# STUDIES IN THE SYNTHESIS OF SEPARATION PROCESSES 

A Dissertation<br>Presented to<br>The Faculty of the Chemical Engineering Department University of Houston Houston, Texas 77004

In Partial Fulfillment
of the Requirements for the Degree Doctor of Philosophy in Chemical Engineering

## by

Ravindra Nath
September, 1977

To Rosa
for her deep understanding and for her constant encouragement

The author would like to express his gratitude to his advisor, Prof. R. L. Motard for his guidance and firm support throughout what has been the most enjoyable perjod of my academic life.

For financial support during this work, the author is indebted to the Chemical Engineering Department. Valuable assistance received in various forms from the faculty and staff of the department of Chemical Engineering is greatfully acknowledged.

Greatful acknowledgements are extended to Frofessors James E. Bailey, Roy Jackson, Robert B. Anderson and John F. Andrews for serving on the oral examination committee.

Finally, the author would like to express his sincere appreciation to Ms. Sandi White for typing this entire manuscript, her patience and assistance cannot be fully acknowledged.

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#### Abstract

Problems related to the synthesis of separation sequences have been considered in this dissertation. The main emphasis has been on the synthesis of shaxp separation sequences. The synthesis of a separation sequence implies the creation of an arrangement of separation units that will isolate species from a given multicomponent fced stream at a minimum cost. The products are specified in terms of desired recoveries and purities. An evolutionary approach is used. The synthesis problem is decomposed into two phases, 1) creation of an initial feasible structure, and 2) evolution of the structures.

A heuristic procedure for the creation of an initial structure is developed. The reuristic rules embody the knowledge of the general behavior of separation units and separation sequences in a form which is suitable for computer implementation. Starting from the feed stream, a systematic application of the eight heuristic rules creates a good initial structure. In the evolutionary phase, the initial structure is successively modified by the application of five evolutionary rules. The evolutionary rules are applied in a hierarchical manner until no modification can be detected. The structure thus obtained is termed the "optimal structure" ard is not changed in the later work.


The products isolated from the optimal structure do not usually satisfy the specified product recoverjes and purities. Therefore, the split fractions of some of the components are adjusted to satisfy the product performance specifications. Inalytical expressions for product recovery and purity as a function of system structure have been obtained and a gradient method has been developed. The cost versus reflux ratio for a distillation unit is nonconvex near the optimum. A surrogate cost function which foilows the actual cost function very closely and has continuous derivatives is obtained by regression. The gradient of the surrogate cost function is used to direct the search for the optimun reflux ratio for each separation unit in the structure. A bisection algorithm is presented.

Several hydrocarbon separation problems have been successfully synthesized as examples of the proposed. synthesis procedure.

A preliminary investigation of the nonsharp synthesis problem has also been made. A graphical procedure to create an initial structure has been developed for nonsharp separation problems.

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| $\mathrm{A}_{1}, \mathrm{~A}_{2}$ | regression coefficients for Equation 6.1-1 |
| :---: | :---: |
| $C_{i}$ | species in product i |
| $C, C_{i}$ | cost of column (\$/yr) |
| CDS | Coefficient of Difficulty of Separation |
| D | flow rate of distillate product |
| $\mathrm{D}_{\mathrm{i}}$ | a set of components, each of which is a key component when $j \in C_{i}$ is the other key component |
| $\mathrm{dc}_{i}$ | distribution coefficient for specie $i$ |
| F | flow rate of feed streami |
| $\mathrm{f}_{\mathrm{i}}$ | flow rate of component $i$ in feed stream |
| HK | refers to the heavy key |
| ITER | iteration counter |
| L | flow rate of bottom product |
| LK | refers to the light key |
| $\max$ | short form of maximum |
| M | number of desired products |
| MS | number of separators using an MSA |
| MSA | Mass Separating Agent |
| ns | refers to nonsharp separations |
| N | number of components, or number of stages |
| $\mathrm{N}_{\mathrm{m}}$ | minimum number of stages |
| $\mathrm{N}_{S}$ | number of possible configurations |
| $\mathrm{N}_{\text {usp }}$ | number of possible unique subproblems |
| $\mathrm{N}_{\text {sa }}$ | number of configurations actually developed |


| $\mathrm{N}_{\text {uspa }}$ | number of unique subproblems actually developed |
| :---: | :---: |
| OPEN | a set whose members are process streams at any given instant in time |
| $p_{i}$ | purity of product i |
| $\mathrm{P}_{\mathrm{i}}$ | flow rate of product i |
| $\mathrm{p}_{\text {ij }}$ | flow rate of specie $j$ in product $i$ |
| $r_{i}$ | recovery of product i |
| $\mathrm{R}_{\mathrm{i}}$ | transformation corresponding to rectification section of separator i |
| $r_{\text {i }}$ | $j$ th component of transformation $R_{i}$ |
| R | reflux ratio |
| $\mathrm{R}_{\mathrm{m}}$ | minimum reflux ratio |
| RL | Ranked List |
| $\mathrm{R}^{\mathrm{n}}$ | the space of real numbers |
| S | refers to sharp separations |
| Ss | refers to semi-sharp separations |
| sp | split fraction |
| S | number of separators available |
| $S_{i}$ | transformation corresponding to stripping section of separator i |
| ST | Separation Type |
| $s^{n}$ | the space of chemical species |
| TAC | Total Annual Cost (\$/yr) |
| V | flow rate of distillate product |
| X | a point in the space $S^{n}$ |
| $\mathrm{x}_{\mathrm{ij}}$ | mole fraction of specie $j$ in product $i$ |
| $\mathrm{x}_{\text {Fj }}$ | mole fraction of specie $j$ in the feed |

## GREEKS

| $\alpha$ | separation factor |
| :---: | :---: |
| B | a positive real number |
| $\delta_{j, i}=1$ | if $j$ has been a key associated with any of the transformations required to produce product i |
| $=0$ | otherwise |
| $\varepsilon$ | small positive quantity, or convergence criterion |
| $\eta_{i}$ | number of times specie $i$ has been a key component in the sequence |
| $\theta$ | $\mathrm{R} / \mathrm{R}_{\mathrm{m}}$ |
| X | additional number of sequences possible using two separation methods, one of which uses an MSA when restriction 1 is relaxed |
| $\Omega$ | number of sequences possible using a separation method when restrictions 1 and 2 are imposed |
| $\partial, \delta$ | infinitesimal change |
| $\Delta$ | small change |

## SUBSCRIPTS

A, B,... refer to components A, B,...
i, j, k, 1 indices

| ih | component just heavier than the heaviest <br> component in product $i$ |
| :--- | :--- |
| il | component just lighter than the lightest <br> component in product $i$ |
| inf | infimum |
| low lower limit |  |

high upper limit
spec specified value
1, 2, 3,... refer to separators $1,2,3, \ldots$

## MATHEMATICAL SYMEOLS

c
subset of
$u$ union with
$\epsilon \quad$ belongs to
甘 for every

* substituted by
> greater than
< less than
$\emptyset \quad$ null set
$\frac{d}{d x}$ derivative wrt $x$
$\Sigma$ summation
\&n natural log
$\log \quad \log$ base 10
$\propto$
proportional to


## Chapter 1

INTRODUCTION

In the course of process design, the problem of: isolating species from a given multicomponent feed stream occurs frequently. The task of feed preparation for the reactor and the task of product purification naturally calls for the synthesis of separation sequences. Also, during the automated design activity [M2], the streams belonging to the ADJUST and SEPARATE secs are candidates for separation tasks. In the present work an attempt is made to systematize the synthesis of separation sequences.

Synthesis of separation sequences implies the creation of an arrangement of separation units that will isolate the desired products from a given feed stream at a minimum cost.

The problem of synthesis of separation schemes is difficult to solve because the number of arrangements which can isolate desired procucts from a given feed is enormous. As a simple example, consider a stream containing three components, $A, B$ and $C$. Isolation of each of the components using दistillation (I) and/or extractive distillation with a solvent $X$ (II) is desired. The ranked lists for the components (ranked acoording to distribution factor, highest first) for both methods are shown below:

```
RL(I) : A B C X
RL(II) : A C B X
```

Figure 1 illustrates a complete enumeration of the nine possible configurations for this case. The number of possible configurations increases exponentially as the number of desired products increases and as the number of types of separators to be considered increases. The number of sequences, in general, is given for an $N$ component feed producing $N$ single component products using $S$ types of separation methods (MS of which use mass-separaingagents (MSA)), by the following inequality:

Arrangements $\geq \Omega(N) \mathrm{s}^{\mathrm{N}-1}+\mathrm{X}(\mathrm{N}) \mathrm{MS} \quad 1-\mathrm{I}$

The first term in Equation l-1 is the number of configurations possible when the MSA is removed immediately after use (restriction 1) by a distillation unit (restriction 2). The second term in Equation l-1 gives the number of additional configurations which are possible due to the relaxing of restriction 1 . The details of the derivations of Equation 1-1 are given in Appendix A.

The total number of configurations for most practical problems is so large that an exhaustive search is computationally infeasible.

In the next sections, previous work in related areas has been reviewed. In the first section, the previous work in the general area of synthesis is briefly reviewed with emphasis on the evolutionary synthesis procedure.


Figure 1
The Nine Possible Arrangements for a Three Component Feed Using Distillation (I) and Extractive Distillation (II)


Figure 1 Continued

In the second section the work in the field of synthesis of separation schemes is reviewed in detail.
1.1 Previous Work on Synthesis

Process synthesis requires the determination of optimal interconnection of processing units as well as the determination of optimal operating conditions for each processing unit. Optimal synthesis thus involves a search for configurational alternatives in addition to a search for design variables. The number of alternatives is enormous and some shortcuts are necessary in order to make the problem computationally feasible for a practical chemical engineering problem. Hendry, Rudd and Seader [H5] have comprehensively reviewed the literature through 1972. Hlavacek [H7] in a similar review has covered the literature througn mid 1975. Basically, four approaches to synthesis have been outlined. A general method of synthesis by decomposition is suggested by Rudd [R4]. The synthesis problem is decomposed into a sequence of smaller and simpler problems which can be solved by available technology. These subproblems, in addition, are connected by tear constraints. Dynamic Frogramming [N1], branch and bound procedures [B3, L2] and the multilevel decomposition of Lasdon [L1, B4] belong to this approach. Synthesis by heuristic methods involves the use of heuristics to decrease the enormous search space. Heuristics are rules of thumb which embody engineering judgement based on design experience. Heuristic rules have
the inherent weakness that they cannot be proven to lead necessarily to the optimal structure. Nonetheless, heuristic rules are quite common in chemical engineering practice and are often used in the design of processes because of the efficiency they give to the search. An alternative approach to synthesis is that of direct optimization. The approach is to imbed all possiole process structures (configurations) into one superstructure by defining all the interconnections which might exist jetween various pieces of equipment. In defining all possible interconnections, many new structural parameters are introduced. These structural parameters are 0-1 type variables and thus make the synthesis problem a mixed integer problem. The solution of large scale mixed integer problems is complicated and the lack of efficient algorithms for solution of such problems restricts the application of this approach to synthesis of fairly small problems.

Another approach to synthesis is by evolutionary procedures. In this approach a feasible initial structure (base case) is successively improved by making evolutionary structural changes. The structural changes to be made are suggested by the application of evolutionary rules to the base case. King, Gantz and Barnes [K2] have applied this synthesis procedure to two cesign problems. In the first example, a demethanizer tower system is synthesized. Starting with a very simple structure, successive structural changes were made to reduce the loss of ethylene in the
overhead stream without increasing the total annual cost of the process. Structural changes to be made mere obtained by a manual end-means analysis of the base case and detailed simulation was performed on a computer implementing the proposed structural modification. The rew structure obtained was improved further by repeating the steps above. Evolution was stopped after significant improvement was made to the initial flowsheet. In the second example, a methane liquifaction process was synchesized. Starting with a simple structure, successive structural changes were made to reduce the energy consumption in the process. During evolution, the flowsheet was examined and the equipment which degraded the largest amount of available energy was replaced by a more promising piece of equipment and the remainder of the process was adapted in a systematic fashion. This evolutionary process was repeated and terminated after significant improvement had been made to the initial structure. Unlike the first example, the complete synthesis logic was automated for the second example. In both examples the evolutionary rules were drawn from considerable engineering experience in the particular processing area. McGalliard and Westerberg [M3] have taken a more theoretical approach to evolutionary synthesis. A procedure based on the two-level method of Lasdon is presented. This procedure is capable of evaluating a small feasible structural modification to a feasible structure without reoptimizing the modified system, The underlying
assumption is that the Lagrange multipliers are fairly insensitive to small structural changes. Using this technique for an initial feasible structure, possible structural modifications can be evaluated quickly. The modification which promises the most improvement is actually reoptimized giving a new structure. The new structure is improved in a similar fashion. The feasibility of this procedure has been demonstrated on two simple heat exchanger synthesis problens.

A somewhat similar approach has been taken by Wilde and Buynoski [W3]. A constrained derivative approach is presented which can evaluate small structural and/or operating condition changes without complete reanalysis of the new system. The constrained derivatives are computed durj.ng optimization of the base case. This approach has been applied to a serial refrigeration system design.

Westerberg, Stephanopoulos and Shah [W2] have systematized the logic of evolutionary synthesis. Four subtasks for the evolutionary synthesis procedure have been identified: finding the initial structure, inventing evolutionary rules, developing a strategy to apply evolutionary rules and a means to compare structures which are generated during evolution. Some guidelines have been provided for inventing evolutionary rules and for developing a strategy to apply these rules. A simple separation problem is illustrated as an example and evolutionary rules for the synthasis of heat exchange
networks have been outlined. In this approach stress is made on the completeness of the evolutionary rules which implies that the rules are such that by a finite application a given structure can be evolved to any other structure. The evolutionary rules make only minimal structural changes. In addition, the evolutionary rules are invented irrespective of the object function. The approach by King et. al. [K2] is significantly different since the objective function is the governing force in the invention of the evolutionary rule. The evolutionary rules in the approach by King et. al. attempt to create structures which make large improvements in the objective function. The approach by Westerberg et. al. is somewhat more mechanical and is suitable for the systems whose behavior is relatively less known. For systems whose behavior is well known, the approach by King is preferable.

## 1. 2 Previous Work on the Synthesis of Separation Sequenses

Lockhart (1947) [L3] studied arrangements of distillation sequences for three different feeds for a natural gasoline plant. Each feed was to be separated into three products, thus requiring two distillation columns, which can be arranged either as a direct or an indirect series. For each of the feeds, the optimum arrangement was given as a function of feed composition. The conclusions drawn apply only to the specific systems considered and have no general applicability.

Harber (1957) [H1] pointed out that "heating requirement" is the single most important variable in aistillation column arrangements. He proposed two heuristics, viz, "difficult separation last" and "near 50-50 splits" for the optimum arrangements. The examples considered were limited to three product feeds.

Rod and Marek (1959) [R2] considered the sequencing problem from the point of view of minimizing total vapor flow in the system. Vapor flows have been calculated by using analytical expressions for the minimum reflux. Several simplifying assumptions were made, consequently the results presented have little practical value.

Heaven (1970) [H3] considered the sequencing problem with a very detailed costing of the distillation units. His studies confirmed the heuristic rules of Harber, for minimum cost sequences. Much of the emphasis was placed on three component feeds and one example considered five component feeds.

Nishimura and Hiraizumi (1971) [N3] have considered the distillation system pattern problem by minimizing a simplified cost function for two restricted cases, when either all components are about the same compcsition, or when one of the components dominates. A three component system is synthesized as an example.

Powers (1971) [P2] has outlined a heuristic method for the creation of a separation scheme. Four heuristics have been proposed. For the process stream under
consideration, all possible separation points are identified and the heuristic rules are used to evaluate the desirability of each separation. Numerical values are assigned by each heuristic to the alternative separations. The alternative with the maximum score is selected as the next separation in the process. This procedure is repeated for each process stream. This algorithm has been applied to four industrial separation problems. In two of the cases, the algorithm produced distillation sequences used by the industry. Unfortunately no comparisons were made with the optimm sequences.

Hendry and Hughes (1972) [H4] have used the Dynamic Programming (DP) method to find the optimum arrangement of distillation and extractive distillation units. A simplification was made; any unit which used a Mass Separating Agent (MSA) had the MSA removed in the inmediate succesor unit. The method is general but has the shortcomings of DP, viz, during suboptimizations the inlet stream composition is assumed, as it is not known exactly when the suboptimizations are performed. This can be a very serious assumption if the separation factors are strongly composition dependent. Also, the computational time requirement is almost prohibitive for big problems. The algorithm, however, guarantees optimality.

Thompson and King (1972) [T3] have presented a systematic method suitable for computer implementation. A "cheapest first" heuristic has been used to create
several good separation sequences to isolate multicomponent. products from a given feed without a large consumption of computer time. In the beginning a feasible produci set is identified based on feed composition and at a typical process temperature. The cheapest separator is picked by comparing predicted costs of alternate separation units. After the sequence is decided, it is simulated and actual costs computed are used to update cost coefficients used for cost prediction. Since computations are performed in the forward direction, the compositions of the streams are known exactly. However, this procedure faces a unique problem of "cycling" for which no satisfactory solution is given. In this work several large scale examples have been considered.

Westerberg and Stephanopoulos (1975) [17] have proposed a branch and bound search technique. Sub-Lagrangians for all possible subsystems are computed first. Based on "choose the potentially cheapest unit first" heuristic, a basic flowsheet is created and dual and primal bounds are computed. Flowsheets whose dual bound exceeds the primal bound of the basic flowsheet are rejected. The remaining flowsheets can be further screened by repetition of the procedure above. The choice of the basic flowsheet and the value of the primal bound for the basic flowsheet are crucial; neither of which is a trivial problem. two example problems have been solved by the proposed method.

In a later paper Stephanopoulos and Westerberg (1976) [S2] have proposed three evolutionary rules for the synthesis of separation processes. These rules are such that, starting from any feasible flowsheet, any other feasible flowsheet can be generated by applications of these rules in finite iterations. Rules 1 and 2 are applied first. Neighboring structures are thus created. Each of the structures is simulated and the one with the cheapest cost is retained. Then, rule 3 is applied to generate a new class of neighbors and the cheapest one is retained. The process above is repeated until no better flowsheet is obtained. In this work, the MSA is treated unlike other products and is isolated in the immediate successor unit after use. Also, the starting structure is crucial in the success of this search scheme. This approach can be improved by using an n-step look-ahead strategy but at the cost of greatly increased computational time.

Freshwater and Henry (1975) [F1] have presented a detailed cost and total energy requirement for three, four and five component systems as a function of configuration. Detailed analyses were made as a function of feed composition. For an $N$ component system $N+2$ different feeds were considerẻ. System feed streams consisted of hydrocarbons in the range $C 4$ through $\mathbf{C 7}$. Only simple distillations units were considered and products were all relatively pure single components. Surprisingly, for most cases considered
the direct sequence was the optimum configuration. The study, however, confirms a direct proportionality between energy requirement and cost.

Rodrigo and Seader (1975) [93] have outlined a modified depth-first method [N1]. Multiplicate'separators are identified and are analyzed no more than once. This approach is computationally superior to the DP algorithm, but still has the shortcomings of the DP algorithm.

In a later paper, Gomez and Seader (1976) [G1]
have further refined the search procedure by using a modified uniform cost method [if2].

In a recent note, Seader and westerberg (1977) [S1]
have proposed a combined heuristic and evolutionary strategy for synthesis of simple separator sequences. Six heuristics have been suggested for the creation of the initial structure and two evolutionary rules have been suggested. Two example problems have been synthesized manually by the proposed strategy. In the first example, the optimum structure is obtained in two evolutionary steps, but in the second example the proposed strategy fails to produce the optimum flowsheet due to the failure of one heuristic.

In another recent paper, Bakshi and Gaddy (1977) [B1] have analysed nine separation problems by exhaustive search over the space of configurations. The reflux ratio for each column and the pressure for the first column in the sequence
has been optimized by a random search technique. Three comonly used heuristics have been tested, but no strategy for the application of these heuristics to solve a synthesis problem has been proposed.

References cited so far in this section deal with the synthesis of conventional separation systems. In addition, the product specification is such that a specie can be specified to be present in only one product. Relaxing the restriction on product specifications to include the cases in which a specie can be specified to be present in more than one products leads to a related synthesis problem. This class of synthesis problems may have nonsharp separation units. There has been no previous work for this class of synthesis problems. A preliminary graphical procedure for nonsharp separation synthesis is developed in Chapter 8.

Another related synthesis problem exists for the cases when complex separation units are considered. The treatment of such problems is more complicated. Research performed in this area is limited to the cases isolating single component products from a ternary feed stream using complex distillation units. Petlyuk (1965) [P1] examined four complex configurations and two conventional configurations (direct and indirect arrangement of two distillation units) for a three component system. The total specific amount of liquid vaporized was used to compare different configurations. Ten different compositions were considerd.

For each composition, complex schemes were better than the conventional schemes. Stupin and Lockhart (1972) [S3] in a case study compared one complex scheme and the two conventional schemes for an equimolar ternary feed stream. The complex scheme had about $20 \%$ less vapor boil-up than the conventional shcemes. Tedder (1976) [T1] has presented a more thorough analysis for ternary feed streans. Six ternary hydrocarbon systems have been considered. For each ternary system, detailed design and costing is performed For seven different compositions and for six complex and two conventional configurations. The results of this study have been summarized on ternary diagrams on which the optimum designs are given as a function of composition.

### 1.3 Problem Definition

Given a feed stream of known conditions (i.e., composition, flow rate, temperature, pressure), systematically synthesize a process that can isolate the specified products from the feed at minimum cost.

```
Min [\Sigma C C ]
i \epsilon I is a feasible separation unit
    Ci is the total annual cost of i
    I is a subset of S
    S is the set of all possible separator
        configruations that can produce the desired
        products
```

The desired products are such that a specie is required to be present in only one product. Each product may be specified in terms of desirєd recovery and/or purity.

The separation types are restricted to conventional distillation and extractive distillation methods. For the extractive distillations the solvents used are to be recycled. The input information is to be kept at a minimum.

### 1.4 Proposed Method

An evolutionary method is presented. The method consists of two phases. In the first phase, a very good starting structure is created by heuristic methods. In the second phase, the starting structure is modified by making evolutionary changes. The evolutionary changes are made by following five evolutionary rules. These rules are applied in a hierarchical manner until no noäification can be detectẻ. The structure thus obtained is termed the "optimal structure" and is not changed in the later work.

The products isolated from the optimal design do not usually satisfy the specified recovery and/or purity restrictions so far. Therffore, the split fractions of the light keys and the heavy keys are udjusted to obtain the specified product recoveries and purities. After this, the reflux ratio of each column in the sequence is optimized by a bisection method.

The overall logi.c diagram for the procedure above is given in Figure 1.4-1.

In the following chapters, each aspect of the proposed method is discussed in detail. Chapter 2 contains a discussion of the heuristic rules for creation of the initial structure and Chapter 3 gives the evolutionary rules for modification of structures. Trarsformations ir the space of species are defined in Chapter 4. In Chapter 5 a procedure to satisfy the product recovery and/or purity specifications is developea. A bisection algorithm for the optimization of operating reflux ratio for a separation unit is described in Chapter 6. Several sample problems which were synthesized by the proposed method are discussed in Chapter 7.

### 1.5 Definitions

Some of the terms used in this dissertation have special meaning and are defined here. A separation factor between two components is the ratio of the distribution coefficients of those two components. A distribution coefficient or distribution factor is the ratio of component mole fraction in the lighter phase to that in the heavier phase, at equilibrium, or, in solvent phase to feed phase, if it applies. A mass separating agent (MSA) is a component added to a separation unit to affect the desired separation. A ranked list is the ranking of components in the feed in order of decreasing distribution
coefficients. Sequence, arrangement, structure, process, flowsheet and configuration have beed used interchangably and refer to an arrangement of separation units. Process stream refers to a stream in the process which needs further processing. OPEN is a set whose elements are process streams at a given time. Column, separation unit and separator are used interchangably to refer to distillation or extractive distillation equipment.


## Chapter 2

CREATION OF INITIAL STRUCTURE

The initial structure in evolutionary synthesis is crucial to the success of the evolutionary synthesis procedure. The initial structure is the starting structure on which small structure changes are made successively. If the starting structure is too unlike the optimum structure it would require many more iterations to converge. Since the evolutionary rules do not guarantee optimality in a rigorous mathematical sense, a structure too unlike the optimum would more probably lead to a local optimum rather than the global optimum. A better initial structure would, on the other hand, arrive at the optimum in less iterations and with a higher probability of reaching the global optimum.

In this chapter we propose a set of heuristic rules that in a systematic way would create a good starting structure. Most of the heuristic rules presented here have been available in the literature, but in a qualitative manner. In this chapter we have attempted to make the rules quantitative and thus suitable for computer implementation.

### 2.1 Separators as List Splitters

For sharp separations, a separator separates the input stream into two output streams, the top stream and the bottom stream. Each stream consists of a list of components and the separator can be viewed as a list splitter which splits the input list into two smaller output lists. The components in the feed stream can be ranked in the order of decreasing distribution factors for a particular separation method. The arranged list is called the ranked list. In the ranked list, the component with the largest value of the separation factor is called the lightest component and the one with the smallest value of the separation factor is called the heaviest component. A split is defined by specifying two adjacent components, the lighter of the two is called the light key and the heavier one is called the heavy key. A sharp separator splits the ranked list corresponding to its input stream into two lists. The list corresponding to the top stream contains the light key and all the lighter components and the list corresponding to the bottom stream contains the heavy key and all the heavier components.

For any multicomponent input strean, usually there are several split points. For example, Figure $2.1-1$ shows the four possible splits for a stream containing five components $A, B, C, D$ and $E$ in crder of decreasing value of distribution factor. Each of the components is to be isolated. Only one of the many possible splits belongs to


Figure 2.1-1
Splits for a Five Component Mixture
the optimal structure.
In the following sections we have presented a systematic procedure that would pick among the possible splits the one that is likely to be in a near optimal structure for a given stream. Repeated application of this procedure starting with the feed stream will result in the creation of the initial structure.

### 2.2 The Heuristic Rules

Heuristic rules for the creation of the initial structure are given below:

1) Favor the smallest product set
2) Favor distillation
3) Easiest separation should be done first
4) A separation method using a mass-separating agent (MSA) cannot be used to isolate another MSA
5) A separation with $\alpha_{\text {LK-HK }}<\alpha_{\text {min }}$ is not acceptable
6) Operating pressure should be close to ambient
7) Set split fractions of the keys to a prespecified value
8) Set operating reflux ratio equal to 1.3 times the minimum reflux ratic for each column.

These heuristic rules are in a hierarchy of degree of detail of the structure. Heuristic rule 1 concerns the product set definition. This rule is simple and is the first step in the creation of the initial structure. The product set is defined without any knowledge of the structure.

Heuristios 2, 3, 4 and 5 form a group of rules (group II) which provides guidelines for selection of the separation method and split point for each stream starting from the feed stream which is not a product stream. Heuristics 5, 6, 7 and 8 form another group of rules (group III) which provides guidelines for the detailed simulation of the design specification obtained by the previous group of rules. Heuristic rule 5 which appears in both the sets is more of an assumption aimed at cutting down the search space. For the present work $\alpha_{\text {min }}$ has been set to a value of 1.1.

In short, heuristic rule 1 fixes the product set. For this product set, and for each process stream in the structure starting from the feed stream group II of the heuristic rules supplies the design alternatives available. The best design alternative is tried for detailed simulation using group III of the heuristic rules. If the design is not feasible, the next best alternative is tried. If the design is feasible, the next process stream (the one which is not a product stream) is considered. A feasible structure may result which is later evolved, or an infeasible structure may result. If the structure is infeasible because a milticomponent product cannot be isolated, the present product set is abandoned and a new product set is defined which splits the multicomponent product which causes the structure to be infeasible. For the new product set the whole procedure is repeated.

In the remaining section we have considered each heuristic rule in detail.

### 2.2.1 Heuristic Rule 1

For a process in which the desired products are all single components, the product set is unique and trivial. If, however, the desired products include one or more multicomponent products, there are more than one product sets. In such cases, during the creation of the initial structure, strong preference is given to the smallest product set. Intuitively, a smaller product set suggests a structure with fewer separation units and probably less total cost.

The smallest product set is, of course, the user supplied product definition. With this product set the creation of the initial structure proceeds (following heuristic rules 2 through 8). In the cases when the initial structure cannot be completed either because a multicomponent product cannot be isolated or because the separation unit isolating the multicomponent product violates heuristic rule 5 , the multicomponent product is split to produce a new product set. With this product set the creation of the initial structure is attempted again.

This heuristic may not lead to the best structure, therefore the heuristic is challenged during the evolution of structures.

### 2.2.2 Heuristic Rule 2

Distillation or methods using energy-separationagents are favored because they minimize the number of separation units in the structure. For each separation unit using a mass-separaiing-agent (MSA) an additional separation unit is required to isolate the MSA. In addition, the internal flow rates are usually much higher for the separator using an MSA. These disadvantages are offset if the separation using the MSA provides a better separation factor, or if it makes the isolation of a multicomponent product feasible which is otherwise infeasible.

During the creation of the initial structure, for any stream under consideration, distillation is tried first. If distillation does not give any feasible design alternative, only then separation methods using an MSA are considered.

This heuristic may not lead to the best process and the application of this heuristic in the creation of the initial structure is subsequently negated by evolutionary changes later on.

### 2.2.3 Hemristic Rule 3

During the creation of the initial structure, for each stream having more than one possible split, we are faced with the problem of picking the one that is likely to be in a near optimum structure. We propose here to select the split which is the easiest. The easiest separation is qualitatively defined as the one which in general is in accordance with the following four heuristics.
a) Favor large $\alpha_{\text {LK-HK }}$
b) Favor a balanced column
c) Favor sloppy splits of the keys
d) Favor less distillate product

Each of the above heuristics has merit. We will now consider them one by one. Later on a quantitative formula that embodies the above four heuristics is presented.

The heuristics a and $c$ are widely accepted by the workers in this field. Favoring jaxge $\alpha_{\text {LK-HK }}$ and sloppy splits in the beginning of the synthesis leads to the selection of difficult separations, with low $\alpha_{\text {LK-HK }}$ and high recovery of the keys to be performed towards the end of the synthesis. This is ideal since these difficult separations are best suited when the stream flow rate is low (requiring low diameter for the separator) and when most of the non-key components are absent. The absence of non-key components results in a column with low temperature difference between the top and the bottom of the column thereby making it thermodynamically more efficient [K1].

Heuristic b is favored because it leads to thermodynamically efficient separators. When the amounts of overhead and bottoms products are about the same (halanced column), the refluy ratios in the sections above and below the feed will be better balanced and the operation will be more reversible [K1], and as a result the energy requirement would be less. Harbert [H1] calls this heuristic "the advantage of $50-50$ split" and justifies it on the basis of minimum heat requirement.

Heuristic $d$ favors, other things being equal, a separator with less distillate product. The operating costs for a column vary directly with the amount of distillate. Consequently the split with the smaller amount of distillate implies lower operating expenses and is preferred if other things are equal. A sequence generated by this heuristic alone would result in a direct sequence of separators.

If, for a split, all four heuristics were favored, we have a good choice and can be reasonably sure that the separation would lead to a good structure. However, in most cases, the heuristics will be in conflict. For example, if, for a given stream, the split that gives the largest $\alpha_{\text {IJK-HK }}$ is not balanced and the split that gives a balanced column has a poor $\alpha_{\text {LK-HK }}$, then the two heuristics (a and b) point toward different decisions. Such conflicts can be resolved ky giving each split a numerical value
proportional to the difficulty of separation. This value should be such that it represents the four heuristics in a quantitative fashion. We propose here such a function, called the coefficient of difficulty of separation (CDS)

$$
\mathrm{CDS}=\frac{\log \left(\frac{s p_{L K}}{1-s p_{L K}} \cdot \frac{s p_{H K}}{1-s p_{H K}}\right)}{\log \alpha_{L K-H K}} \cdot \frac{V}{V+L} \cdot\left(1+\left|\frac{V-I}{V+L}\right|\right)
$$

The first term is the number of theoretical stages and takes into account heuristics $c$ and $d$ realistically. The second term is the fraction distillate and accounts for heuristic d. The last term is a penalty term which penalizes unbalanced columns. When $V=I_{1}$, the column is balanced and this term is unity. For any other values of V and L , the term is always greater than 1 . The last term is a mathematical analog of heuristic b.

With this CDS function in hand we are in a position to evaluate each possible split for a stream in a quantitative way. The split with the least value of $C D S$ is tried for detailed simulation; if it is infeasible, then the split with the next smallest value is tried. This decisionmaking procedure is used for each stream that needs to be processed in the structure, resulting in the creation of the initial structure.
2.2.4 Heuristic Rules 4 and 5

Heuristic rule 4 pronibits the use of a separation using an MSA to isolate another MSA. This is inline with heuristic rule 2, favoring distillation. Moreover, by this rule, we have eliminated the possibility of absurd sequences having an indefinite number of columns in which an MSA is isolated using another MSA which is isolated using another MSA and so forth.

Heuristic rule 5 is more of an assumption, separators with $\alpha_{L K-H K}$ less than $\alpha_{\text {min }}$ are rejected. This assumption is quite sensible since very low values of $\alpha$ result in extremely expensive columns. For the present study $\alpha_{\min }$ is arbitrarily set to a value of 1.1 .

## 2.2-5 Heuristic Rules 6,7 and 8

These rules provide guidelines for selecting the operating conditions for a separation unit. Operating pressure is set close to the ambient, the reflux ratio is set to 1.3 times the minimum and the design of the column is performed for prespecified values of recovery for each key. After the best structure has been obtained by evolution, some of the operating conditions are optimized.

### 2.3 The Proposed Procedure

The proposed procedure for the creation of the initial structure is shown in Figure 2.3-1. In the flowsheet, the number within parenthesis refars to the heuristics
employed in the particular processing. In Chapter 7, this procedure is illustrated in detail for some of the example problems.



S? $\equiv$ All Separation Methods Considered?

Figure 2.3-1 Continued

## Chapter 3

## EVOLUTION OF STRUCTURES

Evolution of structures is the second step in the synthesis procedure by evolutionary methods. The initial structure created in the first step is successively modified by the application of the evolutionary rules. The evolutionary rules suggest structural modifications which usually question the validity of heuristics or other assumptions used in the creation of the initial structure. If the assumptions or heuristics were not appropriate, corrective measures are taken by the evolutionary ruies.

The evolutionary rules are applied in an hierarchical order. If a particular rule does not suggest any structural modification, then the next evolutionary rule is acplied. The evolution stops when no more modifications are possible. If, however, an evolutionary rule suggests a modification, the downstream structure is destroyed and a new structure is created by implementing the proposed change. The upstream structure remains unchanged. If the new structure created by implementing the proposed structure change is superior to the starting structure, then the new structure replaces the starting structure and is evolved further. In the other case, when the new structure is inferior to the starting one, the starting structure is restored in the computer memory and is evcived further.

The evolutionary rules used in the present work are discussed in the next section and the strategy for applying these rules is given in the section following the next cne.

### 3.1 The Evolutionary Rules

The evolutionary rules used in the proposed method are as follows:

Rule l: Challenge heuristic l
Rule 2: Examine the neighboring structures, if
a) the $\operatorname{CDS}$ is within $10 \%$
b) refrigeration is required to condense the reflux

Rule 3: Challenge heuristic 2
Rule 4: Examine neighbors to decide if the MSA removal should be delayed

Rule 5: Challenge heuristic 3, if
a) $R_{m i n}$ of the immediate successor $\gg$ $R_{\text {min }}$ of the unit under consiaderation
b) the cost of the immediate successor >> the cost of the unit under consideration

In the remaining portions of this section we will consider each evolutionary rule in detail.

### 3.1.1 Evolutionary Rule 1

For the creation of the initial structure, the smaliest feasible product set was chosen in accordance with heuristic 1. To retain the smallest product set, sometimes a separation unit using an MSA was used in the process. A separation unit using an MSA needs an additional separator to isolate the MSA (for recycle). For such cases, there is a possibility which could lead to a superior flowsheet. This possibility is to break the multicomponent product which makes use of a separation using an MSA necessary in the process into two products. The two products defined by breaking the multicomponent prodact may both be isolated using distillation units, in which case the new process will have exactly the same number of separation units and may be superior. Evolutionary rule 1 checks for such possibilities in the structure undergoing evolution.

A simple example illustrating the application of evolutionary rule 1 is considered next. For a ternary feed stream containing species $A, B$ and $C$, isolation of species A and B as product 1 and specie $C$ as product 2 using two separation methods is desired. The separation methods available are distillation (I) and extractive distillation using solvent X (II). The ranked list corresponding to these two separation methods is given below:
$R=(I): A C B X$
$R L(I I): A B C X$

The initial. structure for this problem is shown in Figure 3.1.1-1 as structure 1. Evolutionary rale 1 is applicable; the product set is altered by breaking the multicomponent product. A structure for this new product set is shown as structure 2 in Figure 3.1.1-1. In some cases, the new structure would be ecomonically superior to the starting structure.

### 3.1.2 Evolutionary Rule 2

This evolutionary rule takes into consideration some of the shortcomings of the CDS function. The CDS function defined in Section 2.2.3 is an evaluation function which assigns a numerical value proportional to the difficulty of separation for each possible split of a process stream. This evaluation is approximate since it does not consider the operating reflux ratio and the operating pressure of the separation unit in the evaluation. This approximation to some extent is compensated for in the following rules:

Rule 2a: Because of the approximate nature of the CDS function, it cannot be used to distinguish between very competitive design alternatives. To sompensate for this, designs with CDS values within $10 \%$ of each other are treated alike. Therefore, during the creation of a structure, the splits which are within $10 \%$ of the one selected for the creation of the structure are stored. During evolution these alternative splits are considered to create additional structures.
structure $1:$

structure 2:


Figure 3.1.1-1
Evolution of Structure 1 by the
Application of Evolutionary Rule 1

Rule 2b: The cost of refrigeration to condense the reflux is extremely high. The CDS function cannot predict the presence of refrigeration for a separation and consequently is not a good representation of the difficulty of separation in such cases. To rectify this shortcoming, during the creation of a structure a separation using refrigeration to condense the reflux is tagged and during evolution, for these tagged separations, other design alternatives are tried to create new structures.
3.1.3 Evolutionary Rule 3

During the creation of the initial structure, strong preference was given to the use of distillation units in the flowsheet, in accordance with heuristic 2. Evolutionaxy rule 3 questions this heuristic. For each distillation unit in the scheme, alternative separation units using an MSA are considered. Separation methods using an MSA require an additional separation unit to isolate the MSA for recycle. A separation unit using an MSA will become economically superior to a distillation unit, only if, the separation unit using the MSA would have a separation factor ( $\alpha$ ) between the I (r and the $H K$ sufficiently larger than the one for distillation. How much larger should the value of $\alpha$ be for the separation using an MSA compared to the value of of for distillation? No rigorous answer can be given to this question, however, a semi-quantitative analysis vill give an approximate
answer to this question. Kemenber that the minirum number of stages, $N_{m}$, for a separation is

$$
N_{\mathrm{m}}=\ln \frac{s p_{L K}}{1-s p_{L K}} \cdot \frac{s p_{H K}}{1-s p_{H K}} / \ln (\alpha)
$$

The numerator is fixed, therefore

$$
N_{m} \propto \frac{1}{\ell n \alpha}
$$

As a first approximation, we can assume that the actual number of stages, $N$, also has a similar proportionality,

$$
N \propto \frac{1}{\ln \alpha}
$$

If $\alpha$ for the separation using an MSA has a magnitude equal to the square of $\alpha$ for distillation, then the number of stages for the separation unit using an MSA would be half the number of stages for the distillation unit. To a first approximation, the cost of the separation using an MSA would be about half of the cost of the distillation unit. In this case the combined cost of the separation unit using an MSA and the separation unit isolating the MSA may be less than the cost of the distillation unit.

Based on the above semi-quantitative reasoning, the following criteria for consjdering a separation using an MSA instead of distillation for a split is recommended,

$$
\alpha_{\text {MS } \bar{A}} \geq \alpha^{1.95}
$$

where, $\alpha_{\text {MSA }}$ refers to the separation factor between the LK and IKK for the separation method using the MSA and $\alpha$ refers to the separation factor between the LK and $H K$ for distillation.

For a process stream, in general, several splits are possible. The criterion akove is generalized for such streams:

$$
\text { all } \begin{aligned}
& \operatorname{Max} \operatorname{splits}\left(\alpha_{\text {MSA }}\right) \geq \\
& \operatorname{Max} \\
& \text { allits } \\
& \text { splits }
\end{aligned}
$$

i.e., a separation using an MSA may be a superior alternative to distillation if the value of the largest $\alpha$ for the separation using an MSA is at least equal to the 1.95 power of the value of the largest $\alpha$ for distillation for the stream under consideration.

### 3.1.4 Evolutionary Rule 4

The MSA is generally a fairly heavy polar solvent with a low value of distribution coefficient. And since during the creation of structures, strong preference is given to easy separations in accordance with heuristic 3, there is a strong tendency to isolate the MSA immediately after its use in a separation unit. At times, this leads to structures in which there are two or more separation units using the same MSA which are arranged such that the top stream from the separator isolating the MSA, for
the first separator using an MSA, is fed to the second separator using the $M S A$ and so on. Structure 1 in Figure 3.1.4-1 shows one such structure in which each of three products, $A, B$ and $C$, is isolated in the presence of solvent $X$. Four separation units are used as shown. The same result can be obtained using fewer separation units by delaying the isolation of the MSA. The flowsheet obtained by delaying the isolation of the MSA for structure 1 is shown in structure 2 in Figure 3.1.4-1. Structure 2 has one separaさion unit less than structure 1 and would be more economical. Evolutionary rule 4 searches for patterns in which the isolation of the MSA can be delayed and creates better structures by delaying the isolation of the MSA.

### 3.1.5 Evolutionary Rule 5

For multistage structures which are generated by the present synthesis program, the easiest separation at any stage will not always lead to the optimum structure. The conclusion above is inspired by the fact that for acyclic multistage systems the cheapest subsystem at each stage will not lead to the overall cheapest system (the Optimality Principle [B2]). An easy separation at a particular stage may in fact make the next separation very difficult and may lead to a flowsheat more expensive than the one obtained when both the separations are moderately difficult. Evolutionary rule 5 is based on the above logic. In a flowsheet, the occurences of an easy separation
structure 1:

structure 2:


Figure 3.1.4-1
Application of Evolutionary Rule 4 on Structure 1
followed by a very difficult one are checked and for each such occurence new flowsheets are created by trying alternate separations instead of the easy separation.

For the flowsheet undergoing evolution, all pairs of a separation unit and its immediate successor units are checked to find if ore of the following conditions is met:
a) the minimum reflux ratio of the immediate successor is much greater than (for example, nine times) the minimum reflux ratio of the unit under consideretion
b) the cost of the immediate successor units is much greater than (for example, five times) the cost of the unit under consideration.

If either of the conditions above are true for a separation unit and its immediate successor unit then it is an indication that a rather difficult separation follows an easy one. The split for the easy separation is changed which also alters the split for the difficult separation. A new structure is created as a result of these changes and may be superior to the starting structure.

### 3.2 Evolutionary Strategy

Each of the evolutionary rules described in the previous section suggests a structure modification to improve the starting structure. The evolutionary rules can be applied in a variety of ways. A strategy to apply these rules is given next.

The definition of the product set is the single most important decision in the synthesis of separation sequences. For the creation of the initial structure the product set was defined on the basis of heuristic rule 1. Evolutionary rule 1 questions the validity of this heuristic rule and is applied before any other evolutionary rule to resolve the question of the product set definition. Evolutionary rules 2, 3, 4 and 5 are treated equally, but of course cannot all be applied at the same time. Therefore, starting from the feed stream downward, evolutionary rule 1 is applied first. If any modification is suggested by this rule, then it is adapted in the star※ing structure and a new structure is produced. The new structure or the starting one, whichever is superior, is evolved further by applying rule 2 to the portion of the structure not checked by rule 2 in the earlier application. Evolutionary rule 3 js applied starting from the feed stream downward, after no further structural modifications are suggested by rule 2 . If rule 3 suggests a modification, it is adapted to the structure undergoing evolution and a new structure is produced. The new structure or the structure undergoing evolution, whichever is superior, is evolved further. Rule 2 is applied again only to the modified portion of the structure. Rule 3 is applied again to the portion of the structure not checked by rule 3 in the earlier application. This process is repeated by applying all the evolutionary rules. Figure 3.2-1 gives a schematic represertation of this strategy.


## Chapter 4

## THE SPACE OF CHEMICAI SPECIES

### 4.1. The Space $\mathrm{S}^{\mathrm{n}}$

Let n be a fixed positive integer and let
$s^{n}$ denote the totality of ordered $n$-tuples ( $x_{1}, \ldots, x_{n}$ ) of real numbers such that $x_{i} \geq 0, i=1, \ldots, n$. If $x=\left(x_{1}, \ldots, x_{n}\right)$ and $y=\left(y_{1}, \ldots, y_{n}\right)$ are two such $n$-tuples and $\beta$ is a positive real number, define

$$
\begin{aligned}
x+y & =\left(x_{1}+y_{1}, \ldots, x_{n}+y_{n}\right) \\
\beta x & =\left(\beta x_{1}, \ldots, \beta x_{n}\right)
\end{aligned}
$$

Then $S^{n}$ becomes a space of chemical species, Each n-tuple in this space denotes a stream of $n$ conponents having a flow rate $F=\sum_{i=1}^{n} x_{i}$ and the composition of the $i^{\text {th }}$ scecie is $x_{i} / F$.

Mathematically, the space $S^{n}$ is a positive convex cone with vertex at the origin [Vi]. $s^{n}$ is also the positive orthand of the space of real numbers $R^{n}$. Figure 4.1-1 gives an abstract representation of $s^{n}$.
4.2 Transformations in $\mathrm{S}^{\mathrm{n}}$

Physically, a separator transforms a feed stream into two new streans, one from the top of the column, called the top product; and the other from the bottom of the column, called the bottom product. The top and the bottom products


Figure 4.1-1
The Space $s^{n}$
have compositions different from the feed stream. Therefore in the $S^{n}$ space a separation unit can be represented by two transformations $R_{i}$ and $S_{i}$.

In Figure $4.2-1, F=\left(f_{1}, \ldots, f_{n}\right)$ is the feed to a separation unit i. The transformation $R_{i}$ is represented by $R_{i}=\left(r_{i 1}, \ldots, r_{i n}\right)$ where $r_{i j}, l \leq j \leq n$, is the fraction of component $j$ in the feed that goes to the top product $A$. Note that $0 \leq r_{i j} \leq 1, \forall i$. The point $A$ in the space $S^{n}$ is $\left(a_{1}, \ldots, a_{n}\right)$ such that

$$
a_{j}=f_{i} \cdot r_{i j}
$$

or

$$
A=R_{i}(F)=\left(f_{1} r_{i l}, \ldots, f_{n} r_{i n}\right)
$$

Similarly, the bottom product $B$ is

$$
B=s_{i}(F)=\left(f_{1} s_{i l}, \ldots, f_{n} s_{i n}\right)
$$

Note that $R_{i}$ and $S_{i}$ themselves belong to the space $s^{n}$. Material balance over the column requires that: material in = material out. Thus,

$$
R_{i}+S_{i}=(1, \ldots, 1)
$$

### 4.3 Composition of Transformations

Each transformation in the space $\mathrm{S}^{\mathrm{n}}$ is a mapping such that

$$
\begin{array}{ll}
R_{i}: & s^{n} \rightarrow s^{n} \\
s_{i}: & s^{n} \rightarrow s^{n}
\end{array}
$$



Figure 4.2-1
Abstract Representation of a Separator in $s^{n}$

Therefore for each $X$ in the space $S^{n}, Y=R_{i}(X)$ belongs to $\mathrm{S}^{\mathrm{n}}$. So it makes sense to talk of a transformation $R_{j}$ on $Y$. Again $R_{j}(Y)$ belongs to $S^{n}$.

$$
R_{j}(Y)=R_{j}\left(R_{i}(X)\right)=R_{j} R_{i}(X)
$$

Thus $R_{j}$ and $R_{i}$ can be combined to produce a new transformation $R_{j} R_{i}$, called the product or composition of $R_{j}$ and $R_{i}$ in that order. Note that the composition here is such that

$$
R_{j} R_{i}(X)=R_{i} R_{j}(X)
$$

Figure 4.3-1 shows a sequence of separators in $s^{n}$ producing $A, B, C, D$ and $E$ from the feed $F$.

$$
\begin{aligned}
& A=R_{1}(F) \\
& B=R_{3} R_{2} S_{1}(F) \\
& C=S_{3} R_{2} S_{1}(F) \\
& D=R_{4} S_{2} S_{1}(F) \\
& E=S_{4} S_{2} S_{1}(F)
\end{aligned}
$$

### 4.4 A Special Cless of Transformations

In the next cr:apter we will talk much about an ideal separator which is defined as follows:

For a feed $F$ having $n$ components with $L K$ and HK as the light key and the feary key respectively and $\operatorname{sp}_{\text {LK }}$ and $\operatorname{sp}_{H K}$ as the specified split fraction of the light and the heavy key respectively. An ideal separator produces a top product which contains the specified fraction ( $\operatorname{sp}_{\mathrm{LK}}$ ) of


Figure 4.3-1
A Sequence of Separators in $S^{n}$
the light key and all the species jighter than the light key. The hottom product likewise has all the species heavier than the heavy key and the specified fraction $\left(s p_{H K}\right)$ of the heavy key.

If the ranked list of the $n$ components is
1, 2, .... IK, HK, ..., n, the transformations for an ideal separator take the following form:

$$
\begin{aligned}
& R_{i}=\left(1,1, \ldots, 1, s p_{L K}, 1-s p_{H K}, 0, \ldots, 0\right)_{4,4-1} \\
& s_{i}=\left(0,0, \ldots, 0,1-s p_{L K^{\prime}}, s p_{H K}, 1, \ldots, 1\right)_{4.4-2}
\end{aligned}
$$

Definition: We will define the key associated with $\mathrm{R}_{\mathrm{i}}$ as the light key LK and the key asscciated with Si as the heavy key EK.

## Chapter 5

THE PROELEMS OR PRODUCT SPECIFICATTONS

### 5.1 Introduction

In the treatment so far, we have arbitrarily fixed the split fractions of the light and heavy key in eacin column to a prespecified fraction without any concern for the overall product specifications. Generally, however, pexformance specifications are made for the desired products in terms of the product recoveries and the purities. The recovery, $r_{i}$, of product $i$ is the proportion of the components entering in the feed which leaves in the product. The purity, pi, of product $i$ is the proportion of the desired componencs in the product stream. Mathematically,

$$
\begin{array}{ll}
r_{i}=\frac{\underline{P}_{i} \sum x_{i j}}{F \Sigma Y_{i j}} & j \in c_{i} \\
p_{i}=\sum x_{i j} & j \in C_{i}
\end{array}
$$

where

$$
\begin{aligned}
& P_{i}=f \text { fow rate of product } i \\
& f=\text { flow rate of the feed stream } \\
& x_{i j}=\text { nole fraction of component } j \text { in product }: \\
& x_{f j}=\text { mole fraction of component } j \text { in the feed } \\
& C_{i}=\text { desired species in product } i
\end{aligned}
$$

Now we are facec: with the problen of computing the values of the split Eractions for each specie which would satisfy the process performance suecifications.

To hande this problem, first, a theoretical
investigation will be made to obtain a functional dependence of product recoveries and purities on split fractions. For the sake of simplification only ldeal separation units are considered in this analysis. Later, we will see how this assumption affects the results obtained by simplified analysis.

### 5.2 Theoretical Investigation for Single Component Products

We will start this analysis by considering uncomplicated schemes of separation units. For each scheme we will consider a multicomponent feed. Each of the components in the feed will be isolated as a single component product.
I) DIRECT SEQUENCE

The feed consists of $N$ components, $A, B, C, \ldots, N$. The ordering of components in descending order of separation coefficients is $A, B, C, \ldots, N$.

$$
F=\left(f_{A}, f_{B}, \ldots, f_{N}\right)
$$

For the sequence of Figure 5.3-1, the various transformations are,

| $\mathrm{R}_{1}$ | $=\left(s p_{A^{\prime}}\right.$ | $1-\mathrm{SP}_{\mathrm{B}^{\prime}}$ | 0, | 0, |  | 0, | 0, | $0)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $s_{1}$ | $=\left(1-s p_{A}{ }^{\prime}\right.$ | $s \mathrm{P}_{\text {A }}$ 。 | 1. | 1, |  | 0, | 0, | 0) |
| $\mathrm{R}_{2}$ | $=1 \quad 1$, |  | $1-s p c^{\prime}$ | 0, |  | 0 , | 0, | $0)$ |
| $\mathrm{S}_{2}$ | $=10$, | $1-\mathrm{SF}_{\mathrm{B}^{\prime}}$ | $s p_{C^{\prime}}$ | 1, |  | 1, | 1 | 1) |



Figure 5.2-1
A Direct Sequence of $N-1$ Separation Units


Product $A$ is obtained by the single tranformation $R_{1}$ on the feed and is

$$
\begin{aligned}
& A=\left(f_{A} s p_{A}, f_{B}\left(1-s p_{B}\right), 0, \ldots, 0\right) \\
& r_{A}=s p_{A} \\
& p_{A}=\frac{f_{A} s p_{A}}{f_{A} s p_{A}+f_{B}\left(1-s p_{B}\right)}
\end{aligned}
$$

Product B is obtained by composite transformations $R_{2} S_{1}$ on the feed

$$
\begin{aligned}
& B=\left(f_{A}\left(1-s p_{A}\right), f_{B} s p_{B}^{2}, f_{C}\left(1-s p_{C}\right), 0, \ldots, 0\right) \\
& r_{B}=s p_{B}^{2} \\
& p_{B}=\frac{f_{B} s p_{B}^{2}}{f_{A}\left(1-s p_{A}\right)+f_{B} s p_{B}^{2}+f_{C}\left(1-s p_{C}\right)}
\end{aligned}
$$

similarly

Procuct C
Transformation: $\mathrm{R}_{3} \mathrm{~S}_{2} \mathrm{~S}_{1}$.
associated keys: C C B

$$
r_{C}=s p_{C}^{2}
$$

$$
p_{C}=\frac{f_{C} s p_{C}^{2}}{f_{B} s p_{B}\left(1-s p_{B}\right)+f_{C} s p_{C}^{2}+f_{D}\left(1-s p_{D}\right)}
$$

Product $\mathrm{N}-2$
Transformation: ${ }^{R}{ }_{N-2} S_{N-3} \cdots S_{2} S_{1}$
associated keys: $\mathrm{N}-2 \mathrm{~N}-2 \ldots \mathrm{C}$ B

$$
r_{N-2}=s p_{\mathrm{N}-2}^{2}
$$

$$
p_{N-2}=\frac{f_{N-2} s p_{N-2}^{2}}{f_{N-3} s p_{N-3}\left(1-s p_{N-3}\right)+f_{N-2} s p_{N-2}+f_{N-1}\left(1-s p_{N-1}\right)}
$$

Product $\mathrm{N}-1$
Transformation: $R_{N-1} S_{N-2} \ldots S_{2} S_{1}$
associated keys: $N-1 \quad N-1 \ldots$ C $B$

$$
r_{N-1}=s p_{N-1}^{2}
$$

$$
p_{N-1}=\frac{f_{N-1} s p_{N-1}^{2}}{f_{N-2} s p_{N-2}\left(1-s p_{N-2}\right)+f_{N-1} s p_{N-1}^{2}+f_{N}\left(1-s p_{N}\right)}
$$

Product $N$

| Transformation: | $S_{N-1}$ | $S_{N-2}$ | $\cdots$ | $S_{2}$ | $S_{1}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| associated keys: | $N$ | $N-1$ | $\ldots$ | $C$ | $B$ |

$$
\begin{aligned}
& r_{N}=s p_{N} \\
& p_{N}=\frac{f_{N} s p_{N}}{f_{N-1} s p_{N-1}\left(1-s p_{N-1}\right)+f_{N} s p_{N}}
\end{aligned}
$$

Generalization: based on the foregoing analysis we can conclude the following:

$$
\begin{align*}
& r_{i}=s p_{i}^{\eta_{i}} \\
& p_{i}=\frac{5.2-1}{f_{i-1} s p_{i-1}^{\eta_{i-1}^{-1}}\left(1-s p_{i-1}\right)+f_{i} s p_{i}^{\eta_{i}}} \\
&+f_{i+1}\left(1-s p_{i+1}\right)
\end{align*}
$$

where $\quad \eta_{i}=$ number of times component $i$ has been a key component in the sequence.
II) INDIRECT SEQUENCE

A six component feed is analysed. The components are $A, B, C, D, E, F$ in the decreasing order of separation coefficients.

$$
F=\left(f_{A}, f_{B}, f_{C}, f_{D}, f_{E}, f_{F}\right)
$$

The indirect sequence for this feed is shown in Figure 5.2-2. The various transformations are
$\left.\begin{array}{llllllll}R_{1}= & 1, & 1, & 1, & 1, & s p_{E^{\prime}} & 1-s p_{F}\end{array}\right)$


Figure 5.2-2
An Indirect Sequence of Separation Units


## Product F

Transformation: $S_{1}$
associated key: F

$$
r_{F}=s p_{F}
$$

$$
p_{F}=\frac{f_{F} s p_{F}}{f_{E}\left(l-s p_{E}\right)+f_{F} s p_{F}}
$$

Product E
Transformation: $\quad S_{2} R_{1}$
associated keys: E E
$r_{E}=s p_{E}^{2}$
$p_{E}=\frac{f_{E} s p_{E}^{2}}{f_{D}\left(1-s p_{D}\right)+f_{E} s p_{E}^{2}+f_{F}\left(1-s p_{F}\right)}$

Product D Transformation: $S_{3} R_{2} R_{1}$
associated keys: D D E

$$
r_{D}=s p_{D}^{2}
$$

$$
p_{D}=\frac{f_{D} s F_{D}^{2}}{f_{C}\left(1-s p_{C}\right)+f_{D} s p_{D}^{2}+E_{E} s p_{E}\left(1-s p_{E}\right)}
$$

Product $C$
Transformation: $S_{4} R_{3} R_{2} R_{1}$
associated keys: C C D E

$$
\begin{aligned}
& r_{C}=s p_{C}^{2} \\
& p_{C}=\frac{f_{C} s p_{C}^{2}}{f_{B}\left(1-s p_{B}\right)+E_{C} s p_{C}^{2}+f_{D} s p_{D}\left(1-s p_{D}\right)}
\end{aligned}
$$

Product B
Transformation: $\quad S_{5} R_{4} R_{3} R_{2} R_{1}$
associated keys: $B \quad B \quad C \quad D \quad E$

$$
\begin{aligned}
& r_{B}=s p_{B}^{2} \\
& p_{B}=\frac{f_{B} s p_{B}^{2}}{f_{A}\left(1-s p_{A}\right)+f_{B} s p_{B}^{2}+f_{C} s p_{C}\left(1-s p_{C}\right)}
\end{aligned}
$$

Product A
Transformation: $\quad R_{5} R_{4} R_{3} R_{2} R_{1}$
associated keys: A B C D E

$$
\begin{aligned}
& r_{A}=s p_{A} \\
& p_{A}=\frac{f_{A} s p_{A}}{f_{A} s p_{A}+f_{B} s p_{B}\left(1-s p_{B}\right)}
\end{aligned}
$$

Generalization:

$$
\begin{aligned}
r_{i}= & s p_{i}^{\eta_{i}} \\
p_{i}= & \frac{f_{i} s p_{i}^{\eta_{i}}}{f_{i-1}\left(1-s p_{i-1}\right)+f_{i} s p_{i}^{\eta_{i}}+f_{i+1}^{s p_{i+1}^{n_{i+1}}}} \begin{aligned}
-1 \\
\left(1-s p_{i+1}\right)
\end{aligned} \\
& f_{0}=0 \\
& f_{N+1}=0
\end{aligned}
$$

III) SYMMETRIC SEQUENCES

First we will consider a symmetric sequence consisting of three columns and processing a feed consisting of four components $A, B, C$ and $D$. The feed is

$$
F=\left(f_{A}, f_{B}, f_{C^{\prime}}, f_{D}\right)
$$

The ordering of components in descending order of separation coefficients is $A, B, C, D . \quad$ The various transformations for the sequence in Figure 5.2-3 are:
$R_{1}=\left(\quad 1, \quad \operatorname{sp}_{B^{\prime}}, 1-\operatorname{sp}_{C^{\prime}} \quad 0\right)$
$S_{1}=\left(\quad 0,1-s p_{B}, \quad s p_{C}\right.$,
1)
$R_{2}=\left(\operatorname{sp}_{A}, 1-s p_{B}, \quad 0,0\right)$
$s_{2}=\left(1-s p_{A}, \quad s p_{B^{\prime}} \quad 1\right.$,
1)
$R_{3}=\left(1, \quad 1, \quad s p_{C}, 1-s p_{D}\right)$
$s_{3}=\left(0, \quad 0,1-s p_{C}, \quad s p_{D}\right)$

Product A Transformation: $R_{2} R_{1}$
associated keys: A B

$$
\begin{aligned}
& r_{A}=s p_{A} \\
& p_{A}=\frac{f_{A} s p_{A}}{f_{A} s p_{A}+f_{B} s p_{B}\left(1-s p_{B}\right)}
\end{aligned}
$$



Figure 5.2-3
A Symmetric Sequence of Three Separation Units

Proãuct B

$$
\begin{array}{ll}
\text { Transformation: } & S_{2} R_{1} \\
\text { associated keys: } & B \quad B
\end{array}
$$

$$
r_{B}=s F_{B}^{2}
$$

$$
p_{B}=\frac{f_{B} s p_{B}^{2}}{f_{A}\left(I-s p_{A}\right)+f_{B} s p_{B}^{2}+f_{C}\left(I-s p_{C}\right)}
$$

Product C
Transformation: $R_{3} S_{1}$
associated keys: C C
$r_{C}=s p_{C}^{2}$

$$
p_{C}=\frac{f_{C} s p_{C}^{2}}{f_{B}\left(1-s p_{B}\right)+f_{C} s p_{C}^{2}+f_{D}\left(1-s p_{D}\right)}
$$

Product D
Transformation: $S_{3} S_{1}$ associated keys: D C

$$
r_{D}=s p_{D}
$$

$$
p_{D}=\frac{f_{D} s p_{D}}{f_{C} s p_{C}\left(1-s p_{C}\right)+f_{D} s p_{D}}
$$

The expression for purity seems to be a combination of the purity expressions of the direct and indirect sequence.

We conjecture at this stage that

$$
\begin{align*}
r_{i}= & s p_{i}^{\eta_{i}} \\
p_{i}= & \frac{f_{i-1}\left[s p_{i-1}^{\left.\eta_{i+1}^{-1}\right]^{\delta} s p_{i}^{\eta_{i}}}\right]^{\eta_{i}^{i}}\left(1-s p_{i-1}\right)+f_{i} s p_{i}^{\eta_{i}}}{} \\
& \left.+f_{i+1}\left[s p_{i+1}^{\eta}\right]^{-1}\right]_{i+1, i}^{\left.\delta i-s p_{i+1}\right)}
\end{align*}
$$

where

$$
\begin{aligned}
\delta_{k_{r} i} & =1 \quad \text { if } i-1 \text { has been a key associated with } \\
& \text { any of the transformations required } \\
& =0 \quad \text { to produce product } i \\
f_{0} & =f_{N+1}=0
\end{aligned}
$$

Now we will consider an eight component feed to the symmetric sequence of separation units. The sequence is shown in Figure 5.2-4.

$$
F=\left(f_{A}, f_{B^{\prime}}, f_{C}, f_{D^{\prime}}, f_{E^{\prime}}, f_{F}, f_{G}, f_{H^{\prime}}\right)
$$

Transformations associated with the various units in the sequence are given below.

| $\mathrm{R}_{1}=1$ | I, | 1, | 1, | $s P_{D}$, | $1-s p_{E}$, | 0, | 0 , | $0)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $S_{1}=1$ | 0 , | 0 , |  | $\mathrm{SP}_{\mathrm{D}}{ }^{\prime}$ | $s p_{E}$, | 11 | 1, | 1) |

$R_{2}=\left(i, \quad s p_{B}, l-s p_{C}, \quad 0, \quad 0, \quad 0, \quad 0\right.$,
0)
$s_{2}=\left(0,1-s p_{B} \quad s p_{C} \quad 1, \quad 1, \quad 1, \quad 1\right.$,
1)
$R_{3}=\left(1,1, \quad 1, \quad 1, \quad 1, \quad s p_{F^{\prime}}, 1-s p_{G}\right.$,
$S_{3}=\left(0, \quad 0, \quad 0, \quad 0, \quad 0,1-s p_{F^{\prime}} \quad s p_{G^{\prime}}^{\prime}\right.$
$R_{4}=\left(\begin{array}{llllll}s p_{A}, & 1-s p_{B}, & 0, & 0, & 0, & 0,\end{array}\right.$
$S_{4}=\left(1-s p_{A}, \quad s p_{B}, \quad 1, \quad 1, \quad 1, \quad 1, \quad 1\right.$,
1)


Figure 5.2-4
Symmetric Sequence of Seven Separation Units


## Product A

Transformation: $\quad \mathrm{R}_{4} \mathrm{R}_{2} \mathrm{R}_{1}$
associated keys: A B D

$$
r_{A}=s p_{A}
$$

$$
p_{A}=\frac{f_{A} s p_{A}}{f_{A} s p_{A}+\varepsilon_{B} s p_{B}\left(1-s p_{B}\right)}
$$

Product B
Transformation: $\quad S_{4} R_{2} R_{1}$
associated keys: B B D
$r_{B}=s p_{B}^{2}$

$$
p_{B}=\frac{f_{B} s p_{B}^{2}}{f_{A}\left(1-s p_{A}\right)+f_{B} s p_{B}^{2}+f_{C}\left(1-s p_{C}\right)}
$$

Product C
Transformation: $\quad \mathrm{R}_{5} \mathrm{~S}_{2} \mathrm{R}_{1}$
associated keys: C C D

$$
\begin{aligned}
& r_{C}=s p_{C}^{2} \\
& p_{C}=\frac{f_{C} s p_{C}^{2}}{f_{B}\left(1-s p_{B}\right)+f_{C} s p_{C}^{2}+f_{D} s p_{D}\left(1-s p_{D}\right)}
\end{aligned}
$$

Product D
Transformation: $\quad S_{5} S_{2} R_{1}$
associated keys: D C D

$$
r_{D}=s p_{D}^{2}
$$

$$
p_{D}=\frac{f_{D} s p_{D}^{2}}{f_{C} s p_{C}\left(1-s p_{C}\right)+f_{D} s p_{D}^{2}+f_{E}\left(1-s p_{E}\right)}
$$

Product E
Transformation: $\mathrm{R}_{6} \mathrm{R}_{3} \mathrm{~S}_{1}$ associated keys: E F E

$$
r_{E}=s p_{E}^{2}
$$

$$
p_{E}=\frac{f_{E} s p_{E}^{2}}{f_{D}\left(1-s p_{D}\right)+f_{E} s p_{E}^{2}+f_{F} s p_{F}\left(1-s p_{F}\right)}
$$

Product $F$
Transformation: $S_{6} \mathrm{R}_{3} \mathrm{~S}_{1}$
associated keys: F F E

$$
\begin{aligned}
& x_{F}=s p_{F}^{2} \\
& p_{F}=\frac{f_{F} s p_{F}^{2}}{f_{E} s p_{E}\left(1-s p_{E}\right)+f_{F} s p_{F}^{2}+f_{G}\left(1-s p_{G}\right)}
\end{aligned}
$$

Product G
$\begin{array}{llll}\text { Transformation: } & \mathrm{R}_{7} & \mathrm{~S}_{3} & \mathrm{~S}_{1} \\ \text { associated keys: } & \mathrm{G} & \mathrm{G} & \mathrm{E}\end{array}$
$r_{G}=s p_{G}^{2}$
$p_{G}=\frac{f_{G} s p_{G}^{2}}{f_{F}\left(1-s p_{F}\right)+f_{G} p_{G}^{2}+f_{H}\left(I-s p_{H}\right)}$

Transformation: $S_{7} S_{3} S_{1}$
associated keys: H G E

$$
r_{H}=s p_{H}
$$

$$
P_{H}=\frac{f_{H} s p_{H}}{f_{G} s p_{G}\left(1-s p_{G}\right)+f_{E} s p_{H}}
$$

Conclusion: The recovery and purity for this sequence can be predicted by equations 5.2-1 and 5.2-4.

In retrospect we notice that equations 5.2-1 and 5.2-4 also predict correctly the recovery and purity expressions for direct and indirect sequences of separation columns.

Since a general separation scheme is a combination of the direct, the indirect and the symmetric sequences, we can safely conclude that Equetions 5.2-1 and 5.2-4 can be used to predict recovery and purity of single component products produced by any separation sequence.

### 5.3 Analysis for Multicomponent Products

So far the analysis has been restricted to the cases where only single components products have been considered. Now we will relax this constraint and consider cases involving multicomponent products, to obtain analytical expressions for the recovery and the purity of products.

For the purpose of analysis we will consider here a direct sequence of separators, Figure 5.3-1, processing seven components and producing five products.


Figure 5.3-1
A Direct Sequence Froducing Multicomponent Products

Feed $=\left(f_{A}, f_{B}, f_{C}, f_{D}, f_{E}, f_{F}, F_{G}\right)$

Components $A$ and $B$ and components $D$ and $E$ are produced as multicomponents products.

Transformations corresponding to various separators are:

| $\mathrm{R}_{1}=$ | 1, $\mathrm{sp}_{\mathrm{B}^{\prime}} \mathrm{l}^{-s p_{C}}{ }^{\prime}$ | 0 , | 0 , | 0 , | 0) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{s}_{1}=($ | $0,1-s p_{B}, \quad s p_{C}$, | 1, | 1, | 1, | 1) |

$R_{2}=\left(1, \quad 1, \quad s p_{C}, 1-s p_{D}, \quad 0,0,0\right)$
$s_{2}=\left(0, \quad 0,1-s p_{C}, \quad s p_{D}, \quad 1, \quad 1\right.$
1)
$R_{3}=\left(1, \quad 1, \quad 1, \quad 1, \quad s p_{E}, 1-s p_{F}, \quad 0\right)$
$s_{3}=\left(0,0, \quad 0, \quad 0,1-s p_{E^{\prime}} \quad s p_{F^{\prime}} \quad 1\right)$
$R_{4}=\left(1, \quad 1, \quad 1, \quad 1, \quad 1, \quad s p_{F}, 1-s p_{G}\right)$
$S_{4}=\left(\quad 0, \quad 0, \quad 0, \quad 0, \quad 0,1-\mathrm{sp}_{\mathrm{F}}, \quad \mathrm{sp}_{\mathrm{G}}\right.$ )

Product \#1
Transformation: $R_{1}$
associated key: B

$$
\begin{aligned}
& r_{1}=\frac{f_{A}+f_{B} s p_{B}}{f_{A}+f_{B}} \\
& p_{I}=\frac{f_{A}+f_{B} s p_{B}}{f_{A}+f_{B} s \underline{D}_{B}+f_{C}\left(1-s p_{C}\right)}
\end{aligned}
$$

Proauct \#2
Transformation: $\quad \mathrm{R}_{2} \mathrm{~S}_{1}$
associated keys: C C

$$
\begin{aligned}
& r_{2}=s p_{C}^{2} \\
& p_{2}=\frac{f_{C} s p_{C}^{2}}{f_{B}\left(1-s p_{B}\right)+f_{C} s p_{C}^{2}+f_{D}\left(1-s p_{D}\right)}
\end{aligned}
$$

Product \#3 Transformation: $R_{3} S_{2} S_{1}$

> associated keys: E D C
$r_{3}=\frac{f_{D} s p_{D}+f_{E} s p_{E}}{f_{D}+f_{E}}$
$p_{3}=\frac{f_{D} s p_{D}+f_{E} s p_{E}}{f_{C} s p_{C}\left(1-s p_{C}\right)+f_{D} s p_{D}+f_{E} s p_{E}+f_{F}\left(1-s p_{F}\right)}$

Product \#4
Transformation: $\mathrm{R}_{4} \mathrm{~S}_{3} \mathrm{~S}_{2} \mathrm{~S}_{1}$ associated keys: $F$ F D C $r_{4}=s p_{F}^{2}$
$p_{4}=\frac{f_{F} s p_{F}^{2}}{f_{E}\left(1-s p_{E}\right)+f_{F} s p_{F}^{2}+f_{G}\left(1-s p_{G}\right)}$

Product \#5
Transformation: $S_{4} S_{3} S_{2} S_{1}$
associated keys: G F D C
$r_{5}=s p_{G}$
$p_{5}=\frac{f_{G} s p_{G}}{f_{F} s p_{F}\left(1-s p_{F}\right)+f_{G} s p_{G}}$

All the above equations for recovery and purity can be derived from the following equations. In the equations,
i\& refers to the component just lighter then the lightest component in product $i$ and ih reiers to the component just heavier than the heaviest component in product i.

$$
r_{i}=\frac{\sum f_{j} p_{j}^{\eta_{j}}}{\sum f_{j}} \quad j \in c_{i} \quad \frac{\sum f_{j} s p_{j}^{\eta_{j}}}{\left.f_{i \ell}\left[s p_{i \ell}^{\eta_{i \ell}}\right]^{-i}\right]^{\delta_{i \ell, i}}\left(1-s p_{i \ell}\right)+\sum f_{j} s p_{j}^{\eta_{j}}+f_{i h}\left(1-s p_{i h}\right)}
$$

From the equations above we can now deduce expressions for the recovery and the purity of products produced in any arbitrary sequence of separation units.

$$
\begin{align*}
r_{i}= & \frac{\sum f_{j} s p_{j}^{\eta_{j}}}{\sum f_{j}} \quad j \in c_{i} \\
p_{i}= & \frac{\sum f_{j} s p_{j}^{\eta_{j}}}{\left.f_{i \ell}\left[s p_{i \ell}^{\eta_{i \ell}}\right]^{-1}\right]_{i \ell, i}^{\delta_{i \ell}}\left(1-s p_{i \ell}\right)+\Sigma f_{j} s p_{j}^{\eta_{j}}} \\
& +f_{i h}\left[s p_{i h}^{\eta_{i h}}\right]^{\delta_{i h_{1}, i}}\left(1-s p_{i n}\right)
\end{align*}
$$

### 5.3.1 Some Important Derivatives

Derivatives are important since they give the direction of maximum change of a function. In Section 5.6 and 5.7 we will need to change $r_{i}^{\prime} s$ and $p_{i}$ 's. Here we will get analytical expressions for the derivatives of $r_{i}$ and $p_{i}$.
5.3.1.1 Derivatives of $r_{i}$

The general expression is:

$$
\partial r_{i}=\frac{1}{\sum f_{j}}\left(\sum{\underset{f}{j}}^{n_{j}}{ }^{\sigma p_{j}}{ }_{j}^{-1} \delta s p_{j}\right) \quad j \in C_{i} \quad \text { 5.3.1.1-1 }
$$

For a single component product the equation above is simply

$$
\begin{aligned}
\partial r_{i} & =\eta_{j} s p_{j}^{\eta_{j}^{-l}} \delta s p_{j} \\
\delta s p_{j} & =\frac{\delta r_{i}}{\eta_{j} s p_{j} \eta_{j}^{-1}}
\end{aligned} \quad j \in c_{i}
$$

and for small changes

$$
\Delta s p_{j}=\frac{\Delta r_{i}}{\eta_{j} s p_{j}}
$$

For a multicomponent product, some of the $\eta$ 's may be zero. Assume $\eta_{\ell}=0, \ell \subset j$ and $\eta_{k} \neq 0 \quad k \subset j, k \cup \ell=j$. In this case the expression for the derivative is

$$
\partial r_{i}=\frac{1}{\sum f_{j}}\left(\sum f_{k} \eta_{k} s p_{k}^{\eta_{k}^{-1}} \delta s p_{k}\right)
$$

Assume that all $\delta s p_{k}$ are equal, then

$$
\delta r_{i}=\frac{1}{\Sigma f_{j}}\left(\Sigma f_{k} n_{k} s p_{k}^{n_{k}-1}\right) \hat{o s p_{k}}
$$

and for small changes

$$
\begin{align*}
& \Delta s p_{k}=\frac{\Delta r_{i}\left(\Sigma f_{i}\right)}{\sum f_{k} \eta_{k} s p_{k}^{r_{k}}} \\
& \Delta s p_{2}=0
\end{align*}
$$

The equation above implies that the increments $\Delta \mathrm{sp}_{j}$ will increase the recovery of product $i$ by $\Delta r_{i}$ for small changes in the $\Delta s p_{j}{ }^{\prime} s$ and in $\Delta r_{i}$. (Note that the $\Delta s p_{j}{ }^{\prime} s$ calculated above are only one of the many possibilities for achieving a change $\Delta r_{i}$ in the recovery of $i$. )
5.3.1.2 Partial Derivatives of $p_{i}$

1) Partial derivative of $p_{i}$ with respect to $s p_{j}$ 's, $s p_{\ell}=0, s p_{k} \neq 0, \ell u k=j, j \in c_{i}$

$$
\begin{aligned}
\partial p_{i} & \left.=\frac{\left(\sum f_{k} \eta_{k} s p_{k}^{\eta_{k}^{-1}} \partial s p_{k}\right)}{[ }-\frac{\left(\sum f_{j} s p_{j}^{\eta} \cdot \Sigma f_{k} \eta_{k} s p_{k}^{\eta_{k}}{ }^{-1} \partial s p_{k}\right)}{[ }\right] \\
& =\frac{\left(\sum f_{k} n_{k} s p_{k}^{\eta_{k}-1} \partial s p_{k}\right.}{[ }\left(1-p_{i}\right)
\end{aligned}
$$

where [ ] represents the denominator in Equation 5.3-3.

Assume that all $s p_{k}^{\prime}$ s are equal, then

$$
\partial p_{i}=\frac{\sum f_{k} \eta_{k} s p_{k}^{\eta_{k}-1}}{[ }\left(1-p_{i}\right) \delta s p_{k}
$$

$$
\begin{aligned}
\Delta s p_{k} & =\frac{\Delta p_{i}}{\left(1-p_{i}\right) p_{i}} \cdot \frac{\sum f_{j} s p_{j}^{\eta_{j}}}{\sum f_{k} \eta_{k} s p_{k}^{\eta_{k}}} \\
\Delta s p_{\ell} & =0
\end{aligned}
$$

for a single component product, the above reduces to

$$
\Delta s p_{j}=\frac{\Delta p_{i}}{\left(1-p_{j}\right) p_{j}} \frac{s p_{j}}{\eta_{j}} \quad j \in c_{i}
$$

2) Partial derivative of $p_{i}$ with respect to $\operatorname{sp}_{i \ell}, f_{i \ell}>0$

Case $1 \quad \delta_{i \ell, i}=0$

$$
\begin{aligned}
\partial p_{i} & =+\frac{\sum f_{j} s p_{j}^{\eta_{j}}}{[]^{2}} \cdot f_{i \ell} \partial s p_{i \ell} \\
& =p_{i}^{2} \frac{f_{i \ell}}{\sum f_{j} s p_{j}^{\eta_{j}}} \partial s p_{i \ell}
\end{aligned}
$$

for small changes

$$
\Delta s p_{i \ell}=\frac{\Delta p_{i}}{p_{i}^{2}} \frac{\sum f_{j} s p_{j}^{\eta_{j}}}{f_{i \ell}}
$$

Case $2 \quad \delta_{i \ell, i}=1$

$$
\partial p_{i}=\frac{\sum f_{j} s p_{j}^{\eta_{j}}}{[]^{2}} \cdot{ }_{f_{i \ell}}\left[\eta_{i \ell}{s p_{i \ell}}_{\eta_{i \ell}}^{-1}-\left(\eta_{i \ell}^{-1}\right) \operatorname{sp}_{i \ell}^{\eta_{i \ell}}\right] \delta s p_{i \ell}
$$

$$
\Delta s p_{i \ell}=\frac{\Delta p_{i}}{p_{j}^{2}} \frac{f_{i \ell}\left[n_{i \ell} s p_{i \ell}^{n_{i \ell}}-\left(n_{i \ell}^{-1}\right) s p_{i \ell}^{n_{i \ell}}\right]}{\sum f_{j} s p_{j}^{n}}
$$

3) Partial derivative of $p_{i}$ with respect to $s p_{i n}$

Equations are similar to 5.3.1.2-2 and 5.3.1.2-3 except that in replaces il.

### 5.4 Conclusion of 5.2 and 5.3 and Fxtension to to a General Process

In an arbitrary process there is an additional factor which complicates the analysis very much. This factor is "changes of the properties" (sc also the ordering; due to 1) the changes in composition and 2) the addition of an MSA in a separation unit. The expression for recovery of a product will remain unchanged. However, no general conclusion can be drawn for the expression for purity of a product.

Therefare in conclusion we can say that Equation 5.3-1 is true in all cases whereas Equation 5.3-3 is true strictly for structures where the ordering of components remains unchanged.

From the foregoing analysis we have obtained functional dependence of the recovery and the purity of a product on the split fraction of various species in the system. This functional dependence is

$$
\begin{array}{lll}
r_{i}=f\left(s p_{j}\right) & j \in C_{i} & 5.4-1 \\
p_{i}=f\left(s p_{i \ell}, s p_{j}, s p_{i h}\right) & j \in C_{i} & 5.4-2
\end{array}
$$

The recovery of a product thus depends only on the split fraction of components in the product. A change in the split fraction of one of the components in a product will not affect the recovery of any other product. In this sense the $r_{i}$ 's are decoupled.

The purity of a product depends on the split fractions of the components in the products and the split fractions of the neighboring components. Therefore a change in the split fraction of a component in a product will also change the purity of some of the neighboring products. In this sense the $p_{i}$ 's are coupled.

### 5.5 Recovery and Purity for Products Produced in Sequences of Actual Separators

So far the discussion has been limited to sequences of ideal separators. The analysis has been performed using ideal transformation as defined by Equation 4.4-1. The implicit assumption in the definition of these transformations was that all the components lighter than the light key are recovered completely in the distillate and the components heavier than the heavy key are recovered completely in the bottoms. In an actual separator, however, both distiliate and bottoms will contain at least some amount of each component in the feed stream. So the transformations corresponding to an actual separation unit
would have the following form:


The $\varepsilon_{j}$ 's will depend on the relative separation coefficjent of $j$, the number of plates in the column $i$ and the recoveries of the keys. The cases in which we are interested are the ones in which the recoveries of the key components are generally high and also the relative separation coefficient between neighboring components is usually not very close to one. In these cases $\varepsilon_{j}$ 's are relatively small in magnitude, nonetheless, not always zero.

How do the recoveries and purities of the product from an actual separator sequence compare with the estimated recoveries and purities from the same configuration of ideal separators? A simple qualitative analysis will reveal the following,
i) The actual recovery of a product will always be less than or at most equal to that predicted by Equation 5.3-1.
2) The actual purity of a product will always be less than or at most equal to trat predicted by Equation 5.3-2.

The presence of $\varepsilon_{j}$ 's has a tendency to degrade the product to some extent. Therefore, the desired product specification can be obtained by increasing the necessary split fractions in the design. This is the approach taken in the following two sections.

### 5.6 The Problem of Specified Recoveries

For the problem defined in Section 1.3 we
will add an extra restriction: the recoveries of all the products produced are such that

$$
r_{i}=r_{i}
$$

However, for numerical calculations, the following criteria will be used

$$
r_{i_{\text {low }}} \leq r_{i} \leq r_{i_{\text {high }}}
$$

where $r_{i_{l o w}}$ and $r_{i_{h i g h}}$ are specified.
The following iterative procedure is proposed to solve the problem above. A logic diagram for this procedure is given in Figure 5.6-1.


Figure 5.6-1
Procedure to Solve the Problem of Specified Recoveries

### 5.6.1 Initial Estimates of spi

It has been found that the problem is relatively insensitive to the initial guess of the values of $s p_{i}$. Since the configuration is not known to start with, we can safely assume

$$
s p_{j}=r_{i_{\text {spec }}} \quad j \in c_{i}
$$

for each single component product. For multicomponent products, assume $s p_{j}=r_{i s p e c} j \in C_{i}$. However, if the process configuration is known better initial values of the $s p_{i} ' s$ can be estimated.
5.6.2 Modification of $\mathrm{sp}_{\mathrm{i}}{ }^{\prime} \mathrm{s}$

Based on the initial estimates by the method above, the actual recovery for some of the products will, in most cases, fall short of the specification, for instance

$$
r_{i}=r_{i}-\Delta r_{i}
$$

An improvement of $\Delta r_{i}$ in the recovery of product $i$ will obtain the required recovery for us. The improvement of $\Delta r_{i}$ can be achieved by modifying the $s p_{j}$ by $\Delta s p_{j}, j \in C_{i}$. The $\Delta s p_{j}{ }^{\prime} s$ can be computed by formulas in Section 5.3.1.1.

Such changes will be made corresponding to each product which does not satisfy specification constraints. With these new values of the $\mathrm{sp}_{i}$ 's the optimal design is simulated again. Actual recoveries are compared and for the
products which do not satisfy recovery constraints corresponding $\Delta s F_{j}$ changes are made. The process is repeated until required recovery specifications are mat.

### 5.7 The Problem of Specified Purities

The problem under consideration is a variation of the synthesis problem (as defined in Section 1.3). An additional constraint on the design has been imposed,

$$
p_{i} \geq p_{i} \text { spec }
$$

for every product.
An iterative procedure similar to that in Section 5.6 is proposed. The logic diagram is given in Figure 5.7-1. Important aspects of the procedure are discussed below.
5.7.1 Initial Estimates of $s p_{i}{ }^{\prime s}$

The initial choice of $s p_{i}$ 's is a difficult task compared to the previous problem. However, there are some guidelines. If the amounts of all the components in the feed are approximately equal, it would be all right to select $s p_{i}=\min p_{j}$. If the amounts of various components vary greatly, then there are no rules of thumb to follow except to pick an $\operatorname{sp}_{i}$ that is fairly low.
5.7.2 Modification of $5 p_{i}{ }^{\prime} s$

Based on the initial estimates of $s p_{i}$ 's, the actual purities of some of the products will usually fall short of


Figure 5.7-1
Procedure for Solving the Problem of Specified Purities
the specification, for instance

$$
p_{i}=\rho_{i}-\Delta p_{i}
$$

The next step would be to increase the appropriate $s p_{i}$ 's to affect an increase equal to $s p_{i}$ in purity. The problem, however, is complicated since the $\Delta p_{i}$ depends on three variables: 1) $s p_{j} j \in C_{i}$ 2) $s p_{i \ell}$, the split fraction the component just lighter than the lightest component in the product $i$ and 3$) ~ s p_{i n}$, the split fraction of the component just heavier than the heaviest component in the product i.

Therefore a change in one $\mathrm{sF}_{i}$ may in fact change the purity of three products. For this reason, all three variables will not be modified simultaneously, instead they will be modified one at a time in the following ordex:

1) $\operatorname{sp}_{j}{ }^{\prime s} \quad j \in C_{i}$
2) $s p_{i \ell}$ or $s p_{j h}$ whichever is the adjacent key for the separator in which product i is isolated
3) $s p_{i h}$ or $s p_{i \ell}$ whichever is not adjusted in

Step 2.
All the adjustments are made according to the Equations in Section 5.3.1.2.

## Chapter 6

## ECONOMIC OPTIMIZATICN OF REELUX RATIO FOR A COLUMN

### 6.1 Simplified Cost Model for a Distillation Column

Reflux ratio is an important design variable for a đistillation column. Reflux ratio affects both the operating cost and the investment cost of the column. The cost of the cooling medium depends on the cooling duty, which is approximately proportional to the term $D(R+1)$ and the cost of heating mediun is directly related to the same term. The investment costs for the condenser and the reboiler are also directly proportional to the heat duties respectively. Therefore we can approximate the cost of utilities and heat exchange equipment as $A_{1} D(R+1)$. The diameter of the column is proportional to the term $[D(R+I)]^{\frac{1}{2}}$ when operating at total reflux, approximately similar dependence is assumed for operations other than that at the total reflux. The investment cost for the column is proportional to the volume of the column and can be expressed as $A_{2} D(R+1) N$. Based on the analysis above, the total cost for a distillation column can be given by the following relation

$$
C=D(R+1)\left(A_{1}+A_{2} N\right)
$$

A similar cost equation has been proposed by Happel. and Jordan (p. 385). The constants in their equations can be estimated by the knowleßge of various cost factors. No such claim is made here; the constants $A_{1}$ and $A_{2}$ are purely empirical and are obtained by regression.

Equation 6.1-1 fits the cost data very well as is shown in Figure 6.1-1.
$N$ and $R$ are related by the well known Gillilands correlation. Usjng this relation, $N$ can be expressed as a function of R. By this elimination, Equation 6.1-1 can be expressed as a function of $R$ only.

Several analytical expressions for the Gillilands correlation have appeared in the literature. An equation presented by Molokanov et.al. [M4] fits the data satisfactorily over the whole range. This equation will be used in the present work to eliminate $N$ in terms of $R$ in Equation 6.1-1. Molokanov's equation is

$$
Y=1-\exp \left(\frac{1+54.4 x}{11+117.2 x} \cdot \frac{x-1}{\sqrt{x}}\right)
$$

where $X=\frac{R-R_{m}}{R+1} \quad$ and $\quad Y=\frac{N-N_{m}}{N+1} \quad 6.1-3$

Equations 6.1-2 and 6.1-3 give the following

$$
N=\left(1+N_{m}\right) \exp \left(\frac{1+54.4 x}{11+117.2 x} \cdot \frac{x-1}{\sqrt{x}}\right)-1 \quad 6.1-4
$$



Figure 6.1-1
$C / D(1+N)$ Versus $N$
substituting 6.1-4 into 6.1-1. gives $C$ às a function of $R$;

$$
\begin{align*}
C=D(R & +1) A_{1}-A_{2}\left(1+N_{m}\right) \\
& \cdot \exp \left(\frac{1+54.4 x}{11+117.2 x} \cdot \frac{x-1}{\sqrt{x}}\right)
\end{align*}
$$

Now define a new variable

$$
\theta=\mathrm{R} / \mathrm{R}_{\mathrm{m}}
$$

Equation 4.1-5 can be rewritten as

$$
\begin{array}{r}
C=D\left(\theta R_{m}+1\right) A_{1}-A_{2}+A_{2}\left(1+N_{m}\right) \\
\cdot \exp \left(\frac{1+54.4 x}{11+117.2 x} \cdot \frac{x-1}{\sqrt{x}}\right)
\end{array}
$$

where $\quad x=\frac{(\theta-1) R_{m}}{\theta R_{m}+1}$

The derivative $d C / \partial \theta$ is

$$
\begin{align*}
& \frac{d C}{d \theta}= \frac{d C}{d x} \cdot \frac{d x}{d \theta} \\
& \begin{aligned}
\frac{d C}{d x}= & \frac{D\left(1+F_{m}\right)}{1-x} \cdot A_{2}\left(1+N_{m}\right) \exp \left(\frac{1+1-7}{11+117.2 x} \cdot \frac{54.4 x}{\sqrt{x}}\right] \\
& \cdot\left[\frac{1}{1-x}-\frac{11-235.8 x+8053.68 x^{2}+6375.68 x^{3}}{2 x \sqrt{x}(11+117.2 x)^{2}}\right] \\
& +\frac{D\left(1+R_{m}\right)}{(1-x)^{2}}\left(A_{1}-A_{2}\right) \\
\frac{d x}{d \theta}= & \frac{R_{m}(1-x)^{2}}{1+R_{m}}
\end{aligned}
\end{align*}
$$

The minimum of $C$ occurs when $d C / d \theta=0$. A closed form solution for $d C / d \theta=0$ is not possible, so a numerical method would be used to obtain the optimum $\theta$.

## 6. $2 \frac{\text { A Bisection Method for Minimizing a }}{\text { Univariable Convex Function }}$

The minimum for a differentiable univariable convex function $C(x)$ can be computed to any numerical accuracy (< $\varepsilon$ ) in a very efficient manner by the following bisection algorithm.

STEP 1 Get $x_{1}$ such that $\left.\frac{d C}{d x}\right|_{x_{1}}>0 ;$ and

$$
x_{2} \text { such that }\left.\frac{d C}{d x}\right|_{x_{2}}<0
$$

$\underline{\text { STEP } 2}$ new point $x_{3}=\frac{x_{1}+x_{2}}{2}$
if $\left.\frac{\mathrm{dC}}{\mathrm{dx}}\right|_{\mathrm{x}_{3}}=0, \mathrm{x}^{*}=\mathrm{x}_{3} \quad \operatorname{STOP}$
if $\left.\frac{d C}{d x}\right|_{x_{3}}>0, \quad x_{1}=x_{3}, \quad$ GO TO STEP 3
if $\left.\frac{d C}{d x}\right|_{x_{3}}<0, \quad x_{2}=x_{3}, \quad$ GO TO STEP 3
$\underline{\text { STEP } 3}$ if $x_{2}-x_{1}<\varepsilon, x^{*}=\frac{x_{1}+x_{2}}{2}$ STOP
otherwise go to STep 2
$x^{*}$ is the required value of $x$ which minimizes $C(x)$. Figure 6.2-1 gives a graphical interpretation of the bisection method.


Figure 6.2-1
The Bisection Method

### 6.3 A Procedure for Cptimizing Feflux Ratio for a Column

As is noted in Section 6.1, the annual cost of a column is a function of a single variable, $\theta$. $A$ typical plot of cost versus $\theta$ is shown in Figure 6.3-1. The actual cost curve $S$ (connected by •) is not smooth in the region of interest. This is becalise in reality $N$, the number of stages in the column, can only take integer values. However, the cost curve $S^{\prime}$ corresponding to Equation 6.1-1 (the coefficients $A_{1}$ and $A_{2}$ are computed by least square curve fitting of actual cost) is smooth and convex in the region of interest.

No efficient method can be envisioned to find the infinimum of the nonconvex function S. However, the function $S^{\prime}$ can be handled much more easily. Moreover, in general, the minimum of $S^{\prime}$ is around the infinimum of $S$.

The method proposed here consists of searching for the minimum of S by a slight modification of the bisection method presented in Gection 6.2. The algorithm is given below.

STEP 1 simulate design at $\theta_{1}=\theta_{\text {min }}$

$$
\begin{aligned}
& \bar{c}=\left.c\right|_{\theta_{1}} \\
& \bar{\theta}=\theta_{1}
\end{aligned}
$$

$$
\theta=\theta_{2}=1.3
$$

STEP 2 simulate design at given $\theta$

$$
\text { if }\left.C\right|_{\theta}<\bar{C}, \quad \bar{c}=\left.c\right|_{\theta}, \quad \bar{\theta}=\theta
$$



Figure 6.3-1
Cost Versus Refluy Ratio for a Typical Column

STEP 3 compute $A_{1}$ and $A_{2}$ by linear regression
$\underline{\text { STEP } 4}$ if $\left.\frac{d C}{d \theta}\right|_{\theta_{I}}<-\varepsilon_{S}$
GO TO STEP 5
otherwise $\theta *=\theta_{1}$
GO TO STEP 7
$\underline{\operatorname{STEP} 5}$ if $\left.\frac{d C}{d \theta}\right|_{\theta_{2}}>\varepsilon_{S}$ GO TO STEP 6
if $\left.\frac{d C}{d \theta}\right|_{\theta_{2}}<-\varepsilon_{s}, \quad \theta_{1}=\theta_{2}$

$$
\theta=\theta_{2}+1.2 \cdot \theta_{2}
$$

GO TO STEP 2
otherwise
GO TO STEP 7
$\underline{\operatorname{STEP} 6} \quad \theta=\theta_{3}=\frac{\theta_{1}+\theta_{2}}{2}$
if $\left.\left|\frac{d C}{d \theta}\right|_{\theta_{3}} \right\rvert\,<\varepsilon_{S}, \theta *=\theta_{3} \quad$ GO TO STEP 7
if $\left.\quad \frac{\mathrm{dC}}{\mathrm{d} \theta}\right|_{\theta_{3}}<0, \quad \theta_{1}=\theta_{3} \quad$ GO TO STEP 2
if $\left.\cdot \frac{d C}{d \theta}\right|_{\theta_{3}}>0, \theta_{2}=\theta_{3} \quad$ GO TO STEP 2

STEP 7 simulate design at $\theta^{*},\left.C\right|_{\theta *}=C^{*}$

$$
\begin{array}{lll}
\text { if } C^{*}<\bar{C} & \theta_{\text {inf }}=\sigma^{*} & \text { STOP } \\
\text { otherwise } & \theta_{\text {inf }}=\bar{\theta} & \text { STOP }
\end{array}
$$

$\theta$ * is the minimum of $S^{\prime}$. $e_{\text {min }}$ is the minimum acceptable value of $\theta$ (recormended value $=1.05$ ). $\varepsilon_{s}$ is the tolerance in the value of the slope such that $|d C / d \theta|<\varepsilon_{s} \Rightarrow>$ optimum (recommended value of $\varepsilon_{s}$ is 50). The algorithm gives $\theta_{\text {inf }}$ which is the best estimate for the optimum reflux ratio.

## Chapter 7

## SAMPLE SEEARATION SEQUENCES

In this chapter, we will apply the evolutionary synthesis procedure described earliex to problems existing in the literature. In doing this, we will illustrate the synthesis procedure in detail. In the following sections six problems from the literature have been solved. For each problem the various methods used to solve the problem are also compared at the end of each section.

The organization of various routines in the syrthesis program (ESP-SSP) is given in Figure 7.1. During creation of initial structure, MAIN calls PICK to select the next separation to be made at any point in the sequence. PICK decides the separation types to be considered. Key components and coefficient of difficulty of. separation (CDS) are computed by MULTIC. If more than one design specification (separator type, LK, HK, CDS) exists, then PICK arranges them in the order of increasing CDS. Separator simulation and cost calculations are performed by DETAIL. After the initial structure has been created, STORED is called to store the initial structure in memory. Evolution of structures is performed next by calling EVLUTN, which suggests structure modifications. MATN recreates a new structure by implementing the proposed


Figure 7.1
Organization of Various Routines in ESP-SSP
modification. STORED is called agiin, the new structure is compared with the best structure so far. If the new structure is better, then it is stored in the memory for future reference. If, however, the new structure is worse, STORED restores the best structure. ADJST is called after no more evolutionary changes are possible. ADJST modifies the split fractions of key comoonents to satisfy product recovery specifications. ADuSTP is called next and it further modifies the split fractions such that both the product purity and recovery constraints are met. SIMLTR is called next and optimizes the reflux of each column in the structure.

Each figure in the following sections shows a struciure. The large boxes represent separation units. There are two numbers in each bow, the first one is the separator number and the other one within parentheses is the separation method type. Directed lines are streams in the structure. The stream number for each stream is the number on the directed line. If the process is feasible, the total annual cost (TAC) is given in $\$ / y r$ beneath the structure.

### 7.1 Example 1: C6 Separation

Consider the 66 separation synthesis problem described by Rodrigo and Seader [R3]. The feed stream consists of three C 6 components, each of which is to be isolated in a fairly pure form. Ordinary distillation and

Table 7.1-1
Examole 1: Problem Definition

FEED (stream 1):

| component | component name | mole fraction |
| :---: | :--- | :---: |
| 1 | n-Hexane | .3333 |
| 2 | Benzene | .3333 |
| 3 | Cyclohexane | .3334 |


| Total flow rate | $=170.1 \mathrm{~kg}-\mathrm{mole} / \mathrm{hr}$ |
| ---: | :--- |
| Temperature | $=37.8^{\circ} \mathrm{C}$ |
| Pressure | $=1.033 \mathrm{~kg} / \mathrm{sq} \mathrm{cm} \mathrm{abs}$. |

DESIRED PRODUCTS:

| product | component | minimum <br> recovery | minimum <br> purity |
| :---: | :---: | :---: | :---: |
| 2 | 1 |  | $98 \%$ |
| 3 | 2 |  | $93 \%$ |
| $98 \%$ |  |  |  |
| 3 | 3 |  | $98 \%$ |

Separation methods available are:
I) Di.stillation
II) Extractive distillation using phenol (component 4)

Initial ordering of components at $54.4^{\circ} \mathrm{C}$

| $I$ | $I I$ |
| ---: | ---: |
| $I$ | 1 |
| 2 | 3 |
| 3 | 2 |
| 4 | 4 |

extractive distillation using phenol as the rass-separatingagent (MSA) are suitable. The details of the problem are given in Table 7.1-1.
7.1.1 Creation of Initial Structure

$$
\text { OPEN }=\{1\}
$$

The feed stream is considered first. MULTIC returns two designs:

Design \#l: $\quad L K=1 \quad H K=2 \quad S T=I \quad \alpha=1.36 \quad C D S=1.222$ Design \#2: $\quad L K=2 \quad H K=3 \quad S T=I \quad \alpha=1.18 \quad C D S=4.461$

The first design has a lower CDS value and is tried for detailed simulation by calling subroutine DETAIL. DETAIL returns a feasible design producing two new streams, 2 and 3. Stream 2 contains mostly product 1, and stream 3 contains the rest. Stream 3 needs further processing. The OPEN set is updated to

$$
\text { OPEN }=\{3\}
$$

Stream 3 is considered next, MULTIC for this stream returns only one cesign:

Design \#l: LK $=2 \quad \mathrm{HK}=3 \quad \mathrm{ST}=\mathrm{I} \quad \alpha=1.18 \quad \operatorname{CDS}=2.508$

This design is tried for detailed simulation. During detailed simulation the properties are recomputed. At operating conditions, the $\alpha_{L K-H K}$ is 1.04 which is below the acceptable level. Consequently, this design is abandoned.
and the control is returned to the MAJN progran to search for alternate designs. MULTIC returns an additional design:

Design \#l: LK $=3 \mathrm{HK}=2 \mathrm{ST}=\mathrm{II} \alpha=1.76 \quad \operatorname{CDS}=.750$

This design is considered for detailed simulation. DETAIL returns a feasible design resulting in two new streams, 4 and 5. Stream 4 contains product 3 and stream 5 contains product 2 and the MSA used in separator 2. Now, OPEN is updated to

$$
\text { OPEN }=\{5\}
$$

For stream 5, MULTIC returns only one design:

Design \#1: $\quad L K=2 \quad H K=4 \quad S T=I \quad \alpha=14.4 \quad C D S=.117$

For this design specification, DETAIL returns a feasible design. Two new streams, 6 and 7, are generated. Stream 6 contains product 2 and stream 7 has the MSA which is recycled back to separator 2. There are no more streams left which need further processing; OPEN $=\{\varnothing\}$. The initial structure has been created and shown in Figure 7.1-1. The total annual cost (TAC) for this structure is $274,803 \$ / \mathrm{yr}$. STORED is called and this structure is saved for future reference.


TAC $=274,803 \$ / \mathrm{Yr}$

Figure 7.1.1-1
Example 1: Initial Structure

### 7.1.2 Evolution of Structures

Routine EVIUTN is called to search for possible modifications to the initial structure, Fule l does not apply. Rule 2 does not suggest any changes. Rule 3 suggests that a change of separation method for separator 1 may result in a Detter structure. Consequently, the structure downstream of stream 1 is destroyed. Synthesis is restarted by implementing the proposed modification to the initial structure. A new structure $E-1$ is created. This structure has a $T A C=214,675 \$ / \mathrm{Yr}$ and is shown in Figure 7.1.2-1. STORED is called again. Since the structure E-1 is better than the initial structure, structure $E-1$ is saved for future reference. Now structure $E-1$ is evolved. Evolutionary rules 2 and 3 do not suggest any change. Rule 4, however, suggests that a change in the split for separator 2 to delay the MSA removal may improve the structure. Consequently, the structure downstream of separator 2 is destroyed. Synthesis is restarted by implementing the proposed modification to structure E-1. A new structure $E-2$ is created. This structure has a TAC $=158,699$ \$/yr and is shown in Figure 7.1.2-2. STORED is called and structure $\mathrm{E}-2$ is saved for future reference. Now the evolution of structure $E-2$ is attempted but evolutionary rules $2,3,4$ and 5 do not suggest any modification. Consequently, structure E-2 cannot be improved further. Rocirigo and Seader [R3] have obtained the same structure as the optimal structure.


TAC $=214,675 \$ / \mathrm{yr}$

Figure 7.1.2-1
Example 1: Structure E-1

$T A C=158,599 \$ / \mathrm{yr}$

Figure 7.1.2-2
Example 1: Structure E-2, Optimal Structure
7.1.3 Satisfying Product Specifications

So far in the syrthesis we nave arbitrarily set the split fractions of the light and heavy key in each column to a prespecified fraction (.98 for each key in this case). With this assumption, however, the recovery and purity specifications for each product are not met. Now the split fraction of the keys will be changed in accordance with the algorithm presented in Chapter 5 to satisfy the product specifications. First, we will obtain the required recovery for each product and then adjustments will be made to satisfy the purity specifications as well.

Table 7.1.3-1 shows the steps taken to attain the recovery specifications. The top half of the table shows the recoveries of each product for each iteration of $A D J S T$, and the bottom half shows the split fraction for each component for each iteration. Therefore, each column specified by iteration counter ITER should be interpreted as a simulation of optimal structure. The total annual cost (TAC) for this simulation is given in the last column of Table 7.1.3-1. In the existing structure (the one corresponding to $I T E R=0$ ), the recoveries of products 2 and 3 are below the specified level and accordingly, the split fraction of components in these products is increased according to Equation 5.3.1.1-1. The modified values of the $s p_{i}$ 's are shown in the column corresponding to ITER=1. The recoveries for each product obtained because of this change are shown in the colum corresponding to $I T E R=1$.

```
                    Table 7.1.3-1
Example l: Iterations of ADJST
```

| product i | j. $\epsilon \mathrm{C}_{\mathrm{i}}$ | Recovery |  |
| :---: | :---: | :---: | :---: |
|  |  | ITER=0 | ITER=1 |
| 1 | 1 | 98.000 | 98.000 |
| 2 | 2 | 96.020 | 98.023 |
| 3 | 3 | 96.040 | 98.010 |
| 4 | 4 | 99.500 | 99.500 |
| component i | $\eta_{i}$ | Split Fraction |  |
|  |  | ITER=0 | ITER=1 |
| 1 | 1 | . 98000 | . 98000 |
| 2 | 2 | . 98000 | . 99010 |
| 3 | 2 | . 98000 | . 99000 |
| 4 | 1 | . 99500 | . 99500 |
|  | TAC (\$/yr) | 158,699 | 169,952 |

Since all the recoveries are now within tolerable limits of the specified value, no more iterations are required. After the recoveries for each product are at the desired level, changes are made to obtain the desired purity for each product. Table 7.1.3-2 shows the steps taken to obtain the purity specification. Table 7.1.3-2 is organized similar to Table 7.1.3-1. After the recovery satisfaction, the purity of each product is shown in the column corresponding to ITER=0. Both products 2 and 3 fall short of the desired level. The split fractions of the components in products 2 and 3 are incremented by Formula 5.3.1.2-1. The new values of the split fractions are shown in the column corresponding to $\operatorname{ITER}=1$. Simulation is performed incorporating these new values. The TAC changes to 181,498 \$/yr. The resulting purity values are shown in the column corresponding to ITER=1. Even now products 2 and 3 do not meet the desired level. The $\mathrm{sp}_{\mathrm{i}}$ 's of the components corresponding to products 2 and 3 in the first position of column 3 are incremented in accordance with Formula 5.3.1.2-2. The incremented values are shown in the column corresponding to ITER=2. Simulation of the optimal structure is performed and the corresponding values of the purity for each product is shown in the column corresponding to ITER=2. The cost of the structure increases to 190,519 \$/yr. Still, the purity of product 3 is not at the desired level. Now the split fraction of the

Table 7.1.3-2
Example l: Iterations of ADJSTP

component corresponding to product 3 in the second position of column 3 is incremented in accordance with Equation 5.3.1.2-2 to the values shown in the column corresponding to ITER=2. Simulation is performed for these new values of the split fraction. The purity of each product for this case is shown in the column corresponding to ITER=2. Notice that now the purity of constraints is satisfied. The TAC is 190,535 \$/yr.

### 7.1.4 Economic Optimization of Reflux Ratio

So far the reflux ratio of each column was
arbitrarily set to 1.3 times the corresponding minimum reflux ratio for that column. After the product specifications are satisfied the synthesis program optimizes the reflux ratio for each column using the algorithm given in Section 6.3. The optimum values are given in Table 7.1.4-1. Figure 7.1.4-1 is the space of structures for this problem, showing in particular the initial structure and the structures obtained during evolution. The structures are shown in detail in Figure l-1.

Simulation of the optimum structure with the optimum values of reflux ratios is performed next. The total annual cost is $186,489 \$ / \mathrm{yr}$, which shows an improvement of $2.12 \%$.

The proposed mehtod is compared with two other
methods in Table 7.l.4-2. The proposed method is clearly computationally superior to the other two methods. $\mathrm{N}_{\mathbf{s}}$ is the number of possible sequences; $N_{u s p}$ is the number of unique subproblems; $N_{s a}$ is the number of sequences developed; and $N_{\text {uspa }}$ is the number of unique subproblems analysed.

## Table 7.1.4-1

Example 1: The Optimum Reflux Ratios

| Separator | Feed Stream   <br> 1 1  | Optimum $R / R_{m}$ <br> 2 |
| :---: | :---: | :---: |
|  | 3 | 1.144 |
| 3 | 5 | 1.560 |
| 2 |  | 1.050 |

Table 7.1.4-2
Example 1: Comparison of Various Methods

```
\(\mathrm{N}_{\mathrm{S}}=9\)
\(N_{\text {usp }}=16\)
```

Method
Rodrigo and Seader [R3] OBS*
Gomez and Seader [G1] PBOS ${ }^{\dagger}$
PROPOSED METHOD

${ }^{\mathrm{N}_{\text {supa }}}$
10

3
6

[^0]

Figure 7.1.4-1

### 7.2 Example 2: Light Hydrocarbon Separation

Consider the hydrocarbon separation problem
studied by Heaven [H3]. The feed stream consists of five light hydrocarbons in the range $C 3$ to $C 5$, each of which is to be isolated in relatively pure form. The details of the problem are given in Table 7.2-1.

### 7.2.1 Creation of Initial Structure

$$
\text { OPEN }=\{1\}
$$

The feed stream is considered first. MULTIC returns four designs:

Design \#l: $\quad L K=3 \quad H K=4 \quad S T=I \quad \alpha=2.385 \quad C D S=.482$
Design \#2: $L K=2 \quad H K=3 \quad S T=I \quad \alpha=1.380 \quad C D S=.842$
Design \#3: LK = $4 \mathrm{HK}=5 \mathrm{ST}=\mathrm{I} \alpha=1.265 \quad \mathrm{CDS}=3.040$
Design \#4: $L K=1 \quad H K=2 \quad S T=I \quad \alpha=2.511 \quad C D S=.087$

Design 4 has the lowest $C D S$ and is tried for detailed simulation. DETAIL returns a feasible design. Streams 2 and 3 are produced. Stream 2 contains mostly product 1 and stream 3 contains the rest. The OPEN set is updated to

$$
\text { OPEN }=\{3\}
$$

For stream 3, MULTIC returns three designs, which are given below:

Table 7.2-1<br>Example 2: Problem Definition

FEED (stream 1):

| component | component name | mole fraction |
| :---: | :--- | :---: |
|  | Propane | .05 |
| 2 | i-Butane | .15 |
| 3 | n-Butane | .25 |
| 4 | i-Pentane | .20 |
| 5 | n-Pentane | .35 |


| Total flow rate | $=907.2 \mathrm{~kg}$-mole $/ \mathrm{hr}$ |
| ---: | :--- |
| Temperature | $=37.8^{\circ} \mathrm{C}$ |
| Pressure | $=7.03 \mathrm{~kg} / \mathrm{sq} \mathrm{cm} \mathrm{abs}$. |

DESIRED PRODUCTS:

| product | Component | minimum recovery | minimum purity |
| :---: | :---: | :---: | :---: |
| 1 | 1 | 98\% | 98\% |
| 2 | 2 | 98\% | 98\% |
| 3 | 3 | 98\% | 98\% |
| 4 | 4 | 98\% | 98\% |
| 5 | 5 | 98\% | 98\% |

Separation method available:
I) Distillation

Initial ordering of components at $54.4^{\circ} \mathrm{C}$

| Design \#1: | $L K=3$ | $H K=$ | $S T=I$ | $\alpha=2.385$ | $C D S=.474$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| Design \#2: | $L K=2$ | $H K=3$ | $S T=I \quad \alpha=1.380$ | $C D S=.690$ |  |
| Design \#3: | $L K=4$ | $H K=5$ | $S T=I \quad \alpha=1.265$ | $C D S=2.852$ |  |

Design 1 has the lowest value of $C D S$ and is tried for detailed simulation. DETAIL returns a feasible design. Streams 4 and 5 are generated. Stream 4 contains products 2 and 3 and stream 5 contains products 4 and 5. Both the streams need further processing. OPEN is updated to

$$
\text { OPEN }=\{4,5\}
$$

Stream 4 is considered next. MULTIC returns one possible design which is simulated using DETAIL and a feasible design is returned. Two new streams, 6 and 7, are generated. Stream 6 contains mostly product 2 and stream 7 contains mostly product 3. OPEN is updated to

$$
\text { OPEN }=\{5\}
$$

For stream 5, MULTIC returns only one design which is feasible and two new streams, 8 and 9, are generated. Stream 8 contains product 4 and stream 9 contains product 5 . OPEN is updated and is now empty. The initial structure has been created and is given in Diagram 7.2.1-1. The total annual cost for this structure is $542,745 \$ / y r$.


```
TAC = 542,745 $/yr
```

Figure 7.2.1-1
Example 2: Initial and Optimal Structure

### 7.2.2 Evolution of Structures

Evolutionary rules are appiied to the initial structure by calling EVLUTN. Rules 1 and 3 do not apply. Rules 2, 4 and 5 do not suggest any modifications. Consequently the initial structure cannot be improved. Heaven [H3] by an exhaustive enumeration has obtained the same structure as the optimum structure.

### 7.2.3 Satisfying Product Specifications

Recovery constraints are satisfied by calling ADJST. The various iterations are shown in Table 7.2.3-1. The format of the table is described in detail in Section 7.1.3. For this problem two iterations lead to a set of values of the split fractions of the components that satisfy the product recovery specifications. Product purity constraints are satisfied next by calling ADJSP. The various iterations are shown in Table 7.2.3-1. Again in two iterations a set of values of the split fractions are obtained that satisfy the product purity and recovery specifications.

### 7.2.4 Economic Optimization of Reflux Ratio <br> The operating reflux ratio for each column in the

 structure is optimized by the bisection algorithm given in Section 6.3. The optimum values are given in Table 7.2.4-1. The table also gives the operating pressure of each column as obtained by heuristic rule number 6. Rathore, Van Wormer and Powers [ Fi 1 ] have optimized the oferating pressure in```
                        Table 7.2.3-1
Example 2: Iterations of ADJST
```



Table 7.2.3-2
Example 2: Iterations of ADJSTP


Table 7.2.4-1
Example 2: The Optimum Reflux Ratios

| Separator | $\frac{\text { Feed Stream }}{1}$ |  | $\frac{\text { Optimum } R / R_{\text {min }}}{}$ |
| :---: | :---: | :---: | :---: | | Pressure |
| :---: | :---: | :---: |
| $\left(\mathrm{kg} / \mathrm{cm}^{2} \mathrm{abs}\right)$ |

Table 7.2.4-2
Example 2: Comparison of Various Methods

$$
\begin{aligned}
& N_{s}=14 \\
& N_{\text {usp }}=20
\end{aligned}
$$

| Method | ${ }^{\mathrm{N}_{5}{ }_{\text {a }}}$ | ${ }^{\text {Nuspa }}$ |
| :---: | :---: | :---: |
| total <br> Heaven [H3] enumeration | 14 | 20 |
| Rathore, et.al. [R1] DP* |  | 20 |
| Rodrigo and Seader [R3] OBS |  | 20 |
| Gomez and Seader [G1] PBOS |  | 13 |
| PROPOSED MEHTOD | 1 | 4 |

[^1]each column. The values of the optimum pressure reported are very close to the ones obtained by the synthesis program. This problem has been studied by several authors. Table 7.2.4-2 gives a comparison of the various methods in the literature. The present method is computationally superior to other methods.

### 7.3 Example 3: Hydrocarbon Separation I

Consider the hydrocarbon separation problem considered by Rodrigo and Seader (example 3) [R3]. The feed stream consists of six components, a mixture of paraffins and olefins each of which is to be isolated in relatively pure form using ordinary distillation. The details of the problem are given in Table 7.3-1.

### 7.3.1 Creation of the Initial Structure

$$
\text { OPEN }=\{1\}
$$

The feed stream is considered first. MULTIC returns five designs:

| Design \#1: | $\mathrm{LK}=5$ | $\mathrm{HK}=2$ | $\mathrm{ST}=\mathrm{I}$ | $\alpha=1.202$ | $\mathrm{CDS}=2.091$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| Design \#2: | $\mathrm{LK}=1$ | $\mathrm{HK}=5$ | $\mathrm{ST}=\mathrm{I}$ | $\alpha=3.456$ | $\mathrm{CDS}=.219$ |
| Design \#3: | $\mathrm{LK}=2$ | $\mathrm{HK}=6$ | $\mathrm{ST}=\mathrm{I}$ | $\alpha=2.722$ | $\mathrm{CDS}=.512$ |
| Design \#4: | $\mathrm{LK}=6$ | $\mathrm{HK}=3$ | $\mathrm{ST}=\mathrm{I}$ | $\alpha=1.246$ | $\mathrm{CDS}=3.775$ |
| Design \#5: | $\mathrm{LK}=3$ | $\mathrm{HK}=4$ | $\mathrm{ST}=\mathrm{I}$ | $\alpha=2.964$ | $\mathrm{CDS}=1.126$ |

Design 3 has the least value of $C D S$ and is tried for detailed design. DETAIL returns a feasible design. Two

Table 7.3-1
Example 3: Problem Definition

FEED (stream I):

| component |  | component name |  |
| :---: | :--- | :--- | :--- |
|  |  | Ethane | fraction |
| 2 | Propane | .20 |  |
| 3 | Butane | .20 |  |
| 4 | Pentane | .15 |  |
| 5 | Propene | .15 |  |
| 6 | 1-Butene | .15 |  |
|  |  | .15 |  |


| Total flow rate | $=453.59 \mathrm{~kg}$-mole $/ \mathrm{hr}$ |
| ---: | :--- |
| Temperature | $=37.8^{\circ} \mathrm{C}$ |
| Pressure | $=1.0333 \mathrm{~kg} / \mathrm{cm}^{2} \mathrm{abs}$. |

DESIRED PRODUCTS:
$\left.\begin{array}{ccccc}\text { product } & \text { component } & & \begin{array}{l}\text { minimum } \\ \text { recovery }\end{array} & \end{array} \begin{array}{c}\text { minimum } \\ \text { purity }\end{array}\right]$

Separation method available is:
I) Distillation

Initial ordering of components at $54.4^{\circ} \mathrm{C}$
new streams, 2 and 3, are generated. Stream 2 contains product 1 and stream 3 has the rest. OPEN is updated to

$$
\text { OPEN }=\{3\}
$$

Stream 3 is considered next. MULTIC returns four designs:

Design \#l: $L K=2 \quad H K=6 \quad S T=I \quad \alpha=2.722 \quad C D S=.415$
Design \#2: $\mathrm{LK}=5 \mathrm{HK}=2 \mathrm{ST}=\mathrm{I} \alpha=1.202 \mathrm{CDS}=1.379$
Design \#3: LK = $6 \quad \mathrm{HK}=3 \mathrm{ST}=\mathrm{I} \alpha=1.246 \quad \mathrm{CDS}=2.960$
Design \#4: $\quad L K=3 \quad H K=4 \quad S T=I \quad \alpha=2.964 \quad C D S=1.016$

Design 1 has the lowest value of $C D S$ and is tried for detailed simulation. DETAIL returns a feasible design. Two new streams, 4 and 5, are generated. Stream 4 contains products 5 and 2 , and stream 5 contains products 6,3 and 4. OPEN is updated to

$$
\text { OPEN }=\{4,5\}
$$

Stream 4 is considered next. MULTIC returns only one design which is tried for detailed simulation. DETAIL returns a feasible design. Two new streams, 6 and 7, are generated. Stream 6 contains product 5 and stream 7 contains product 2 . OPEN is updated to

$$
\text { OPEN }=\{5\}
$$

Stream 5 is considered next. MULTIC returns two designs:
$\begin{array}{llllll}\text { Design \#1: } & \mathrm{LK}=6 & \mathrm{HK}=3 & \mathrm{ST}=\mathrm{I} & \alpha=1.246 & \mathrm{CDS}=1.692 \\ \text { Design \#2: } & \mathrm{LK}=3 & \mathrm{HK}=4 & \mathrm{ST}=\mathrm{I} & \alpha=2.964 & \mathrm{CDS}=.673\end{array}$

Design 2 is tried for detailed simulation and found feasible. Streams 8 and 9 are generated. Stream 9 contains product 4 and stream 8 contains the rest. OPEN is updated to

$$
\text { OPEN }=\{8\}
$$

For stream 8, MULTIC returns only one design which is feasible. Streams 10 and 11 are generated. Stream 10 contains product 6 and stream 11 contains product 3. OPEN is updated and is now empty. The initial structure has been created and is given in Figure 7.3-1. The total annual cost is 748,178 \$/yr. Srored is called and the initial structure is saved for future reference.

### 7.3.2 Evoluation of Structures

EVLUTN is called to evolve the initial structure. Rule 1 does not apply for this problem. Rule 2 suggests a change in the split for separator 1. The next best design (i.e. Design 2) for stream 1 is tried for detailed simulation and is feasible. The rest of the structure is generated by using the heuristic rules for the creation of the initial structure. Structure $E-1$ is created and is shown in Figure 7.3.2-1. This structure has a total annual cost of 685,189 \$/Yr and is supericr to the initial structure. STORED is called and structure $E-1$ is saved for future reference.

$\mathrm{TAC}=748,178 \$ / \mathrm{yr}$

Figure 7.3.1-1
Example 3: Initial Structure


$$
\mathrm{TAC}=685,189 \$ / \mathrm{yr}
$$

Figure 7.3.2-1
Example 3: Structure E-1

Structure E-1 is evolved next. Rule 2 suggests a change in the split for separator 2 . The structure downstream of separator 2 is destroyed. The proposed change is implemented and the remaining structure recreated. This results in a new structure, structure E-2. Structure E-2 is given in Figure 7.3.2-2. This structure has a total annual cost of $805,105 \$ / \mathrm{yr}$ which is greater than structure E-1. The evolutionary change did not lead to a better desi.gn. STORED is called again and structure E-1 is restored.

Structure E-1 is evolved again. Rule 3 does not apply. Rules 2 and 4 do not suggest any alterations. Rule 5 suggests a change of split (key specification) for separator 3. The structure downstream from separator 3 is destroyed. The design for separator 3 is changed according to the proposed modification. The structure downstream of 3 is created by heuristics. Structure $\mathrm{E}-3$ is thus created and is shown in Figure 7.3.2-3. This structure has a total annual cost of 630,454 \$/Yr. STORED is called and structure $\mathrm{E}-3$ is saved for future reference. Evolution of structure E-3 is attempted next. Rule 3 does not apply and rules 4 and 5 fail to suggest any modifications. Consequently, structure E-3 cannot be improved further. Rodrigo and Seader [R3] have obtained the same structure by the ordered branch search procedure.

$\mathrm{TAC}=805,105 \$ / \mathrm{yr}$

Figure 7.3.2-2
Example 3: Structure E-2


Figure 7.3.2-3
Example 3: Structure E-3, Optimal Structure

### 7.3.3 Satisfying Product Sivecifications

ADJST is called nexi to alter the split fractions of the keys by the method given in Section 5.6.2. Three iterations are required. Table 7.3.3-1 gives the details of these iterations. The format of the table is the same as described in Section 7.1.3.

ADJSTP is called next to satisfy purity specifications. Table 7.3.3-2 gives the details of each iteration. 7.3.4 Economic Optimization of Reflux Ratio

Reflux ratios for each column in the structure are optimized by the algorithm given in Section 6.3. The optimum values are given in Table 7.3.4-1.

Table 7.3.4-2 compares the varicus methods that have been employed to solve this problem. The proposed method is superior to any other method available.

### 7.4 Example 4: Hydrocarbon Separation II

Consider a variation of the previous problem as given by Westerberg and Stephanopoulos [W1] for a feed stream consisting of six hydrocarbons. Four products in relatively pure form are to be isolated using ordinary distillation and extractive distillation using tetrahydrofuran. The details of the problem are given in Table 7.4-1.

Table 7.3.3-1
Example 3: Iterations of ADJST

| product i | $j \in C_{i}$ | Recovery |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | ITER $=0$ | ITER=1 | ITER=2 | ITER=3 |
| 1 | 1 | 98.000 | 98.000 | 98.000 | 98.000 |
| 2 | 2 | 95.497 | 98.381 | 97.951 | 98.006 |
| 3 | 3 | 95.687 | 98.245 | 97.994 | 98.001 |
| 4 | 4 | 98.000 | 98.000 | 98.000 | 98.000 |
| 5 | 5 | 95.574 | 98.357 | 97.961 | 98.005 |
| 6 | 6 | 96.040 | 98.010 | 98.010 | 98.010 |
| component i | $\eta_{i}$ | Split Fraction |  |  |  |
|  |  | ITER=0 | ITER=1 | ITER=2 | ITER=3 |
| 1 | 1 | . 98000 | . 98000 | . 98000 | . 98000 |
| 2 | 2 | . 98000 | . 99277 | . 99085 | . 99110 |
| 3 | 2 | . 98000 | . 99180 | . 99057 | . 99060 |
| 4 | 1 | . 98000 | . 98000 | . 98000 | . 98000 |
| 5 | 2 | . 98000 | . 99238 | . 99058 | . 99078 |
| 6 | 2 | . 98000 | . 99000 | . 99000 | . 99000 |
|  | TAC (\$/yr) | 630,454 | 748,008 | 730,389 | 730,546 |

Table 7.3.3-2
Example 3: Iterations of ADJSTP


Table 7.3.4-1
Example 3: The Optimum Reflux Ratios


[^2]Table 7.4-1.
Example 4: Problem Definition

FEED (stream l):

| components | component name | mole fraction |
| :---: | :--- | :---: |
| 1 | Ethane | .20 |
| 2 | Propane | .20 |
| 3 | Butane | .15 |
| 4 | Pentane | .15 |
| 5 | Propere | .15 |
| 6 | l-Butene | .15 |


| Total flow rate | $=453.59 \mathrm{~kg}$-mole $/ \mathrm{hr}$ |
| ---: | :--- |
| Temperature | $=37.8^{\circ} \mathrm{C}$ |
| Pressure | $=1.0333 \mathrm{~kg} / \mathrm{cm}^{2} \mathrm{abs}$. |

DESIRES PRODUCTS:

| product | Component (s) | minimum recovery | minimum purity |
| :---: | :---: | :---: | :---: |
| 1 | 1 | 98\% | 98\% |
| 2 | 2 | 98\% | 98\% |
| 3 | 3, 4 | 98\% | 98\% |
| 4 | 5,6 | 98\% | 98\% |

Separation methods available are:
I) Distillation
II) Extractive distillation usirg Tetrahydrofuran (component 7)

Initial ordering of components at $54.4^{\circ} \mathrm{C}$

| $I$ | $I I$ |
| :--- | ---: |
| 1 | 1 |
| 5 | 2 |
| 2 | 5 |
| 6 | 3 |
| 3 | 6 |
| 4 | 4 |

### 7.4.1 Creation of Initial Structure

$$
\text { OPEN }=\{1\}
$$

For stream 1, MULTIC returns two designs:

Design \#1: $\quad \mathrm{LK}=1 \quad \mathrm{HK}=5 \quad \mathrm{ST}=\mathrm{I} \quad \alpha=3.456 \quad \mathrm{CDS}=.219$
Design \#2: $\quad \mathrm{LK}=6 \mathrm{HK}=3 \quad \mathrm{ST}=\mathrm{I} \alpha=1.246 \quad \mathrm{CDS}=3.775$

Design 2 is simulated and is feasible. Streams 2 and 3 are generated. Stream 2 is mainly product 1 and stream 3 contains the rest. OPEN is updated to

$$
\text { OPEN }=\{3\}
$$

For stream 3, MULTIC returns only one design:

Design \#l: $\quad L K=6 \quad H K=3 \quad S T=I \quad \alpha=1.246 \quad C D S=2.960$ This design is simulated and found to be feasible. Streams 4 and 5 are generated. Stream 5 is mainly product 3 and stream 4 contains the rest. OPEN is updated to

$$
\text { OPEN }=\{4\}
$$

Stream 4 is considered next. No design is possible using separation method I without product splitting, consequently other separation methods are explored. MUITIC returns the following design:

Design \#l: $\quad \mathrm{LK}=2 \mathrm{HK}=5 \quad \mathrm{ST}=\mathrm{II} \alpha=1.071 \quad \mathrm{CDS}=5.407$

This design, however, is not acceptable since the value of $\alpha$ is too small. Since no design alternatives now exist, PICK determines that the breaking of product 4 is necessary. Consequently, product 4 is broken and a new product set is defined as given below:

| Product Set 2 |  |
| :---: | :---: |
| $\frac{\text { Product }}{1}$ | $\frac{\text { Components }}{}$ |
| 2 | 1 |
| 3 | 2 |
| 4 | 6,4 |
| 5 | 5 |

The incomplete structure with the initial product set is shown in Figure 7.4.1-1.

For product set 2, the procedure for creation of the initial structure is repeated. By following the heuristic rules a feasible initial structure is created. The structure is shown in Figure 7.4.1-2. The total annual cost for this structure is 663,385 \$/yr. STORED is called and the feasible initial structure is saved for future reference.


Figure 7.4.1-1
Example 4: Infeasible Structure Using Initial Product Set


$$
\mathrm{TAC}=663,385 \$ / \mathrm{yr}
$$

Figure 7.4.1-2
Example 4: Initial Feasible Structure Using Product Set 2
7.4.2 Evolution of Structures

The initial structure is evolved. Rule 1 does not suggest any modification. Ruie 2 , however, suggests a change of split for separator l. This modification is implemented and structure E-l is created. Structure E-l is shown in Figure 7.4.2-1. This structure has a total annual cost of $600,395 \$ / \mathrm{yr}$ and is superior to the initial structure. Structure E-1 is saved by calling STORED.

Structure E-1 is evolved next. Rule 2 suggests a change of split for separator 2. This modification is implemented and Structure E-2 is created. Structure E-2 is shown in Figure 7.4.2-2. This structure has a total annual cost of $720,311 \$ / y r$ and is not as good as Structure E-1. STORED is called and structure E-l is restored.

Structure E-1 is evolved again. However, the evolutionary rules do not suggest any additional modifications. Structure E-l cannot be improved any further. Westerberg and Stephanopoulos [ ] have obtained the same structure as the optimal structure by a branch and bound procedure.

$\mathrm{TAC}=600,395 \$ / \mathrm{Yr}$

Figure 7.4.2-1
Example 4: Structure E-l Using Product Set 2, Optimal Structure

$\mathrm{TAC}=720,311 \$ / \mathrm{yr}$

Figure 7.4.2-2
Example 4: Structure E-2 Using Product Set 2
7.4.3 Satisfying Product Specifications

Table 7.4.3-l gives the four iterations of ADJST required to satisfy the product recovery specifications. Table 7.4.3-2 gives the three iterations of ADJSTP required to satisfy the product purity specifications. The format of these tables have been explained earlier.

### 7.4.4 Economic Optimization of Reflux Ratio

The operating reflux ratio for each column in the optimum structure is optimized by the bisection algorithm in Section 6.3. The optimum values are given in Table 7.4.4-1.

Table 7.4.4-2 gives a comparison of three methods that have been used to solve this problem. Again, the proposed method is computationally superior to the others.

### 7.5 Example 5: n-Butylene Purification System

Consider the n-butylene purification problem studied in detail by Hendry and Hughes [H4]. The feed stream is the stabilized output from a butane hydrogenation unit in a butadiene processing plant and consists of six components. Four products are to be isolated in relatively pure form. Ordinary distillation and extractive distillation using furfural as the MSA are suitable. The details of the problem are given in Tabie 7.5-1.

Table 7.4.3-1
Example 4: Iterations of ADJST


Table 7.4.3-2
Example 4: Iterations of ADJSTP

| product i | $\underline{j \in C_{i}}$ | $\mathrm{k} \in \mathrm{D}_{\mathrm{j}}$ | Purity |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | ITER=0 | ITER=1 | ITER=2 | ITER=3 |
| 1 | 1 | 5 | 99.074 | 99.534 | 99.533 | 99.550 |
| 2 | 2 | 5, 6 | 98.461 | 99.425 | 99.431 | 99.431 |
| 3 | 3, 4 | 6 | 99.498 | 99.868 | 99.870 | 99.870 |
| 4 | 6 | 3, 2 | 95.067 | 95.165 | 98.545 | 98.545 |
| 5 | 5 | 2, 1 | 96.230 | 96.262 | 96.691 | 98.014 |
| component i | $\eta_{i}$ |  |  | Split | ction |  |
|  |  |  | ITER=0 | ITER=1 | ITER=2 | ITER=3 |
| 1 | 1 |  | . 98000 | . 98000 | . 98000 | . 99037 |
| 2 | 2 |  | . 99110 | . 99110 | . 99456 | . 99456 |
| 3 | 2 |  | . 96257 | . 96257 | . 99327 | . 99327 |
| 4 | 0 |  | . 98000 | . 98000 | . 98000 | . 98000 |
| 5 | 2 |  | . 99078 | . 99525 | . 99525 | . 99525 |
| 6 | 2 |  | . 99000 | . 99741 | . 99741 | . 99741 |
|  | TAC (\$/Yr) |  | 654,143 | 719,846 | 786,920 | 791,921 |

> Table 7.4.4-1

Example 4: The Optimum Reflux Ratios


[^3]Tabie 7.5-1
Example 5: Problem Definition

FEED (stream 1):

| component | component name | mole fraction |
| :---: | :---: | :---: |
| 1 | Propane | . 0147 |
| 2 | n -Butane | . 5029 |
| 3 | Butene-1 | . 1475 |
| 4 | Trans-butene-2 | . 1563 |
| 5 | Cis-Butene-2 | . 1196 |
| 6 | Pentane | . 0590 |
| $\begin{aligned} \text { Total flow rate } & =303.04 \mathrm{~kg} \text {-mole } / \mathrm{hr} \\ \text { Temperature } & =53.89^{\circ} \mathrm{C} \\ \text { Pressure } & =5.62 \mathrm{~kg} / \mathrm{cm}^{2} \mathrm{abs} . \end{aligned}$ |  |  |

DESIRED PRODUCTS:

| product | component (s) |  | minimum <br> recovery | minimum <br> purity |
| :---: | :---: | :---: | :---: | :---: |
| 2 | 1 |  | $98 \%$ | $98 \%$ |
| 3 | 2 |  | $98 \%$ | $98 \%$ |
| 4 | $3,4,5$ |  | $98 \%$ | $98 \%$ |
|  | 6 |  | $98 \%$ | $98 \%$ |

Separation methods available are:
I) Distillation
II) Extractive distillation using Furfural (component 7)

Initial ordering of components at $54.4^{\circ} \mathrm{C}$

| $I$ | $I I$ |
| ---: | ---: |
| 1 | 1 |
| 3 | 2 |
| 2 | 3 |
| 4 | 4 |
| 5 | 5 |
| 6 | 6 |
| 7 | 7 |

### 7.5.1 Creation of Initial Structure

The synthesis program creates an initial structure by following the heuristic rules of Chapter 2. The initial structure has a total annual cost of $1,171,322 \$ / \mathrm{yr}$ and is shown in Diagram 7.5-1. STORED is called and the initial structure is saved for future reference.
7.5.2 Evolution of Structures

Evolution of the initial structure is attempted by calling EVLUTN. Rule 1 suggests the breaking up of product 3. The new product set is given below:

## Product Set 2

| Product | Components |
| :---: | :---: |
|  | 1 |
| 2 | 2 |
| 3 | 4,5 |
| 4 | 6 |
| 5 | 3 |

Using the product set above, the procedure for the creation of the initial structure is repeated and gives a new structure, structure E-1. Structure E-1 is shown in Figure 7.5.2-1. This structure has a total annual cost of 669,844 \$/yr and is superior to the initial structure. STORED is called and structure E-1 is saved for future reference.


$$
\mathrm{TAC}=1,171,322 \$ / \mathrm{yr}
$$

Figure 7.5.1-1
Example 5: Initial Structure Using Initial Product Set

$\mathrm{TAC}=669,844 \mathrm{~S} / \mathrm{yr}$
Figure 7.5.2-1
Example 5: Structure E-1 Using Product Set 2

Structure E-I is evolved next. Rules 2, 3 and 4 do not suggest any modifications. Rule 5, however, suggests changing the split in separator 1 . The structure downstream of separator 1 is destroyed. The proposed modification is implemented and a new structure, E-2, is created. This structure has a total annual cost of 658,737 \$/yr and is superior to structure E-1. STORED is called and structure $E-2$ is saved for future reference.

Structure E-2 is evolved next. Rules 2, 3 and 4 do not suggest any modifications. Rule 5, however, suggests a change in the split for separator 3. The structure downstream of separator 3 is destroyed and the proposed modification is implemented. A new structure, E-3, is created. This structure has a TAC $=701,786 \$ / \mathrm{yr}$ and is shown in Figure 7.5.2-3. . Since structure $\mathrm{E}-3$ is inferior to structure E-2, structure E-2 is restored in memory.

EVLUTN is called to evolve structure E-2.
However, none of the evolutionary rules suggest any modification. Consequently, structure E-2 cannot be improved any further. Hendry [H4] has obtained the same structure as the optimal structure.


$$
\mathrm{TAC}=658,737 \$ / \mathrm{yr}
$$

Figure 7.5.2-2
Example 5: Structure E-2 Using Product Set 2, Optimal Structure


```
TAC = 701,786 $/yr
```

Figure 7.5.2-3
Example 5: Structure E-3 Using Product Set 2

### 7.5.3 Satisfying Product Specifications

ADJST is called to satisfy the product recovery constraints. Four iterations are required to obtain the specified product recovery. The details of the iterations are given in Table 7.5.3-1.

ADJSTP is called next. Two iterations are required to satisfy the product purity constraints. Table 7.5.3-2 gives the relevent details of the iterations.

### 7.5.4 Economic Optimization of Reflux Ratio

The reflux ratio of each column in the structure is optimized by the bisection algorithm in Section 6.3. The optimum values are given in Table 7.5.4-1.

A comparison of the various methods employed to solve this problem is given in Table 7.5.4-2.

Table 7.5.3-2
Example 5: Iterations of ADJSTP

| product i | $\underline{j \in C_{i}}$ | $\underline{k} \in \mathrm{D}_{\mathrm{j}}$ | ITER=0 | Purity <br> ITER=1 | IT'ER=2 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 1 | 3 | 97.276 | 98.012 | 98.012 |
| 2 | 2 | 4, 3 | 99.894 | 99.905 | 99.905 |
| 3 | 4, 5 | 2, 7, 6 | 96.689 | 96.709 | 98.024 |
| 4 | 6 | 5 | 98.795 | 98.795 | 98.795 |
| 5 | 3 | 1, 2 | 99.061 | 99.064 | 99.064 |
| component i | $\eta_{i}$ |  | Split Fraction |  |  |
|  |  |  | ITER=0 | ITER=1 | ITER=2 |
| 1 | 1 |  | . 99785 | . 99785 | . 99785 |
| 2 | 2 |  | . 99782 | . 99782 | . 99782 |
| 3 | 2 |  | . 99722 | . 99798 | . 99798 |
| 4 | 1 |  | . 99789 | . 99789 | . 99789 |
| 5 | 2 |  | . 99795 | . 99795 | . 99795 |
| 6 | 1 |  | . 99447 | . 99447 | . 99447 |
| 7 | 1 |  | . 99500 | . 99500 | . 99745 |
|  | TAC ( $\$ / \mathrm{yr}$ ) |  | 878,840 | 887,997 | 887.870 |

Table 7.5.3-1
Example 5: Iterations of ADJST

| product i | $\underline{j} \in C_{i}$ | ITER=0 | ITER=1 | $\begin{gathered} \text { Recovery } \\ \text { ITER=2 } \end{gathered}$ | ITER=3 | ITER=4 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 1 | 97.229 | 97.986 | 98.000 | 98.000 | 98.000 |
| 2 | 2 | 96.160 | 97.301 | 97.717 | 98.021 | 98.033 |
| 3 | 4, 5 | 95.962 | 97.277 | 97.734 | 97.936 | 98.002 |
| 4 | 6 | 97.559 | 97.994 | 98.000 | 98.000 | 98.000 |
| 5 | 3 | 96.587 | 97.984 | 98.000 | 98.000 | 98.000 |
| 6 | 7 | 99.500 | 99.500 | 99.500 | 99.500 | 99.500 |
| component i | $\eta_{i}$ | Split Fraction |  |  |  |  |
|  |  | ITER=0 | ITER=1 | ITER=2 | ITER=3 | ITER=4 |
| 1 | 1 | . 99000 | . 99771 | . 99785 | . 99785 | . 99785 |
| 2 | 2 | . 99000 | . 99465 | . 99640 | . 99782 | . 99782 |
| 3 | 2 | . 99000 | . 99714 | . 99722 | . 99722 | . 99722 |
| 4 | 1 | . 99000 | . 99510 | . 99690 | . 99757 | . 99789 |
| 5 | 2 | . 99000 | . 99515 | . 99696 | . 99763 | . 99795 |
| 6 | 1 | . 99000 | . 99441 | . 99447 | . 99447 | . 99447 |
| 7 | 1 | . 99000 | . 99500 | . 99500 | . 99500 | . 99500 |
|  | (\$/yr) | 658,737 | 782,652 | 827,265 | 874,700 | 878,840 |

Table 7.5.4-1
Example 5: The Optimum Reflux Ratios

| Separator | Feed Stream |  | Optimum $R / R_{\mathrm{m}}$ <br> 1 |
| :---: | :---: | :---: | :---: |
|  | 1 |  | 1.638 |
| 2 | 2 | 1.269 |  |
| 3 | 3 | 1.112 |  |
| 4 | 6 | 1.716 |  |
| 5 | 9 | 1.300 |  |

Table 7.5.4-2
Example 5: Comparison of Various Methods
$N_{S}=376$
$\mathrm{N}_{\text {usp }}=92$

| Method | ${ }^{\mathrm{NS}_{\text {a }}}$ | $\underline{N u s p}{ }_{\text {a }}$ |  |
| :---: | :---: | :---: | :---: |
| Hendry and Hughes [ $H^{4}$ ] DP | 4 | 64 | certain splits were prohibited, reducing $\mathrm{N}_{\mathrm{S}}=227, \mathrm{~N}_{\mathrm{usp}}=64$ |
| Westerberg and Stephanopoulos [W1] B\&B | 4 | 43 |  |
| Stephanopoulos and | 10 |  | initial structure obtained by B\&B |
| Westerberg [S2] Evolut'ry | $\overline{1} 9$ |  | initial structure obtaine as direct sequence |
| Rodrigo and |  |  | some more splits were prohibited, reducing |
| Seader [R3] OBS | 14 | 23 | $\mathrm{N}_{\mathrm{s}}=33, \mathrm{~N}_{\mathrm{usp}}=30$ |
| Gomez and Seader [G1] PBOS |  | 21 |  |
| Seader and |  |  |  |
| Westerberg [S1] H\&E | 3 | 11 |  |
| PROPOSED METHOD | 4 | 12 |  |

### 7.6 Example 6: Hydrocarbon Separation III

Consider the hydrocarbon separation problem described by Thompson and King (Example 2) [T4]. The problem as stated is in error [T2]; the corrected version is considered next. The feed stream consists of an eight component mixture of paraffins, olefins and aromatic compounds in the range $\mathbf{C 5}$ to $\mathbf{C 7}$. Six products are to be produced in relatively pure form using four separation methods. The details of the problem are given in Table 7.6-1.

### 7.6.1 Creation of Initial Structure

$$
\text { OPEN }=\{1\}
$$

For stream l, MULTIC returns four designs:

Design \#1: $\quad \mathrm{LK}=7 \quad \mathrm{HK}=2 \quad \mathrm{ST}=\mathrm{I} \quad \alpha=1.224 \quad \mathrm{CDS}=1.968$
Design \#2: $\quad \mathrm{LK}=2 \quad \mathrm{HK}=4 \quad \mathrm{ST}=\mathrm{I} \quad \alpha=1.159 \quad \mathrm{CDS}=2.869$
Design \#3: $\quad L K=4 \quad H K=6 \quad S T=I \quad \alpha=1.284 \quad C D S=2.643$
Design \#4: $\quad \mathrm{LK}=6 \mathrm{HK}=3 \mathrm{ST}=\mathrm{I} \quad \alpha=1.927 \quad \mathrm{CDS}=1.453$

Design 4 is tried for detailed simulation. DETAIL returns a feasible design. Two new streams, 2 and 3, are generated. Stream 3 contains mostly product 3 and stream 2 contains the rest. The OPEN set is updated,

$$
\text { OPEN }=\{2\}
$$

Table 7.6-1
Example 6: Eroblem Definition

FEED (stream l):

| Component | component name | mole fraction |  |
| :---: | :--- | :--- | :--- |
|  |  | Pentane | .125 |
| 2 | Hexane | .125 |  |
| 3 | Heptane | .125 |  |
| 4 | Benzene | .125 |  |
| 5 | Toluene | .125 |  |
| 6 | Cyclohexane | .125 |  |
| 7 | Hexene | .125 |  |
| 8 | l-Pentene | .125 |  |

DESIRED PRODUCTS:

| product | component (s) | minimum recovery | minimum purity |
| :---: | :---: | :---: | :---: |
| 1 | 1 | 98\% | 98\% |
| 2 | 2 | 98\% | 98\% |
| 3 | 3, 5 | 98\% | 98\% |
| 4 | 4 | 98\% | 98\% |
| 5 | 6 | 98\% | 98\% |
| 6 | 7, 8 | 98\% | 98\% |

Separation methods available are:
I) Distillation
II) Extractive distillation using Phenol (component 9)
III) Extractive distillation using Tetrahydrofuran (component 10)
IV) Extractive distillation using l-Hexene (component 11)

Takle 7.6 m 1 continued

Initial Ordering of Components at $54.4^{\circ} \mathrm{C}$

| $I$ | $I I$ | $I I I$ | $I V$ |
| ---: | ---: | ---: | ---: |
| 8 | 1 | 1 | 8 |
| 1 | 8 | 8 | 1 |
| 10 | 2 | 7 | 10 |
| 7 | 7 | 11 | 11 |
| 11 | 11 | 2 | 7 |
| 2 | 6 | 10 | 4 |
| 4 | 3 | 4 | 2 |
| 6 | 10 | 6 | 6 |
| 3 | 4 | 3 | 3 |
| 5 | 5 | 5 | 5 |
| 9 | 9 | 9 | 9 |

For stream 2, MULTIC returns three ciesigns:
$\begin{array}{llllll}\text { Design \#1: } & \mathrm{LK}=7 & \mathrm{HK}=2 & \mathrm{ST}=\mathrm{I} & \alpha=1.224 & \mathrm{CDS}=2.019 \\ \text { Design \#2: } & \mathrm{LK}=2 & \mathrm{HK}=4 & \mathrm{ST}=\mathrm{I} & \alpha=1.159 & \mathrm{CDS}=5.101 \\ \text { Design \#3: } & \mathrm{LK}=4 & \mathrm{HK}=6 & \mathrm{ST}=\mathrm{I} & \alpha=1.284 & \mathrm{CDS}=4.695\end{array}$

Design 1 has the smallest value of $C D S$ and is considered for detailed simulation. DETAIL returns a feasible design, generating two new streams, 4 and 5. Stream 4 contains products 6 and l. Stream 5 contains products 2, 4 and 5. The OPEN set is updated,

$$
\text { OPEN }=\{4,5\}
$$

Stream 4 is considered next. MULTIC returns two designs:

Design \#l: $\quad L K=1 \quad H K=8 \quad S T=I I \quad \alpha=1.500 \quad \operatorname{CDS}=.929$
Design \#2: $\quad \mathrm{LK}=1 \quad \mathrm{HK}=8 \quad \mathrm{ST}=\mathrm{III} \alpha=1.116 \quad \mathrm{CDS}=3.420$

Note that separation methods I and IV are not considered since these methods cannot give any design specification without the breaking of product 6. Design 1 is considered for detailed simulation. DETAIL returns an infeasible design. Design 2 is considered next. DETAIL returns a feasible design now. Two new streams, 6 and 7, are generated. Stream 6 contains product 1 and stream 7 contains product 6 and the MSA used. The OPEN set is updated,

$$
\text { OPEN }=\{5,7\}
$$

For stream 5, MULTIC returns two designs:

Design \#I: $\quad L K=2 \quad H K=4 \quad S T=I \quad \alpha=1.159 \quad C D S=2.525$
Design \#2: $\quad \mathrm{LK}=4 \quad \mathrm{HK}=6 \quad \mathrm{ST}=\mathrm{I} \alpha=1.284 \quad \mathrm{CDS}=2.941$

Design $l$ is considered for detailed simulation. DETAIL returns a feasible design and two new streams, 8 and 9, are generated. Stream 8 contains product 2 and stream 9 contains the rest. The OPEN set is updated,

$$
\text { OPEN }=\{7,9\}
$$

For stream 7, the use of separation method I (distillation) does not produce any design specification without breaking product 6. Other separation methods are not used because heuristic 4 is invoked. Consequently, no design specifications is produced and the synthesis cannot proceed any further. The partial structure created so far is shown in Figure 7.6.1-1. PICK breaks product 6 giving a new product set.

Product Set 2

| Product | Components |
| :---: | :---: |
|  | 1 |
| 2 | 2 |
| 3 | 3,5 |
| 4 | 4 |
| 5 | 6 |
| 6 | 8 |
| 7 | 7 |



Figure 7.6.1-1
Example 6: Infeasible Structure Using Initial Product Set

With this new product set, the procedure for the creation of an initial structure is repeated. The initial structure so created is shown in Figure 7.6.1-2. This structure has a total annual cost of $1,305,548 \mathrm{~s} / \mathrm{yr}$. STORED is called and the initial structure is saved for future reference.

### 7.6.2 Evolution of Structures

Evolution of the initial structure is attempted. Rule 1 does not suggest any modification. Rule 2 , however, suggests investigation of the next best design for separator 3. The structure downstream of separator 3 is destroyed. The design for separator 3 is changed and the structure downstream is recreated. Therefore, a new structure $\mathrm{E}-1$ is obtained. This structure has a total annual cost of $1,365,207 \$ / y r$ and is shown in Figure 7.6.2-1. STORED is called and since structure e-l is not as good as the initial structure, the initial structure is restored. The initial structure is evolved again. Evolutionary rule 3 suggests a change in the separation method for separator 2. The structure downstream of separator 2 is destroyed and a new structure is created with separation method II for separator 2. This new structure, E-2, has a total annual cost of $1,152,250 \$ / \mathrm{yr}$ and is shown in Figure 7.6.2-2. Structure $E-2$ is superior to the initial structure and is saved for future reference by calling STORED.


$$
\mathrm{TAC}=1,305,548 \$ / \mathrm{yr}
$$

Figure 7.6.1-2
Example 6: Initial Feasible Structure Using Product Set 2

$\mathrm{TAC}=1,365,207 \$ / \mathrm{yr}$

Figure 7.6.2-1
Example 6: Structure E-1 Using Product Set 2

$\mathrm{TAC}=1,152,250 \$ / \mathrm{yr}$

Figure 7.6.2-2
Example 6: Structure E-2 Using Product Set 2

Structure E-2 is evolved next. Rule 2 does not suggest any modificaticn. Rule 3 suggests a change of separation method for separator 3. The structure downstream of separator 3 is destroyed. The proposed modification is tried, but it results in an infeasible design because the MSA is not soluble with the bottom strean. The incomplete structure is shown in Figure 7.6.2-3. STORED is called again and structure E-2 is restored.

Structure E-2 is evolved again. Rule 3 again suggests a change of separation method for separator 5 . The structure downstream of separator 5 is destroyed. A new structure, $E-3$, is created by implementing the proposed change and recreating the structure downstream from separator 5. This structure is shown in Figure 7.6.2-4 and has a total annual cost of $1,011,157 \$ / \mathrm{yr}$. This structure is better than structure $E-2$ and is saved for future reference by calling STORED.

Structure E-3 is evolved next. Rules 2 and 3 do not suggest any changes. Rule 4, however, suggests a change in split for separator 7 to delay the removal of the MSA. The structure downstream of separator 7 is destroyed. Separator 7 is redesigned including the proposed modification and the downstream structure is recreated. A new structure, E-4, is thus created and is shown in Figure 7.6.2-5. This structure has a total annual cost of 953,078 \$/yr. Since this structure is better than structure $E-3$, STORED is called and structure $\mathrm{E}-4$ is stored.


Figure 7.6.2-3
Example 6: Infeasible Structure During Evolution of Structure E-2


Figure 7.6.2-4
Example 6: Structure E-3 Using Product Set 2

$\mathrm{TAC}=953,078 \$ / \mathrm{yr}$

Figure 7.6.2-5
Example 6: Structure E-4 Using Product Set 2, Optimal Structure

Structure E-4 is evolved next. However, rules 2, 3, 4 and 5 do not suggest any modifications and structure E-5 cannot be improved further. Thompson and King [T4] have obtained the same structure after considerably more effort.

### 7.6.3 Satisfying Product Specifications

ADJST is called next to satisfy the product recovery constraints. Five iterations are required to obtain the specified product recovery. The details of the iterations are given in Table 7.6.3-1. The format of the table has been explained earlier.

ADJSTP is called next. Four iterations are required to satisfy the product purity constraints. In doing so, the recovery constraints are not violated. Table 7.6.3-2 gives the details for each iteration. The total annual cost of the structure increases to $1,217,617 \$ / y r$ because of these adjustments.
7.6.4 Economic Optimization of Reflux Ratio

The reflux ratio of each column in the optimal structure is optimized by the bisection algorithm in Section 6.3. The optimal values are given in Table 7.6.4-1. The total annual cost for the optimum structure incorporating the optimum value of the reflux ratio is $1,178,648 \$ / y r$. This gives an improvement of $3.2 \%$ on TAC because of this optimization.

Table 7.6.4-2 compares the present method with that of the heuristic method of Thompson and King.

| product i | $\underline{j \in C_{i}}$ | Recoveries |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | ITER=0 | ITER=1 | ITER=2 | ITER=3 | ITER=4 | ITER=5 |
| 1 | 1 | 96.040 | 98.010 | 98.010 | 98.010 | 98.010 | 98.010 |
| 2 | 2 | 96.345 | 99.189 | 98.005 | 98.005 | 98.005 | 98.005 |
| 3 | 3, 5 | 98.991 | 98.496 | 98.246 | 98.122 | 98.060 | 98.060 |
| 4 | 4 | 95.874 | 98.150 | 97.999 | 97.999 | 97.999 | 98.000 |
| 5 | 6 | 94.109 | 98.063 | 98.063 | 98.063 | 98.063 | 98.063 |
| 6 | 8 | 95.867 | 98.136 | 98.000 | 98.000 | 98.000 | 98.000 |
| 7 | 7 | 94.119 | 98.054 | 98.054 | 98.054 | 98.054 | 98.054 |
| 8 | 9 | 99.500 | 99.500 | 99.500 | 99.500 | 99.500 | 99.500 |
| 9 | 9 | 99.501 | 99.500 | 99.500 | 99.500 | 99.500 | 99.500 |
| component i | $\eta_{i}$ | ITER=0 | ITER=1 | $\begin{array}{r} \text { Split } \\ I T E R=2 \end{array}$ | ractions ITER=3 | ITER=4 | ITER=5 |
| 1 | 2 | . 98000 | . 99000 | . 99000 | . 99000 | . 99000 | . 99000 |
| 2 | 1 | . 98000 | . 99655 | . 98466 | . 98466 | . 98466 | . 98466 |
| 3 | 1 | . 98000 | . 97009 | . 96513 | . 96267 | . 96145 | . 96145 |
| 4 | 2 | . 98000 | . 99084 | . 99009 | . 99009 | . 99009 | . 99009 |
| 5 | 0 | . 98000 | . 98000 | . 98000 | . 98000 | . 98000 | . 98000 |
| 6 | 3 | . 98000 | . 99350 | . 99350 | . 99350 | . 99350 | . 99350 |
| 7 | 3 | . 98000 | . 99347 | . 99347 | . 99347 | . 99347 | . 99347 |
| 8 | 2 | . 98000 | . 99088 | . 99020 | . 99020 | . 99020 | . 99020 |
| 9 | 2 | . 98000 | . 99500 | . 99500 | . 99500 | . 99500 | . 99500 |
| TAC | (\$/yr) | 953,078 | 76,126 | 1,097,808 | 1,093,811 | 1,093,718 | 93,719 |

Table 7.6.3-2
Example 6: Iterations of ADJSTP


Table 7.6.4-1
Example 6: The Optimum Reflux Ratios

| Separator | Feed Stream | Optimum $\mathrm{R} / \mathrm{R}_{\text {min }}$ |
| :---: | :---: | :---: |
| 1 | 1 | 1.112 |
| 2 | 2 | 1.716 |
| 3 | 3 | 1.300 |
| 4 | 6 | 1.300 |
| 5 | 8 | 1.560 |
| 6 | 9 | 1.430 |
| 7 | 13 | 1.050 |
| 8 | 5 | 1.300 |

Table 7.6.4-2
Example 6: Comparison of Various Methods
$N_{S}>63,000$

| Method | $\mathrm{N}_{\mathbf{s}}$ |  |
| :--- | ---: | :--- |
| Thompson and King <br> $[T 4]$ Heuristic |  |  |
| PROPOSED METHOD | 15 | has problem of "cycling" |

## Chapter 8

NONSHARP SEFARATION SYNTHESIS

The discussion so far has been limited to cases where a specie was present only in one product. In actual plant design activity, it is not uncommon to have product specifications in which some of the species are desired in more than one product. The presence of a specie in more than one product can lead to nonsharp separations in which the recovery of the keys is not close to unity. Nonsharp separations are inherently more economical, making the study of the nonsharp separation synthesis problem worthwhile.

In this preliminary work, an attempt is made to develop a procedure for the creation of an initial structure for nonsharp separation synthesis problems. This study is restricted to cases where a specie is desired in not more than two products. Also, the ordering of the species is assumed to be composition independent. In addition, we will limit ourselves to conventional distillation units. In the next section, we will discuss the concept of material diagrams and various operations and manipulations on these diagrams, classes of product types and an observation based on this classification. In the following two sections we will analyse typical synthesis problems for binary and ternary systems. Conclusions based on this study are presented in Section 8.4 and a sample problem is synthesized in Section 8.5.

### 8.1 Material Diagrams

In this section we will describe the concept of material diagrams, since they will be used extensively in the remaining parts of the chapter. We will define two material diagrams, the first one, called the material diagram (MD), is a graphical representation of the feed stream. Each specie in the feed is represented by a rectangle of fixed height. The width of each rectangle is proportional to its concentration in the stream. Each rectangle thus represents the quantity of a specie in the stream. The rectangles are arranged in order of decreasing separation factor of the corresponding species. Adjacent species are delineated by dotted vertical lines. Figure 8.1-1 is an MD.

Another material diagram, called the material allocation diagram (MAD) is a graphical representation of the desired products on the MD. Each product is delineated on the MAD by solid lines. In the area corresponding to each product the product number is given. Figure 8.1-2 shows an MAD for the MD of Figure 8.1-1. Four products, I, II, III and IV have been delineated.

## 8.1-1 Operation on the MAD

Two operations are defined on the MAD. They are;
a) Horizontal division (HD): corresponds to the physical operation of stream splitting. This operation produces two streams of the same composition, one of which


Figure 8.1-1
A Typical Material Diagram (MD)


Figure 8.1-2
A Material Allocation Diagram (MAD)
is processed further and the other one bypasses processing and goes directly to a product. Graphically, HD is represented by a horizontal line which cuts the MAD into two parts without intersecting a solid vertical line in the interior of the MAD. The two parts have identical composition. A sharp horizontal division (SHD) occurs when the horizontal line touches one of the solid horizontal lines in the interior of the MAD.

A nonsharp HD makes some of the separations semi-sharp or nonsharp. By varying the amount bypassed, the degree of sharpness can be adjusted. A larger bypass would result in sharper separation but would process less material and a smaller: bypass would result in sloppier separation with more material to process. The optimum bypass can be computed by more analytical calculations, however, for the purpose of creation of the initial structure, we will set the bypass which leads to about $90 \%$ recovery of the keys. This assumption is termed heuristic 1. A horizontal division is shown in Figure 8.l.l-1.
b) Vertical division (VD): corresponds to the physical process of separation (such as distillation). This operation produces two streams which are of different compositions. Depending on the MAD, three different separations are possible,

1) A separation along a vertical solid line which coincides with a dotted line. This corresponds to the physical process of sharp separation (s).


Figure 8.1.1-1
A Horizontal Division (HD)


Figure 8.1.1-2
Vertical Divisions of the MAD
2) A separation along a vertical solic line which does not coincide with any dotied line (or along a vertical line which is broken at one of the ends and coincides with a dotted line). This corresponds to the physical process of semi-sharp separation (ss).
3) A separation along an incomplete solid line broken at both the ends, and which coincides with a dotted line. This may correspond to the physical process of nonsharp separation ( ns ), if the following condition, called the condition for nonsharp separation, is met:
"The light product is such that it does not. have any component heavier than the heavy key (HK) and the heavy product is such that it does not have any component lighter than the light key (LK)."

Figure 8.1.l-2 shows each of three vertical divisions and the corresponding physical operation for three component systems.

### 8.1.2 Definitions

Depending on the feed composition and the desired product specification, the boundaries (solid lines) in the MAD can take any of innumerable positions. Some of these topologies are important in analysing the synthesis problems and are defined in this subsection.

Let $N=n$ nober of species in the system, these species are $1,2,3, \ldots N$
$\mathrm{F}=$ total amount of the process stream
$f_{i}=$ amount of specie $i$ in the process stream Note: $F=\sum_{i=1}^{N} f_{i}$
$\mathrm{M}=$ number of desired products. The products are 1, 2, .... M
$P_{j}=$ amount of product $j$. Note: $F=\sum_{j=1}^{M} P_{j}$
$C_{j}=$ species in product $j$
$P_{j k}=$ amount of specie $k \in K_{j}$ in product $j$
$d c_{i}=$ distribution coefficient of $i$

The species in the system are arranged such that

$$
d c_{i-1}>d c_{i}>d c_{i+1} \quad i=2, \ldots, N-1
$$

Decreasing Cascade: A product $j$ is defined to be a decreasing cascade if the desired components in the product are consecutive and are such that the more volatile component is desired in a larger proportion of the inlet amount. Or mathematically,

$$
\frac{P_{j} k-1}{f_{k-1}}<\frac{P_{j k}}{F_{k}} \quad k, k-1 \in C_{j}
$$

Product $j$ is called a semi-decreasjng cascade if one of the inequalities is replaced by $\geq$ in the above equation. In Figure 8.1.2-I, product $I$ is a decreasing cascade. The definitions above are valid when $k_{j}$ has only one component.

Increasing Cascade: A product $j$ is defined to be an increasing cascade if the desired components in the product are consecutive and are such that the less volatile component is desired in a larger proportion of the inlet amount, or

$$
\frac{P_{j k}}{f_{k}}<\frac{P_{j k+1}}{f_{k+1}} \quad k, k+1 \in C_{j}
$$

Product $j$ is called a semi-increasing cascade if one or more of the inequalities is replaced by s in the above equation. In Figure 8.i.2-1, products II and III are both increasing cascades. The definitions above are valid when $C_{j}$ has only one element.

Center Peak: A three component product is defined to be a center peak if the desired components are consecutive and the center specie is required in a larger proportion of the inlet amount than the other two components. Or,

$$
\frac{P_{j k-1}}{f_{k-1}}<\frac{P_{j k}}{f_{k}}>\frac{P_{j k+1}}{f_{k+1}} \quad k-1, k, k+1 \in C_{j}
$$

In Figure 8.1.2-2, product $I$ is a center peak.

Nonuniform Product: A product not classified according to any of the above definitions is a nonuniform product. In Figure 8.1.2-3, product II is a nonuniform product. Uniform Product: A product which is not nonuniform is called a uniform product.

### 8.1.3 Manipulations in the MAD

Without any loss of information the following three manipulations can be performed on an MAD. These manipulations are helpful in solving the synthesis problem. Aligning a product: on the MAD this manipulation makes the adjacent components of a product of uniform hej.ght. Any two component products and ariy center peak product can be aligned.

Centering of a product: this manipulation makes the product fill the entire height of the MAD and the boundaries are as far as possible from the closest visible dotted lines.

Off centering of a product: this manipulation makes the product fill the entire height of the MAD and makes one of the boundaries coincide with one of the outermost boundaries of the MAD.

Figure 8.1.3-3. gives these manipulations on a three component MAD.


Product $I$ is a decreasing cascade Products II and III are increasing cascades

Figure 8.1.2-1
Classification of Products


Product $I$ is a center peak Product II is a nonuniform product

Figure 8.1.2-2
Classificaticn of Products


Figure 8.1.3-1
Manjpulations on an MAD

One very important observation in synthesis is to realize when a multicomponent product cannot be isolated as a single product. In that case the multicomponent product has to be broken into paxts. The following rule gives an early recognition of such products:

Rule 1: A nonuniform product has to be broken such that the parts are uniform products.
8.2 Binary Systems

For binary systems, it is meaningful to consider only two desired products. If there were three products, for example, one of these three products would be superfluous because it could be produced by mixing the other two products. All possible product requirements can be classified in one of the following three ciasses,

1) When one specie is split in both the products
2) When both species are split in both products
3) When none of the species is split

For case 3 there is only one solution and that is isolating each specie by a single sharp separator. For case 1, a semi-sharp separator would isolate the desired products. Case 2 is the most general and is considered in detail. A typical MAD for this case is shown in Figure 8.2-1. Notice that the norizontal divisions are possible at both ends of the MAD. TWO HD's are performed in accordance with heuristic 1. Observe the reduced MAD now, clearly a nonsharp separation would isolate the desired products. The development of the flowsheet is shown in Figure 8.2-1.


Figure 8.2-1

### 8.3 Ternary Systems

The problem becomes slighty more complicated in the ternary syster compared to the binary systern. Many different product specifications are possible. Instead of studying all the different product specifications possible, we will study representative problems from three different classes of product specifications here. In each case the feed consists of three species, $A, B$ and $C$ in order of decreasing distribution coefficient.
8.3.1 One Component Split in Two Products

Consider the problern in which $B$ is split into two products, I and II. A typical MAD for such a problem is shown in Figure 8.3.1-1. Notice that horizontal divisjon is possible and is preformed in accordance with heuristic 1. Also, observe that product II i.s nonuniform and needs to be broken. Product I is centered. Two vertical divisions are possible as shown by $\mathrm{Ss}_{1}$ and $\mathrm{ss}_{2}$ on the MAD. The CDS for both of the vertical divisions is calculated and the easier one (the one with a smaller value of CDS) is performed first. The complete flowsheet for the case when $s_{1}$ is the easier of the two is shown in Figure 8.3.1-1.

Another possible problem in this class is when one of the extreme components (the lightest or the heaviest component) in the system is split into two products. One such problem is shown in Figure 8.3.1-2. HD is possible and is performed in accordance with heuristic 1 . Notice that

initial MAD

centering I


$$
\begin{array}{ll}
\mathrm{LK}=\mathrm{A} & \mathrm{LK}=\mathrm{B} \\
\mathrm{KK}=\mathrm{B} & \mathrm{FiK}=\mathrm{C}
\end{array}
$$

Figure 8.3.1-1
Nonsharp Synthesis for a Ternary System

initial MAD


Figure 8.3.1-2
Nonsharp Synthesis for a Ternary System
product II is a semi-increasing cascade and it may be possible to isolate it without breaking. A careful look at the MAD reveals a serni-sharp separation capable of isolating both the products. This separation is performed and the resulting flowsheet js shown in Figure 8.3.1-2.

### 8.3.2 Two Component Split in Two Products

Consider the case illustrated in Figure 8.3.2-1. Both products I and II are uniform and it may not be necessary to break them. HD is possible and is performed in accordance with heuristic 1. A nonsharp separation is clearly possible and is performed. The complete flowsheet is shown in Figure 8.3.2-1.

Consider another problem in this class as shown in Figure 8.3.2-2. $H D$ is possible and is performed. Notice that product $I$ is nonuniform and needs to be broken. Product II is centered, two semi-sharp separations are possible now. The CDS fox each separation is computed ard the easiest one is performed first. The flowsheet for the case when $s s_{I}$ is the easier of the two is shown in Figure 8.3.2-2.

### 8.3.3 Three Species Split

Consider the synthesis problem shown in Figure 8.3.3-1. Both products I and II are uniform. $H D$ is possible on both enas of the MAD. A little reflection will show that sharp horizontal divisions are preferable on both ends. The MAD after HD's have been performed is shown next. Alignment is


Figure 8.3.2-1
Nonsharp Synthesis of a Sample Problem in 8.3.2

centering II


Figure 8.3.2-2


Figure 8.3.3-1
Nonsharp Synthesis of a Sample Problem in 8.3.3
then performed. One semi-sharp separation i.s required to isolate both products. The completed flowsheet is shown in Figure 8.3.3-1.

Another synthesis problem is shown in Figure 8.3.3-2. Product I is nonuniform and needs to be broken. Notice that $H D$ is possible on both ends of the MAD. Again a little reflection will show that one sharp horizontal division is preferable and the other $H D$ is performed in accordance with heuristic l. The SHD is performed either at the top (case 1) or at the bottom (case 2) of the MAD, whichever bypasses more material. Both cases for this problem are shown in Figure 8.3.3-2.

At this point we would like to propose another heuristic which concerns the decision of sharp horizontal division. The heuristic is

Heuristic 2: For three or more component systems, perform a sharp horizontal division if it does not result in any additional sharp separations.

A three product case is considered next. The MAD under consideration is shown in Figure 8.3.3-3. Product I is a center peak, products II and III are increasing cascades, i.e., all products are uniform and may be isolated without breaking. HD is possible and heuristic 2 indicates a sharp horizontal division. SHD is performed. Now an attempt is made to identify possible separations. Products II and III are off centered and product I is centered. The resulting MAD is shown next. Two separations,

case 1: SHD a.t the top of the MAD

alignment of Pr. II

case 2: SHD at the bottom of the MAD

centering Pr. II


Figure 8.3.3-2
Nonsharp Synthesis of Another Sample Problem in 8.3.3

off centering $\operatorname{Pr} . \operatorname{II}$


Figure 8.3.3-3
Nonsharp Synthesis of a Three Product Problem
$s_{1}$ and $s_{2}$, are possible. The CDS for both separations is evaluated and the easier one is performed first. A complete flowsheet for the case when $\mathrm{ss}_{1}$ is the easier of the two is also shown in Fi.gure 8.3.3-3.

### 8.4 A Procedure for Creation of the Initial Structure Nonsharp Separations

Based on the experience gained in solving synthesis problems for binary and ternary systems in the previous two section and by inductive reasoning along similar lines, a procedure for creation of the initial structure emerges. The various steps for this procedure are given below,

Step 1. Complete the material allocation diagram (MAD) for the problem at hand.

Step 2. Study the products and classify them. Also note which products need to be broken (Rule 1).

Step 3. Examine the MAD for the possibility of horizontal divisions (HD) or sharp horizontal divisions (SHD). Heuristic 1 anā 2 are followed.

Step 4. Perform manipulations on the MAD to identify the various possible separations.

Step 5. Evaluate the CDS for each separation identified in Step 4.

Step 6. Ferform the easiest separation.
Step 7. Jpdate the MAD and repeat Steps 2, 3, 4, 5 anả 6 for each MAD.

Step 8. Translate the operations on the MAD back to physical operations and thus complete the flowsheet.

As the synthesis progresses, the speculation about isolation of multicomponent products for the initial feed made in Step 2 may turn out to be wrong. In that case the synthesis is restarted with this additional information. Such a situation appears in the example considered in the next section.

### 8.5 A Sample Problem

As an example of the procedure in Section 8.4, a four component synthesis problem is solved. The problem is defined in Table 8.5-1 and the corresponding MAD is given in Figure 8.1-2. Notice that products II and III are decreasing cascades, product II is an increasing cascade and product IV, a single component product, can simply be classified as uniform. So each of the four products is uniform and may be isolated without breaking. No horizontal division is possible. The MAD is rearranged and only one separation is identified without breaking of a product. This separation is performed and the MAD is updated as shown in Figure 8.5-1. Now, however, we cannot identify any separation that will not necessitate breaking product I later. Therefore, the initial speculation that product I can be isolated without breaking is incorrect and product $I$ is to be broken. In the light of this new information, the synthesis procedure is restarted. Four separations can be identified now. The CDS for each is evaluated and shown in Figure 8.5-1. Separation $\mathrm{Ss}_{2}$ is the easiest and is performed.

Table 8.5-1<br>Problem Definition

## FEED:

| Component | Component Name | Mole Fraction |
| :---: | :---: | :---: |
| 1 | n-Butane | .25 |
| 2 | n-Pentane | .25 |
| 3 | n-Hexane | .25 |
| 4 | n-Heptane | .25 |

```
Total flow rate = 181.440 kg-mole/hr
Temperature = = 37.8 8
Pressure = 1.0333kg/
```

DESIRED PRODUCTS:

| Product | Component (mole fraction) |  |  |  | Total Flow Rate kg -mole/hr |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1 | 2 | 3 | 4 |  |
| I | . 4615 | . 3846 | . 1539 | - | 58.968 |
| II | . 4444 | . 5556 | - | - | 40.824 |
| III | - | - | . 6657 | . 3333 | 54.432 |
| IV | - | - | - | 1.000 | 27.216 |

Separation Method Available is: A) Distillation
Initial Ordering at $54.4^{\circ} \mathrm{C}$ :

Two MAD's, MAD1 and MAD2, result because of this separation. MADI is consjdered next. HD is possible now and is performed in accordance with heuristic l. One separation, $s s_{1}$, is possible now and is performed. MAD2 is considered next and no horizontal division is possible. MAD2 is rearranged and two semi-sharp separations are identified. The CDS for each separation is computed and $s_{1}$, the easier of the two, is performed next. HD is possible for this new MAD and is performed in accordance with heuristic 1. One semi-sharp separation is identified. This separation is performed next. All products have been isolated and the initial structure is shown in Figure 8.5-1.


Product IV isolated, but
design abandoned


Figure 8.5-1
Nonsharp Synthesis of the Sample Problem


MAD 1


separation performed

separation $s_{1}$ performed



Fjgure 8.5-1 Continued

## Chapter 9

## CONCLUSIONS AND RECOMMENDATIONS

In this dissertation, problems related to the synthesis of separation sequences were examined. The major thrust has been on the synthesis of sharp separation sequences capable of isolating multicomponent products from a multicomponent feed. In addition, the products were specified in terms of desired recoveries and purities. The operating reflux ratio of each separation unit in the sequence was optimized. The problem of synthesis of nonsharp separation sequences was also investigated.

An evolutionary approach to the synthesis of sharp separations has been proposed. The synthesis problem is decomposed into two phases. In the first phase, an initial feasible structure is created by using the heuristic rules. In the second phase, the initial structure obtained in the first phase is successively improved by applying the evolutionary rules. The heuristic rules embody knowledge of the general behavior of separation units and separation sequences, and the evolutionary rules question the validity of these heuristic rules for the particular problem under considexation. This approach closely mimics the problem solving procedures commonly employed by engineers, especially with regard to relatively large systems.

The proposed procedure does not suffer from the shortcomings of the dynamic programming based synthesis procedure [H4]. The calculations are performed in the actual direction of material flow in the process, thus, the composition and properties for each stream under consideration are known. The proposed procedure also does not suffer from the problem of "cycling" [T4], since separation types are not selected on the basis of estimated costs. The proposed procedure is practical and has been tested on several problems. For each problem, the procedure creates the best or the next best separation sequence in a reasonable amount of computational time.

A gradient algorithm has been proposed to satisfy product recovery and purity specifications in Chapter 5. Analytical expressions for product purity and recovery have been obtained as a function of the system structure by analysing several system configurations. Necessary derivatives have been computed and used to modify the split fraction of the key components. The algorithm has been programmed and works on all the test problems.

The cost of a separation unit versus the operating reflux ratio is a noncorivex function. A surrogate cost function which follows the actual cost function very closely and has continuous derivatives is obtained by regression. The gradient of the surrogate cost function is used to direct the search for optimum reflux ratio. A bisection
algorithm has been proposed in Chapter 6. The algorithm works well for every separation unit in the test problems.

A graphical procedure for the synthesis of nonsharp separations is presented in Chapter 8. The procedure creates an initial structure for restricted sample problems. Further work is needed to generalize this graphical procedure.

## Recommendations

The following recommendations are made to extend and improve the work presented in this dissertation:

1) The current procedure is restricted to distillation and extractive distillation methods. A natural extension would be to include other separation methods, such as absorbers, strippers and extractors. In doing this, the CDS function would have to be modified to include the additional separation methods.
2) Shortcut calculation procedures used for the simulation of separation units could be replaced by more rigorous methods.
3) The CDS function defined in this work can be generalized:

$$
\text { CDS }=\left[\frac{\log \left(\frac{s p_{I K}}{I-s p_{I K}} \cdot \frac{s p_{H K}}{I-s p_{H K}}\right)}{\log \alpha_{L K-H K}}\right]^{\beta}\left(\frac{V}{V+L}\right)^{\gamma}\left(1+\left|\frac{V-L}{V+L}\right|\right)^{\delta}
$$

The exponents $\beta, \gamma$ and $\delta$ could be obtained by regression.

An alternative approach would be to let the synthesis program "learn" $\beta, \gamma$ and $\delta$ by incorporating a learning algorithm [M7].
4) The synthesis program can be made interactive, in which case the evolutionary search can be guided by the experience of the user.
5) The present synthesis program synthesizes only the separation processes and can be used in conjunction with general process synthesizers, such as BALTAZAR [M1], for more detailed plant synthesis.
6) The problem of nonsharp synthesis has been barely touched and much needs to be done in this research area. The graphical procedure presented in this work needs to be generalized. An evolutionary approach similar to that for sharp separations is a possible way to modify the initial structure of nonsharp separations.

B1 Bakhshi, V. S. and J. I. Gaddy, "Optimal Synthesis of Separation Systers by Flowsheet Simulation," 70th Annual Meeting of AIChE, New York, Nov., 1977.

B2 Bellman, R. E., Dynamic Programming. Princeton University Press", New Jersey, 1957.

B3 Bertier, P. and B. Roy, "A Solution Procedure for a Class of Problems Having Combinatorial Character," Cahiers du Centre D'Etudes de Recherche Operationelle, 6, p. 202 (1968).

B4 Brosilow, C. and L. S. Lasdon, "A Two Level Optimization Technique for Recycle Processes," AIChE-I. Chem. E. Symposium Series, No. 4, p. 75 (1965).

P1 Freshwater, D. C. and B. D. Henry, "The Optimal Configuration of Multicomponent Distillation Trains," The Chem. Engr. (London), No. 201, p. 533 (1975).

G1 Gomez, A. M. and J. D. Seader, "Separation Sequence Synthesis by a Predictor Based Ordered Search," AIChE J., 22 (6), p. 970 (1976).

H1 Harbert, W. D., "Which Tower Goes Where?" Petroleum Refiner, 36 (3), p. 169 (1957).

H2 Happel, J. and D. G. Jordan, Chemical Process Economics. Marcel Dekker, New York (1975).

H3 Heaven, D. L., "Optimum Sequencing of Distillation Columns in Multicomponent Fractionation." MS thesis, University of California, Berkeley, 1970.

H4 Herdry, J. E. and R. R. Hughes, "Generating Separation Process Flowsheets," CEP, 68 (6), p. 71 (1972).

H5 Hendry, J. E., D. F. Rudd and J. D. Seader, "Synthesis in the Design of Chemical Processes," AIChE J., 19 (1), p. 1 (1973).

P5 Henley, E. J. and J. D. Seader, Multiphase Mass Transfer Operations. John Wiley and Sons, 1977.

H7 Hlavacek, V., "Analysis and Synthesis of Complex Plants: Steady State and Transient Behavior," Symposium, Computers in the Design and Erection of Chemical Plants, Czechosolvakia, 1975.

```
H8 Helpinstill, J. G. and M. VanWinkle. Ind. Eng. Chem.
    Process Des. Devel., 7 (2), p. 213 (1968).
```

```
H9 Haggenmacher, J. E., J. Am, Chem. Soc., 68, p. 1633
    (1946).
```

H10 Halm, R. I. and L. J. Stiel, AIChE J., 16 (1), p. $3, ~$
K1 King, C. J., Separation Frocesses. McGraw-Hill, New
York, 1971.
K2 King, C. J., D. W. Gantz and F. J. Barnes, "Systematic
Evolutionary Process Synthesis," Ind. Eng. Chem。
Process Des. Deve1., 11 (2), p. 271 (1972).

L1 Lasdon, L. S., Optimization Theory for Large Systems. MacMillan Co., New York, 1970.

L2 Lawler, E. L. and D. F. Wood, "Branch and Bound Methods: A Survey," Operations Research, ll (4), p. 699 (1966).

L3 Lockhart, F. J., "Multi-column Distillation of Natural Gasoline," The Petroleum Engineer, No. 8, p. 111 (1947).

M1 Mahalec, V., "Procedures for the Initial Design of Chemical Processing Systems," PhD dissertation, University of Houston, 1976.

M2 Mahalec, V. and R. L. Motard, "Procedures for the Initial Design of Chemical Processing Systerns," Computers and Chemical Engineering, 1 (1), p. 57 (1977).

M3 McGilliard, R. L. and A. W. Westerberg, "Structural Sensitivity Analysis in Design Synthesis," Chem. Eng. J., 4. p. 127 (1972).

M4 Molokanov, Y. K., T. Y. Korabiira, N. I. Mazurina and G. A. Mazurina, "An Approximate Method for Calculating the Basic Parameters of Multicomponent Fractionation," Inter. Chem. Engr., 12 (2), p. 209. (1972).

M5 Maxwell, J., Data Book on Hydrocarbons. .Van Nostrand, New York, 1950.

Mo Motard, R. L. and H. M. Lee, CHESS: User's Guide. Department of Chem. Engr., University of Houston, TX, 1971.

M7 Mandel, J. M. and K. S. Fu, Adaptive, Learning and Pattern Recognition: Theory and Practice. Academic Press, New York, 1970.

M8 Miller, D. G., "A Simple Reduced Equation for the Estimation of Vepor Pressures," J. Phys. Chem, 69 (9), p. 3209 (1965).

N1 Nemhauser, G. L., Introduction to Dynamic Programming. John Wiley and Sons, New York, 1966.

N2 Nilsson, N. J., Problem Solving Methods in Artificial Intelligence. McGraw-Hill, New York, 1971 .

N3 Nishimura, H. and Y. Hiraizumi, "Optimal System Pattern for Multicomponent Distillation Systems," Inter. Chem. Engr., 11 (1), p. 188 (1971).

P1 Petlyuk, F. B., V. M. Platonov and D. M. Slavinshii, "Thermodynamically Optimum Method for Separating Multicomponent Mixtures," Inter. Chem. Engr., 5 (3), p. 555 (1965).

P2 Powers, G. J., "Recognizing Patterns in the Synthesis of Chemical Processing Systems," PhD dissertation, University of wisconsin, 1.971 .

P3 Peters, M. S. and K. D. Timmertiaus, Plant Design and Economics for Chemical Engineers, 2nd ed. McGraw-Hill, New York, 1968.

R1 Rathore, R. N. S., K. A. VanWormer and G. J. Powers, "Synthesis of Distillation Systems with Energy Integration," AIChE J., 20 (5), p. 940 (1974).

R2 Rod, V. and J. Marek, "Separation Sequences in Multicomponent Rectification," Collection Czechosiov Chem. Commun., 24, p. 3240 (1059).

R3 Rodrigo, F. R. and J. D. Seader, "Synthesis of Separation Sequences by Ordered Branch Search," AIChE J., 21 (5), p. 885 (1975).

R't Rudd, D. F., "The Synthesis of System Designs: I. Elementary Decomposition Thsory," AIChE J., 14 (2), p. 343 (1968).

R5 Ried, R. C. and T. K. Sherwood, Properties of Gases and Liquids, 2nd ed. McGraw-Hill, New York, 1966 .

Si Seader, J. D. and A. W. Westerberg, "A Combined Heuristic and Evolutionary Strategy for Synthesis of Simpie Separation Sequences," to be published.

S2 Stephanopoulos, G. and A. W. Westerberg, "Studeis in Process Synthesis - II," CES, 31, p. 195 (1976).

S3 Stupin, W. J. and F. J. Lockhart, "Thermally Couplea Distillation - A Case History," CEP, 68 (10), p. 71 (1972).

T1 Tedder, D. W. and D. F. Rudd, "Parametric Studies in Industrial Distillation," 82nd National AIChE Meeting, Atlantic City, 1976.

T2 Thompson, R. W. Personal communication, 1977.
T3 Thompson, R. W. and C. J. King, "Systematic Synthesis of Separation Schemes," AIChE J., 18 (5), p. 941 (1972).

T4 Thompson, R. W. and C. J. King, Synthesis of Separation Schemes. Technical Report No. LBL-614, Lawrence Berkeley Laboratory, 1972.

V1 Valentine, F. A., Convex Sets. McGraw-Hill, New York, 1964.

W1 Westerberg, A. W. and G. Stephancuoulos, "Studies in Process Synthesis - I," CES, 30, p. 963 (1975).

W2 Westerberg, A. W., G. Stephanopculos and J. V. Shah, "The Synthesis Froblem with Some Thoughts on Evolutionary Synthesis in the Design of Engineering Systems," Symposium on Basic Questions of Design Theory, Columbia University, 1974.

W3 Wilde, D. J. and M. S. Buynoski, "Constrained Derivatives in the Design of a Serial Refrigeration System," Optimization and Design, eds. A. Avriel, M. J. Rijckaert and D. J. Wilde, Prentice Hall, 1973.

W4 Weimer, R. F. and J. M. Prausnitz, Hydrocarion Proc., 44 (9), p. 237 (1965).

## APPENDIX A

## Number of Possible Confjgurations for $N$ Component

 Feed Producing $N$ Single-component ProductsDefine:

$$
\begin{aligned}
N= & \text { number of components in the feed stream } \\
A(N)= & \text { number of possible configurations } \\
S= & \text { number of separation methods available } \\
M S= & \text { number of separation methods available which } \\
& \text { use an MSA (in this work MS }=S-1) \\
\Omega(N)= & \text { number of configurations possible using one } \\
& \text { separation method when restrictions l and } 2 \\
& \text { are imposed } \\
x(N)= & \text { number of configurations possible using two } \\
& \text { separation methods, one of which uses an } \\
& \text { MSA - restriction }] \text { is relaxed } \\
\text { Restriction } 1: & \text { In the configuration, MSA is isolated in } \\
& \text { the successor separation urit after use } \\
\text { Restriction } 2: & \text { In the configuration, a separation method } \\
& \text { using an MSA cannot be used to isolate } \\
& \text { another MSA }
\end{aligned}
$$

Then,

$$
A(N) \geq \Omega(N) S^{N-1}+X(N) \cdot N S
$$

This expression is a strict equality only when $S=1$, or when $S=2, M S=1$ and restriction 2 is imposed. Expression for $\Omega(N)$

A recursion formula for obtaining $\Omega(N)$ has been developed by Henley and Seader [H6] and is reproduced here. For the first separator in the sequence there are $N-1$ split points. Let $j$ be the number of components appearing in the overhead product; then $N$ - j components appear in the bottoms product. If $\Omega(i)$ is the number of sequences for $i$ components, then for the first separator the number of sequences is $\Omega(j) \Omega(N-j)$. But, for the first separator, N - 1 different splits are possible. Therefore, the total number of sequences is

$$
\Omega(N)=\sum_{j=1}^{N-1} \Omega(j) \Omega(N-j)=\frac{[2(N-1)]!}{N!(N-1)!}
$$

For $N$ equal to two, only one sequence is possible. Thus $\Omega(2)=\Omega(1) \Omega(1)$ and $\Omega(1)=1$. For $R=3, \Omega(3)=$ $\Omega(1) \Omega(2)+\Omega(2) \Omega(1)=2$. Values for $N$ up to 7 are given in Table $\mathrm{A}-1$.

Evaluation of $X(N)$
Unfortunately, no closed form equation for $X(N)$ could be derived. The value of $X(N)$ is presented in a tabular form for $\mathbb{N}=3,4,5,6$ and 7 when MS $=1$. This value of $\chi(N)$ has been computed by examining all possible structures when both restrictions 1 and 2 are imposed.

Restriction 1 is then relaxed and the adaitional structures so created are counted. As an example of the computational procedure, the steps for $N=4$ using two separation methods, type I and type II, are given below. The type I method is ordinary distillation and the type II method is an extractive distillation using solvent $X$. We also assume that the solvent is the heaviest component in the system.

For $N=4$, three separation units are required.
Five different interconnections exist for three units. These interconnections are shown in Figure A-1.

Each of the units in any of the interconnections can be either a type I unit or a type II unit. There are eight different ways in which two different units can be arranged. These patterns are shown below:

| Pattern | I | I | I |
| ---: | ---: | ---: | ---: |
| 2 | I | I | II |
| 3 | I | II | I |
| 4 | I | II | II |
| 5 | I | II | II |
| 6 | II | I | I |
| 7 | II | II | I |
| 8 | II | II | II |

For each interconnection, any of these eight patterns can be used. Therefore, there are $8 \times 5=40$ different structures which are possible.

By relaxing restriction 1 , adaitional structures
1)


Figure A-I
Five Possible Interconnections of Three Separation Units [T4]
would be generated. A new structure appears when two or more type II separation units are in a sequence adjacent to each other. In addition, the two units are connected in a direct arrangement. These situations are illustrated in Figure A-2.

Now we will start counting the additional. structures created by considering the five interconnections one by one. For interconnection 1 , pattern 4 will give rise to a new structure. Another new structure would be generated for pattern 7, and three more structures would be generated for pattern 8. Thus, interconnection l leads to five additional structures. Similarly, interconnection 2 gives rise to two additional structures for patterns 4 and 8 . Interconnection 3 gives rise to two additional configurations for patterns 7 and 8. Interconnection 4 does not produce any new structures. Interconnection 5 gives two additional structures for patterns 7 and 8. The total new configurations is eleven.

This procedure is repeated for $N=5,6$ and 7 . The results are shown in Table A-1. Table A-2 shows the total number of structures possible for various values of N and for $\mathrm{S}=1$ and 2.


Additional structure is:


Situation 1


One of the three addi.tional structures is:


Situation 2

Figure $A-2$

Table A-1
$\Omega(N)$ and $X(N)$ as a Function of $N$

| $N$ | $\frac{\Omega(N)}{N}$ | $\underline{X(N)}$ |
| ---: | ---: | ---: |
| 2 | 1 | 0 |
| 3 | 2 | 1 |
| 5 | 5 | 11 |
| 6 | 14 | 100 |
| 7 | 132 | $\sim 711.4$ |

Table A-2
Total Number of Arrangements as a Function of $N$ and $S$

| $N$ | $\frac{S=1}{N}$ | $\frac{S=2}{2}$ | $\frac{S=3}{3}$ |
| ---: | ---: | ---: | ---: |
| 2 | 2 | 9 | 30 |
| 4 | 5 | 51 | - |
| 5 | 14 | 324 | - |
| 6 | 42 | 2200 | - |
| 7 | 132 | $\sim 15562$ | - |

- not computed

APPENDIX B

SAMPLE OUTPUT FOR EXAMPLE 1

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| ¢ E | SS | PP PPP |  | 55 | 55 | PP PPP |
| Leeee | SSsss | PPPPP | －－－ | SS5ss | sSsss | PPPPP |
| と | 5 S | PP | － | 55 | SS | PP |
| ric | SS | PP |  | 55 | 55 | PP |
| tetefte | \＄5555 | PP |  | ssssss | s5sss | pp |

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| 165398. | 1 | 2 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0. | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - | 0 |
| 7月548. | 2 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0. | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 30457. | 2 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0. | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0. | 4 | 0 | 0 | 0 | 0 | $\stackrel{\sim}{4}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

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\hline 56911. & 3 & 2 & 5 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline 7755A. & 3 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
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| 3 | 3 | 2 | 0 | 0 | 1 | 4 | 0 | 1 | 76207. | 3 | 2 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 3 | 0. | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
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| 1 | 1 | 3 | 0 | 4 | 2 | 2 | 2 |  | 7 | 0 |  |  |  | 52296. | 1 | 2 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 0 | 0 | 0 | 0 | 0 |  | 0 |  | 0 | 1 |  |  |  | 0. | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3 | 3 | 2 | 0 | 4 | 1 | 1 | 4 |  | $a$ | 1 |  |  |  | 99826. | 3 | 2 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
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| 5 | 2 | 4 | 4 | 0 | 1 | 1 | 6 |  | c | 3 |  |  |  | 34.368. | 2 | 4 | 0 | 0 | 0 | - | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 6 | 0 | 0 | 1 | 0 | 0 |  | 0 |  | 0 | 3 |  |  |  | 0. | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $\square$ | 0 |
| 7 | c | 0 | 0 | 0 | 6 | , | 0 |  | 0 | 5 |  |  |  | 0. | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|  |  |  |  |  |  |  |  |  | Otal | AL s |  |  |  | 186489. |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | EPGRA | run | * |  | EE | ED. 5 | Ste | meam | A |  |  | OPT | IMUM R/a | MIN |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  |  | 1 |  |  |  |  | 1 |  |  |  |  |  | 1.144 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  |  | 2 |  |  |  |  | 3 |  |  |  |  |  | 1.560 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  |  | 3 |  |  |  |  | 5 |  |  |  |  |  | 1.050 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

Simulatiun or design coraesponding to optimum reflux ratio



```
gfparator i fuk strfak number 3
ASTILLATICN ALPHA = 1.968
\begin{tabular}{|c|c|c|c|c|c|}
\hline Light ker is & \[
\begin{aligned}
& \text { CYCLOMEXAHE } \\
& F E E D \\
& \cdot 10015+04
\end{aligned}
\] & \begin{tabular}{l}
heavy key oistillate \\
-12624+03
\end{tabular} & \[
\begin{aligned}
& \text { IS BENZENE } \\
& \text { BOTTOHS } \\
& .87531+03
\end{aligned}
\] & LB & MOLES/hr \\
\hline \(\cdots-r E x \rightarrow r e\) & . 00219 & -41739 & . 00000 & & \\
\hline creltinexata & . 12416 & .98002 & .00073 & & \\
\hline feicisam & .12485 & . 00259 & .14243 & & \\
\hline Prelon & .74884 & . 00000 & . 85684 & & \\
\hline mbimun meflua ratiou & = .2056C.01 & & & & \\
\hline co'senseg & & & & & \\
\hline  & AREA \(=.5 S 1+53\) & delta \(\mathrm{Y}=\) & . \(776+02\) & temp & -176.39 \\
\hline
\end{tabular}
    GAPCOST = .319.U4 HOURLY OP CUST = *749+00
    0uTy=
    OGTY = 1400.7 TEMP = 256.94
```




```
    EGUILIFRIUMSTZGES: 2R.3U EFFICIENCY = .60571
```



```
    'EAKLY OPEGATINGG COST 15S 39477.00
```

SFPARATOR I FOR STREAM NUGGER 5

```
OISTILLATiOA ALPHA \(=36.558\)
```



| EtFy | ${ }^{\text {chp }}$ | 1.1 | Pkgo | U 1 | Ser. | $H \times$ <br> 50 | msa | LST | $\operatorname{cost}$ |  | PRi | dic |  | 1 N | STR | AM |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| NUH9 | LK | HK | mK | c.K | NUH | Stit | HCL | Sth |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 1 | 1 | 3 | 0 | 0 | 2 | 2 | 7 | 0 | 52296. | 1 | 2 | 3 | 0 | $\bigcirc$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 . | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | 0 | 0 | 0 | 0 | 0 | + | 0 | 1 | 99826. | 3 | 2 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 2 | 4 | 0 | 0 | 1 | 6 | 0 | 3 | 34368. | 2 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |



| efeeme | Sssss | PPPPP |  | 5S5ss | sssss | Ppppp |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| EE | 53 | PP | PP | Ss | Ss | $p \mathrm{p}$ | PP |
| EE | Ss | PP | PP | 55 | 5 S | PP | PP |
| eeeee | sssss | PPPPP |  | Sssss | sssss | PPPPP |  |
| EE | ss | PP |  | 5 S | 55 | PP |  |
| EE | 55 | PP <br> P |  | S5ssss | 55555 | PP <br> $P \mathbf{P}$ |  |
| heeteee | Sssss |  |  |  |  |  |  |



## APPENDIX C

Unit Simulations

Distillation
For a given feed stream and for a specified light key, heavy key and split fraction of the key components, subroutine DISTL performs the simulation. The coding of this routine has been taken from Thompson and King [74], with a small modification.

The minimum number of stages is calculated by FRAC using the Fenske-Underwood Equation. The relative volatilities are calculated based on the activity coefficients of the components at the feed composition and the temperature of the feed, or at $130^{\circ} \mathrm{F}$ if a pressurized column is used. Based on the total-reflux equations the splits of all the components are calculated by routine FRAC2. If the minimum number of stages is less than one, routine LVQ attempts to make the separation in a flash drum or partial condenser. It does this by trying to find the temperature and pressure at which the specified split fractions of the keys are exactly met, if they are not satisfied, or by dividing the improvement in the split fractions if they are more than met. If VLQ fails, the next step is to use a distillation colum. The minimum refiux is calculated using the Underwood equations [K1].

At first the column is set to atmospheric pressure. If the bubble point (by BUBI) of the distillate is greater than $120^{\circ} \mathrm{F}$, so that cooling water can be used in the overhead condenser, then the bubble point and the latent heat (both by BUBL) of the bottoms are calculated. If the maximum allowable temperature (usually $600^{\circ} \mathrm{F}$ ) is not exceeded, the reboiler is sized and osted by RBL. If the maximum temperature is exceeded, a vacuum tower is tried at a reboiler temperature equal to the maximum allowable and a corresponding pressure. Allowing for a pressure drop of one inch of water on each tray, the overhead pressure must be attainable with a one-stage steam ejector, i.e., 1.5 psia. If this is not possible, distillation is not used and a constraint is considered violated. If the Cistillate bubble point is less than $120^{\circ} \mathrm{F}$, a pressure column is used in order to increase the overhead temperature so that cooling water can be used, if possible. If this cannot be done without increasing the pressure beyond $60 \%$ of the critical pressure of the mixing, cooling water is not used. Above $50^{\circ} \mathrm{F}$ steam ejectors provide low-pressure evaporation of water, and below that refrigeration is used at several discrete levels. Capital costs are included for these coolants. If the pressure exceeds 115 psia a partial condenser is used, and the distillate is taken as a vapor product.

Increased pressure increases the cost of the tower, the basic cost of which is taken from a graph in Peters ard Timmernaus [P3]. The cost of plates in excess of 50 is double the normal cost. The actual number of iceal stages is calculated by Molokanov's equation [M4]. The
efficiency is based on a correlation in Maxwell [M5]. The viscosity is obtained through the method of Stiel and Thodos [R5]: eff $=36.3$ (vis, cp $)^{46}$.

Extractive Distillation
Extractive distillation is simulated in the same way as distillation except that the solvent is added to the extent of $67 \%$ mole percent of the total liquid feed. The bottoms composition is also checked by routine MISBI to assure that it corresponds to one homogeneous phase. No direct charge of capital or make-up is made for the solvent.

## Utility Costs

The cost of utilities is as given in Peters and Timmerhaus [P3] p. 776. Water is $\$ 0.02 / 1000$ gal., electricity is $\$ 0.01 / \mathrm{kwhr}, 500 \mathrm{psia}$ steam is $\$ 0.60 / 1000 \mathrm{lb}$, 100 psia steam is $\$ 0.50 / 1000 \mathrm{Ib}$, and exhaust steam is $\$ 0.25 / 1000$ 1b. These utility costs are used as the operating costs in the economic evaluation. The purchased cost of equipment repicesents one-fourth of the installed cost.

## Thermodynamic Routines

All of the thermodynamic routines are based on calculations using the theory of corresponding states. This allows for the estimation of many properties with very little input information needed. The input information that is needed for each component is as follows:

1. molecular weight
2. normal boiling point
3. critical temperature
4. critical pressure
5. an integer characterizing the compound as to structural homomorph.

The above information for each component is obtained from the CHESS [M6] data bank by supplying component identification numbers. The coding of the thermodynamic routines has been taken from Thompson and King [T4]. The calculated activity coefficients which are used in almost all of the routines use a modified form of the regular solution theory [H8]. The two solubility parameters used in this correlation are calculated from the latent heat and the homomorph plots of varying molecular structure of Weimer and Prausnitz [W4]. These homomorph plots are transformed into equations and appear in the routine SOLPAR. The latent heat and the vapor pressure are calculated from the correlation of Miller in routine VP [K8]. The compressibility factor is from Haggenmacher [H9]. The critical compressibility factor and density are from

Halm and stiel [H10]. SETCRIT calculates the critical properties that are not input information. SEPFAC calculates the distribution coefficients of all components based on the feed composition, atmospheric pressure, and the temperature of $130^{\circ} \mathrm{F}$. Limiting activity coefficients at high dilution are used in the solvent phase for extrac-tion, while a mole fraction of 0.667 for the solvent is used in extractive distillation.


[^0]:    *Ordered Branch Search
    †Predictor Based Ordered Search

[^1]:    *Dynamic Programming

[^2]:    *Heuristic and Evoluationary Method

[^3]:    *Branch and Bound Method

