on such a diagram are distinguished by the ratio of two characteristic times, a characteristic relaxation time for the polymer-solvent system and a characteristic diffusion time. Since the situation is analogous to that encountered in the flow behavior of viscoelastic fluids, it is reasonable to expect that a diffusion Deborah number can be defined which corresponds to the Deborah number used to characterize flow of polymeric materials. In this paper we propose a Deborah number which can be used to characterize diffusional transport in amorphous polymer-solvent systems and consider the calculation and utilization of this dimensionless group.

CONCLUSIONS AND SIGNIFICANCE

From examination of the various stable and metastable states of polymers which are invariably observed in amorphous configurations, justification is given for treating such polymers as viscoelastic fluids at all temperatures. A diffusion Deborah number can then be defined in terms of the characteristic length of the diffusion path and the shear modulus and self-diffusion coefficients of the polymer-solvent mixture. Reasonable estimates of the Deborah number can be obtained over wide ranges of conditions, even though the slow orientation of molecules of polymeric materials below T_g causes difficulties in conducting meaningful experiments in this temperature range. Two types of temperature-concentration diagrams depicting polymer-penetrant diffusion can be constructed, and the various regions on these figures are identified by their Deborah number values. The utility of the diffusion Deborah number is demonstrated by using this dimensionless group to anticipate conditions under which thickness anomalies can be expected in sorption experiments for the atactic polystyrene-pentane system.

Investigations of diffusion phenomena in amorphous polymer-solvent systems have shown that it is possible to observe widely differing behavior by traversing a large enough range of temperature, concentration, and polymer molecular weight. Alfrey (1965) and Hopfenberg and Frisch (1969) depicted the different types of diffusional transport of penetrants in high polymers by utilizing a temperature-penetrant concentration diagram. It was later noted (Duda and Vrentas, 1970) that the various regions on this diagram could be distinguished by the ratio of two characteristic times, a characteristic relaxation time for the

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