SIMPLIFIED PROCESS SYNTHESIS OF DISTILLATION SEQUENCES

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by

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THESIS SUMMARY

The problem of finding the optimum sequence of a train of distillation columns to separate a multicomponent mixture has received much previous attention. The solutions to this complicated problem are complex, and probably because of this, little or no progress has been made in solving the common but more difficult problem of finding the optimum sequence of a train of separation methods (for example, distillation combined with liquid-liquid extraction, gas absorption and extractive distillation).

This work introduces simplified methods for optimising a separation by distillation, based upon new concepts. These are "energy flow per unit area of distillation column cross-section" which may be used to produce correlations of distillation column cost, energy cost and optimum reflux ratio, all as functions of pressure or flow parameter; and "the Binary Distillation Total Vapour Load (BDTVL)" which is defined and then used to derive a simple equation for finding the optimum sequence of a train of distillation columns. The equation is shown to represent the most powerful heuristics (rules of thumb) found in the literature.

These simplified procedures are evaluated by means of detailed but conventional design and costing methods which are put into extensive computer programs.

The BDTVL method is also used to develop a simple equation for the screening of solvents in an extractive distillation process.

An extensive test of the BDTVL method showed that it finds the optimum sequence for all the problems used as examples in the more complicated methods of previous work. However, in a further test, mixtures were sought and found where the BDTVL method failed. Even here it is shown that sequences predicted to be optimum by the BDTVL equation are likely to be those most suitable for energy integration. It is proposed that this will form the basis for future work.

KEY WORDS: SEQUENCES OF DISTILLATION; HEURISTICS; PROCESS SYNTHESIS; OPTIMUM DISTILLATION; EXTRACTIVE DISTILLATION.

DEDICATION

Dedicated unto God.

"The fear of the Lord is the beginning of wisdom ..." Prov. 1:7

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Above all, I give all my thanks unto God for keeping us and providing for our needs in one way or another during the course of this work. His grace is indeed sufficient to them that put their trust in Him.

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CHAPTER ONE

INTRODUCTION

Processes for separating multicomponent mixtures into multiple products often consist of a sequence of two or more separators, each of which produces generally two, but sometimes more than two, product or intermediate streams. These processes, usually referred to as separation processes, form a significant portion of the total capital investment in a chemical plant. As such, a great deal of interest has always been generated for their process synthesis. Process synthesis is a step in design where the chemical engineer selects the component parts and how to interconnect them to create his flowsheet.

For separation processes, synthesis may call for three tasks so as to meet the specified process requirements:

(1) Selection of methods of separation,

(2) The development of procedures which will produce optimal or near optimal separation sequences; and

(3) Finding the optimum value for the design variables (e.g reflux ratio in a distillation column).

Our primary concern in this research is on the second task.

For many years now, design engineers have had to face the problem of selecting the least expensive separation sequences for a given multicomponent mixture. This problem is most common in the petroleum and petrochemical industries where it is usually necessary to separate multicomponent mixtures into relatively pure products. This task of selecting the least expensive separation sequence often represents a formidable combinatorial problem. Thompson and King(1972) gives the number of possible sequences for a mixture of M components to be separated into M pure component products as

$$S_E = \frac{[2(M - 1)]\,!}{M\,!\,(M - 1)\,!} \qquad ......(1.1)$$

As can be observed from the Equation (1.1), the results of which are tabulated in Table E1-1 (Appendix E) for up to ten components, the number of possible sequences increases rapidly as the number of components in the feed increases.

Examination of the literature shows that the techniques for determining the optimal sequence of separation processes can be classified into three:

(1) Heuristic techniques: these seek the solution to the problem by means of plausible rules of thumb resulting from the long engineering experience.

(2) Evolutionary techniques: these seek to find a new and hopefully an optimal sequence by modification of previously generated sequences.

(3) Algorithmic techniques: consider the sequencing problem as a minimization problem. They attempt to obtain the best sequence using well-known optimisation methods developed in the area of nonlinear mathematical programming.

These techniques, apart from the heuristic techniques, are complex and time consuming. This is even with the simplifying assumptions which are usually made. In other words, they are usually very rigorous and their applications require a special mathematical background and computational skills and a lot of computer space and time from the user. The problem of distillation sequencing which has received much attention, has become so complex, that the introduction of other separation methods into the sequence would not be an easy one. And it seems unlikely that further progress can be made on the problem of sequencing of distillation columns let alone that of separation processes without some simplification. Therefore, there is still the need to develop simple procedures for the sequencing problem. Some other authors [e.g Stephanopoulos et al(1982)] have made similar observations. Such simple procedures will provide greater understanding of the problem which can lead to process modification. This is rarely, if ever, gained from the other complex computer methods. In particular, quantitative equations or expressions that represent and supplement heuristic rules are expected to be valuable in understanding and identifying the nature of the processes.

As a primary objective of the work, we set out to explore the possibility of finding simple concepts and equations that can aid engineers in the choice of optimum separation sequences. Although much of the work done in the thesis is on ordinary distillation, extractive distillation is also investigated. In parallel with this primary objective is the provision of a comprehensive critical literature survey on the optimum sequencing of separation processes. And because the eventual aim would be to compare the results obtained from the equations that might have been developed with detailed costs of sequences, we also embark on the sizing and costing of ordinary and extractive distillation processes.

The initial stage of the work is the examination of the concept of energy flow per unit area of distillation column; and this resulted in a simple equation for the determination of the optimum reflux ratio to minimum, the optimum number of plates to minimum and the optimum cost of distillation operation per moles of distillate. These were correlated against the column pressure or the Flow Parameter. The effects of many other variables [e.g feed composition, the relative volatility, the recovery fraction and the material of construction] on the optimum reflux ratio and cost of distillation per mole of distillate were therefore investigated and correlated against the flow parameter. These investigations are important since in multicomponent distillation sequencing, we shall be dealing with columns in which these variables become crucial. Above all, the results from this stage of the work made possible the simplifications employed and explanations made in some other parts of the thesis.

Moving on to the optimum sequencing of multicomponent distillation columns, we first investigated the sensitivity of the optimum sequencing to some operating and system variables; and used the results obtained to evaluate the use of heuristics as a technique for determining the optimum sequence of multicomponent distillation columns. These variables include the feed composition, relative volatility between the components, the ratio of reflux to minimum, R/R_m, the recovery fraction and the feed vaporisation. Having observed, both from the literature and the results from this study, that the feed composition and the relative volatility between a pair of adjacent components have dominant effects on the optimum sequencing of distillation columns, the next stage of the work was to develop a quantitative equation that takes into account these two variables. These two variables are those generally used in the heuristic rules. The new equation which we derived, we referred to as the Binary Distillation Total Vapour Load (BDTVL) equation, represents quantitatively the most powerful heuristic rules found in the literature and identifies the optimum sequences for the published examples (up to six component mixtures) which have been solved by other methods.

We believe that although the heuristic techniques may not always guarantee optimality, nevertheless, their development has provided a first breakthrough towards the solution of the problem of finding the optimum sequence of separation processes. These rules are always needed to reduce the computational time and number of search space involved in other techniques. These rules will continue to play significant role in the sequencing of separation process problem. Such quantitative expressions as derived here would help to determine the numerical ranges of accuracy and bounds on the applicability of the heuristics.

The observation of possible failures of the BDTVL method in some extreme conditions of relative volatilities leads to the consideration of the ranges of the applicability of the method and its potentials in energy integration. We did not go too far in the consideration of the energy integration concept however.

Realising that an extractive distillation could be a possible candidate for choice of separation in cases where the relative volatility between the components is close to 1.0, we then extended the BDTVL method to an extractive distillation process. The resulting equation is applied to solvent screening in an extractive distillation; and to find when an extractive distillation will be better than an ordinary distillation.

At the heart of an extractive distillation is the selection of suitable solvents capable of enhancing the relative volatility of the key components to be separated. The screening of solvents is usually done by ranking them in the order of selectivity at infinite dilution, with that solvent with the highest selectivity being the most promising one for the given separation. Inasmuch as this approach for selecting solvents based on selectivity is still useful, our equation produces a new approach of screening solvents which proves better than the approach of selectivity at infinite dilution.

In the process design and costing analysis procedures, standard known equations/methods are employed to size and cost the various aspects of the columns. The rigorous multicomponent design procedure of Naphtali and Sandholm(1971) involving the material, equilibrium and energy balances is used. The costing analysis involves the capital costs of column, condenser, reboiler and the energy costs of the condenser cooling water and reboiler steam cost. The computer programs developed as part of the objective of the research are capable of sizing and costing distillation sequences of three-, four-, five-, and six-component mixtures. These programs are developed into a form of a package using the menu-driven techniques.

The breakdown of the chapters is as follows: In general, it is considered better to discuss the results at the end of each chapter. Conclusions are also given at the end of each chapter.

Chapter Two is the general survey of the literature on the optimum sequencing of separation processes. This chapter provides the reader an understanding of the relevant literature on the topics and a better insight into the problems of sequences of separation processes. A brief review of the determination of the optimum reflux ratio and the screening of solvents for an extractive distillation process are given respectively in Sections 3.2 and 7.2.

Chapter Three considers the concept of the energy flow per unit area of distillation column and the resulting equations which are used to investigate the effects of some variables on the optimum reflux ratio and optimum cost of distillation per mole of distillate, and how these correlate against the total reflux flow parameter.

In chapter Four, the investigation of the sensitivity of the optimum sequence of distillation columns to system variables and the validity of the use of heuristics in sequencing problems is presented.

Chapter Five gives the derivation of the BDTVL method and its applications and comparisons with published work. The limitations of its use and its potentials in energy integration are discussed in chapter Six.

Chapters Seven and Eight contain the extension of the BDTVL method to the extractive distillation process with the aim of applying it to screening of solvents for a given separation.

Chapter Nine contains the design procedures and the major features of the computer programs for sizing and costing the distillation columns. The various equations/methods employed and the computer flowcharts are given in the Appendices.

The general discussions and conclusions which are a summary of most of the conclusions already stated in the various chapters are presented in chapter Ten.

Almost all the tables of results are given in the Appendices which also contain details of the computer flowcharts used in this work. These are bound separately into another volume (VOLUME II).

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In the introductory chapter to this thesis, we stated that our primary concern in this reseach is on the development of procedures which will produce optimal or near optimal sequences of separation proceses. Therefore, the bulk of the literature review is devoted to this aspect. The review considers the use of heuristics (rules of thumb) for finding the optimum distillation sequences and then the optimum sequences of separation processes. Then the Evolutionary techniques and the Algorithmic techniques are reviewed. The survey concludes with a brief review of heat integrated sequences.

2.2 Sequences of separation processes without Heat Integration.

In the last decade and half, many articles including review articles [Hendry et al (1973), Hlavacek (1978), Nishida et al (1981)] have appeared in the literature on this subject. This problem of sequencing of separation processes is complex because of the large number of possible sequences even for relatively simple processes. Take for an example, if a stream is to be divided into three parts then two columns are required. But the feed to the second column can be either the overhead or the bottoms from the first. So we have two possible arrangements. That is, if the 'simple sharp' separation split is assumed. A simple sharp separation unit is one which splits a simple stream feed into two products. A sharp separation unit is one where each entering component exists in only one product stream. This number of possible arrangements increases rapidly with increasing number of components in the original feed. The problem becomes even more complicated when more than one separation method is used. At least more than 20 separation methods are in use today and these are outlined by Porter and Jenkins(1981). And the problem of deciding on the method of separation to be used, before considering the optimum point at which it should be introduced in the sequence, is not trivial.

Thompson and King (1972) give the number of possible sequences for a mixture of M components to be separated into M pure products using R separation methods as

$$S_E = \frac{[2(M-1)]!\ R^{M-1}}{M!(M-1)!} \qquad ....(2.1)$$

Many techniques for obtaining the optimal or near-optimal separation sequences have been developed over the years. They can be classified into

1) Heuristic Techniques (i.e. rules of thumb)

2) Evolutionary Techniques, and

3) Algorithmic Techniques.

These techniques are discussed. First, we review articles on the sequencing of distillation columns; and then sequencing of separation processes.

It should be noted that the words sequence, structure, arrangement, configuration may have been used interchangeably and all refer to an arrangement of separation units. Column, separator and tower are used interchangeably too to refer to a separation equipment.

2.2.1 Heuristic Technique.

The heuristic techniques use rules of thumb resulting from long engineering experience and insight into the physics and chemistry of the separation methods. In the examination of the literature, the following heuristics summarised below are found.

(1) Favour direct sequencing [The direct sequence is that where components are removed one by one as overhead products from a series of distillation columns.]

(2) Save the most difficult separation for last.

(3) Favour 50-50 split. [i.e sequences which give a more nearly equimolar division of the feed between the distillate and bottom products.]

(4) Sequence with the minimum total vapour flow.

(5) Perform the sequence with high recovery fraction last.

(6) Separate the most plentiful component first.

(7) Choose the cheapest as the next separator.

(8) Remove the thermally unstable and corrosive material early.

(9) A separation with $\alpha_{LK-HK} < 1.05$ is not acceptable.

(10) Perform easy separation first.

(11) Favour sequences with the smallest product set.

(12) Avoid separations using a mass-separating-agent (MSA).

(13) Remove a MSA from one of the products in another subsequent separation process.[i.e separations which require the use of species (solvent in most cases) not normally present in the original feed.]

(14) A separation method using a MSA cannot be used to isolate another MSA.

(15) Favour ordinary distillation.

(16) Separate first the components which might undergo undesirable reactions.

(17) Set splits fractions of the key components to the prespecified values.

(18) Avoid extreme processing conditions.

(19) Favour ambient operating pressure.

(20) Favour sequences having the minimum sum of Q T areas.

(21) Choose operating reflux or 1.2 or 1.3 times the minimum.

(22) Avoid vacuum distillation and refrigeration.

We now examine the authors that demonstrate the use of these heuristic rules in the determination of the optimal or near optimal distillation sequences.

The earliest papers known on the sequencing of distillation columns using heuristic techniques were that of Lockhart(1947) and Harbert(1957).

Lockhart(1947) examined the three component mixtures commonly encountered in the processing of natural gasoline. He utilised approximate distillation design methods in conjunction with economic analysis. He concluded that the direct sequence was not optimum when the least volatile component was the predominant constituent of the feed. In this case, he recommended the use of indirect sequence. The indirect sequence is the opposite of the direct sequence.

Harbert(1957) considered the selection of the optimum sequence on the basis of heat duty. This factor, according to him, dominated the economic evaluation of distillation columns. This approach led him to his two rules; (1)"the advantage of minimum quantities for difficult separation". In other words, he implied that the most difficult separation should be performed last. (2) "the advantage of the 50-50 split", implying that a sequence should be sought which favours nearly equimolar division of each column feed into distillate and bottom products. This last rule was believed to be the stronger of the two and the one most ignored in design practice at that time. The author also developed a method of approximating the heat requirement of the various columns but only for a three component feed mixture.

The first known quantitative approach to the optimum distillation sequence problem was undertaken by Rod and Marek(1959). The basis of comparison for the various column arrangements was the total vapour flow. They defined a comparison criterion factor which was taken as the difference in the total overhead vapour flows of a given and standard sequence per unit of feed. The direct sequence was used as the standard; and it followed that any sequence is more advantageous than the standard sequence if the comparison factor was a negative. Based on simplifying assumptions, an algebraic equation was derived for the overhead vapour flow. The authors verified their equation for a ternary mixture of benzene, toluene and ethylbenzene at atmospheric pressure. This mixture does not represent a difficult separation. Their relationship does not include the volatility values for all the components, it cannot therefore reproduce many of the current heuristics especially when the adjacent component volatilities differ much from one and another. When more than three components are involved, the authors suggested lumping the components together into a form of three component mixtures. This was applied to the example considered by Lockhart(1947) and the agreement of both results was considered satisfactory.

As reported by Nishida et el(1981), Heaven(1969) in a computational investigation with economic optimum sizing and costing of distillation columns, identified several heuristic rules. The four general heuristics identified were heuristics numbers 2, 1, 3 and 5.

These heuristics are not entirely new. Some of them have been stated by Harbert(1957). As noted by Freshwater and Henry(1975) later, these heuristics can contradict each other. Therefore, quantitative expressions to represent the heuristics are desirable.

Power(1971) suggested an approach whereby weighting factors are applied to the heuristics for determining optimum column sequencing. The heuristics considered were heuristics numbers 1, 6, 2 and 8.

The weighting factors developed for combining the effects of the above four heuristics were tested by the author on some industrial multicomponent separation problem with favourable results. However, there was no standardised method of determining these weighting factors; their determination relied on intuition and experience. This may render the approach not very useful.

Nishimura and Hiraizumi(1971) undertook an optimisation of sequences of distillation columns of ideal mixtures. Relatively simple functions are used for the cost evaluation function. The function was expressed in terms of volume of a column and heat consumption rate at a reboiler which was considered equal to the cooling rate of a condenser. They formulated the optimisation problem with optimum variables of the sequence and the system parameters. Even for this 'simple' function employed, the mathematics involved cannot be considered simple. The heuristic rules obtained can be summarised as: when everything else is the same, select the direct sequence and remove first the dominant component.[Heuristic 1 and 6]. An example of benzene, toluene and o-xylene was used to illustrate the application of their approach for some different feed compositions. The direct sequence was found to be optimum for some feed compositions, and the indirect sequence for others.

Freshwater and Henry(1975) undertook a computational study to generate quantitative data to illustrate the effects of column sequence on the total annual cost of separation of typical feed component mixtures. They examined the feasibility of the use of heuristics as a possible synthesis technique in the determination of multicomponent distillation sequencing. The specific aim was to investigate the effect on the total annual cost of the sequences of (1) composition of feed. (2) volatility of the components, and (3) degree of recovery of the feed components. They used the result of the investigation to determine under what conditions the benefits obtained by the choice of the optimal sequence would justify the use of the heuristics suggested by Heaven(1969) and that of favouring the predominant component of the feed (Heuristic No. 6).

From the results, the following observations can be made.

(1) Noticeable variation occurred in the cost differences between all possible configurations for a given separation. Smaller variations were in most cases restricted to feeds in which the least volatile components were predominant, while large cost difference occured in the reverse case. Remarkably, however, the magnitude of these variations in many cases was not greater than 10 percent except in high recovery cases.

(2) The direct sequence was optimum in all cases except for cases when one component was predominant.

(3) The absolute value of the cost of all sequences for a given separation varied significantly depending on the feed composition.

(4) Performing the difficult separation last was found in several cases to be the dominant factor.

The authors however noted that although the direct sequence was the optimum for all cases considered in their study, this result might simply have been a consequence of the values of relative volatilities chosen or the degree of difficulty of the separation between the difficult pair of components of the feeds. A conflict was found to exist between heuristics 1 and 6 when one of the components of the difficult pair was predominant.

As an extension of the work of Petlyuk et al(1965) which is considered later in section 2.2.2, Doukas and Luyben(1978) studied the separation of a ternary mixture of benzene, toluene and O-xylene into three products using four different sequences of distillation columns:-

(1) direct sequence configuration.

(2) indirect sequence configuration.

(3) single column with side streams product.

(4) a prefactionator column followed by a sidestream column.

Results were presented for arbitrarily selected relative volatilities of 3:2:1 and 6.7:2.4:1.0. Their studies did not cover a wide spectrum of all possibilies but they observed that;

(1) the single sidestream column is the most economical for low concerntrations of either Benzene or O - xylene.

2) the single sidestream rapidly becomes unneconomical as benzene feed concentration increases above 10%. A Prefractionator column is preferred.

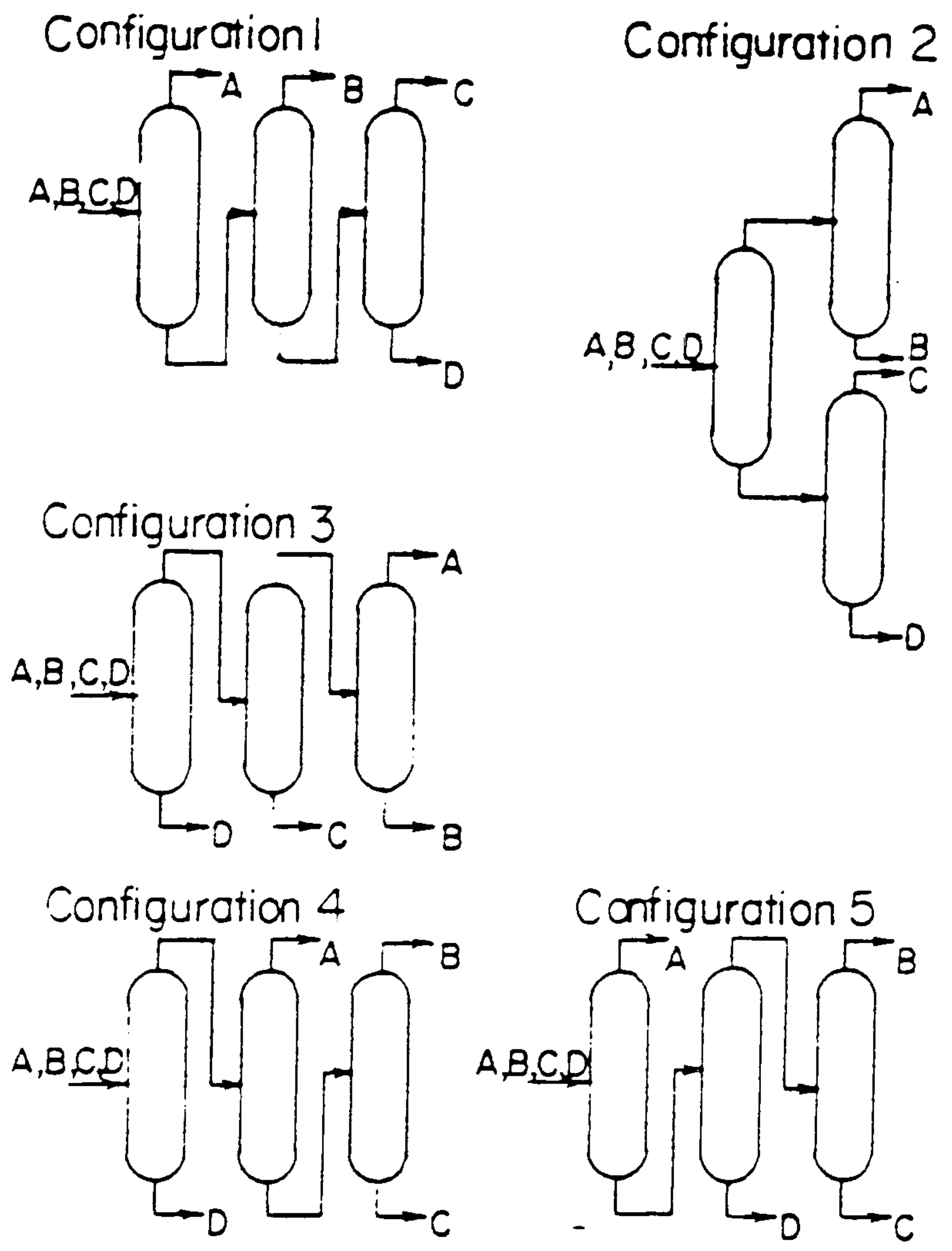
3) the effect of the relative volatilities was pronounced and the differences in cost were primarily in energy consumption.

4) the energy cost account for more than 80% of the total annual cost in most cases.

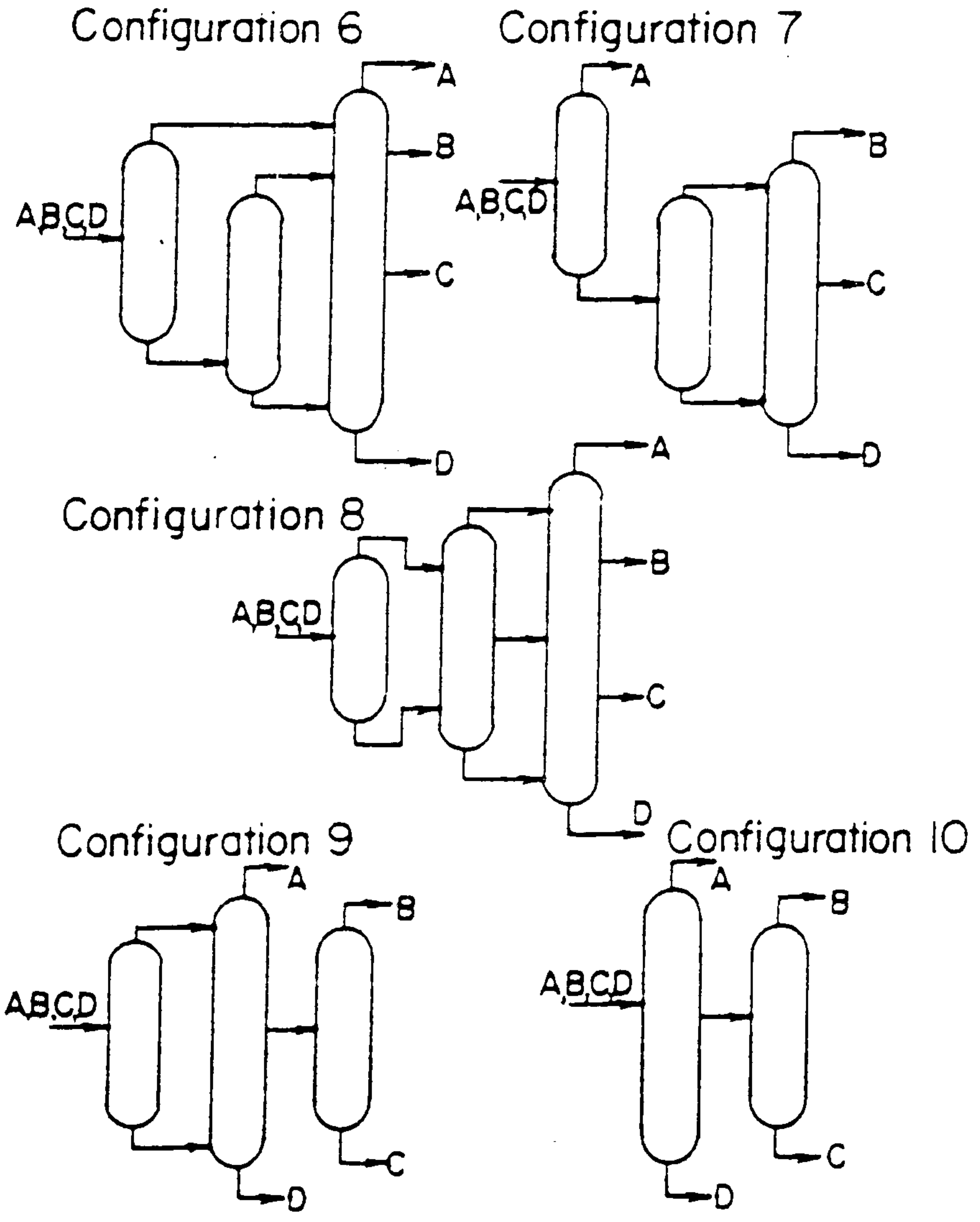
Elaahi and Luyben(1983) evaluated a number of alternative configurations of distillation columns for the separation of four-component mixtures on the basis of energy consumption. The heuristic rules employed are heuristic numbers 2, 1, 3, 5 and 4.

The sequences are shown in Figure 2.1. In the preliminary study, four hypothetical components A,B,C and D with arbitrarily selected relative volatilities of 8:4:2:1 respectively were chosen and examined for five cases of feed compositions. In the results, sequence 1 (i.e the direct sequence) turned out to consume the least energy for the three cases of feed composition (thus favouring heuristics 1 and 4); but other sequences (like sequences 3,4 and 5) competed with 1 as the composition of D was increased. For a feed composition where the heaviest component D is in excess, these sequences 3, 4 and 5 are even better than sequences number 1 (favouring heuristic 4). For the complex configuration comparison, configuration 8 turned out to be the most energy conserving sequence for almost all the cases and this was closely followed by configuration 6. In the study of a specific mixture of propane, isobutane, n-butane and isopentane only one feed composition case is considered.

The authors concluded that the optimum sequence for multicomponent distillation columns is that in which components are partially separated in the initial columns, and the final separation of all components into pure product streams is left for the last column. One must however note that with just one specific example investigated coupled with many assumptions made, it is hard to justify the generalisation of such a result.



A: Simple configurations for four-component separations.



B: **Proposed complex configurations for four-component separations.**

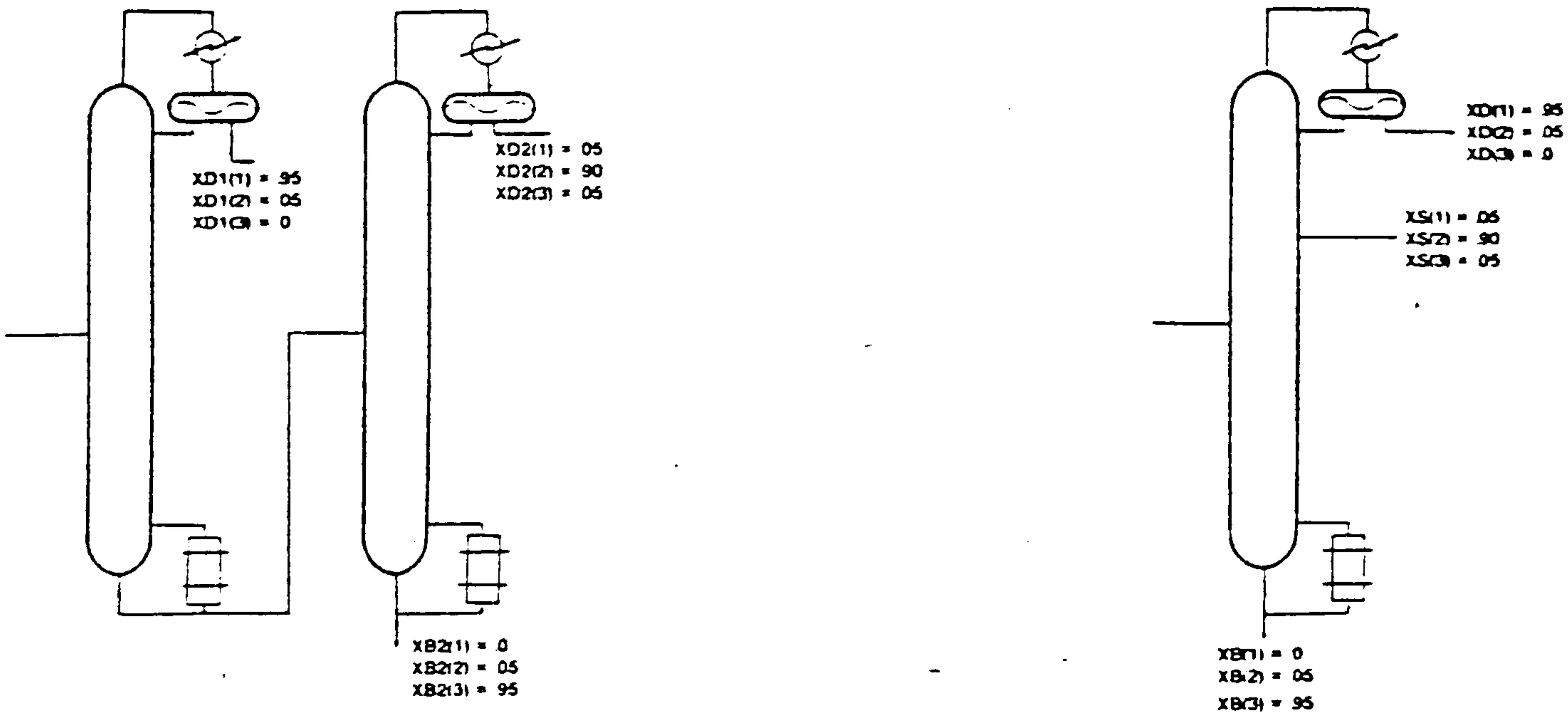
FIG. 2.1 ALTERNATIVE DISTILLATION CONFIGURATIONS USED BY ELAAHI AND LUYBEN (1983)

Alatiqi and Luyben (1985) extended the work of Doukas and Luyben (1978) to the case when the concentration of the intermediate boiling component in the feed is low. This was in an attempt to compare the energy consumption of four different sequences of a mixture of Benzene, Toluene and O -xylene. The four sequences are shown in Figure 2.2. The number of trays in each column was determined from the Fenske - Underwood shortcut method using 1.1 times the minimum reflux ratio. Rigorous steady state simulation of Wang and Henke (1967) was then used to get precise values for energy consumption. Only the energy consumption is considered in the analysis. The results show that

1) the SS configuration (Figure 2.2c) becomes less attrative compared to Figure 2.1a as the intermediate feed concentration becomes smaller.

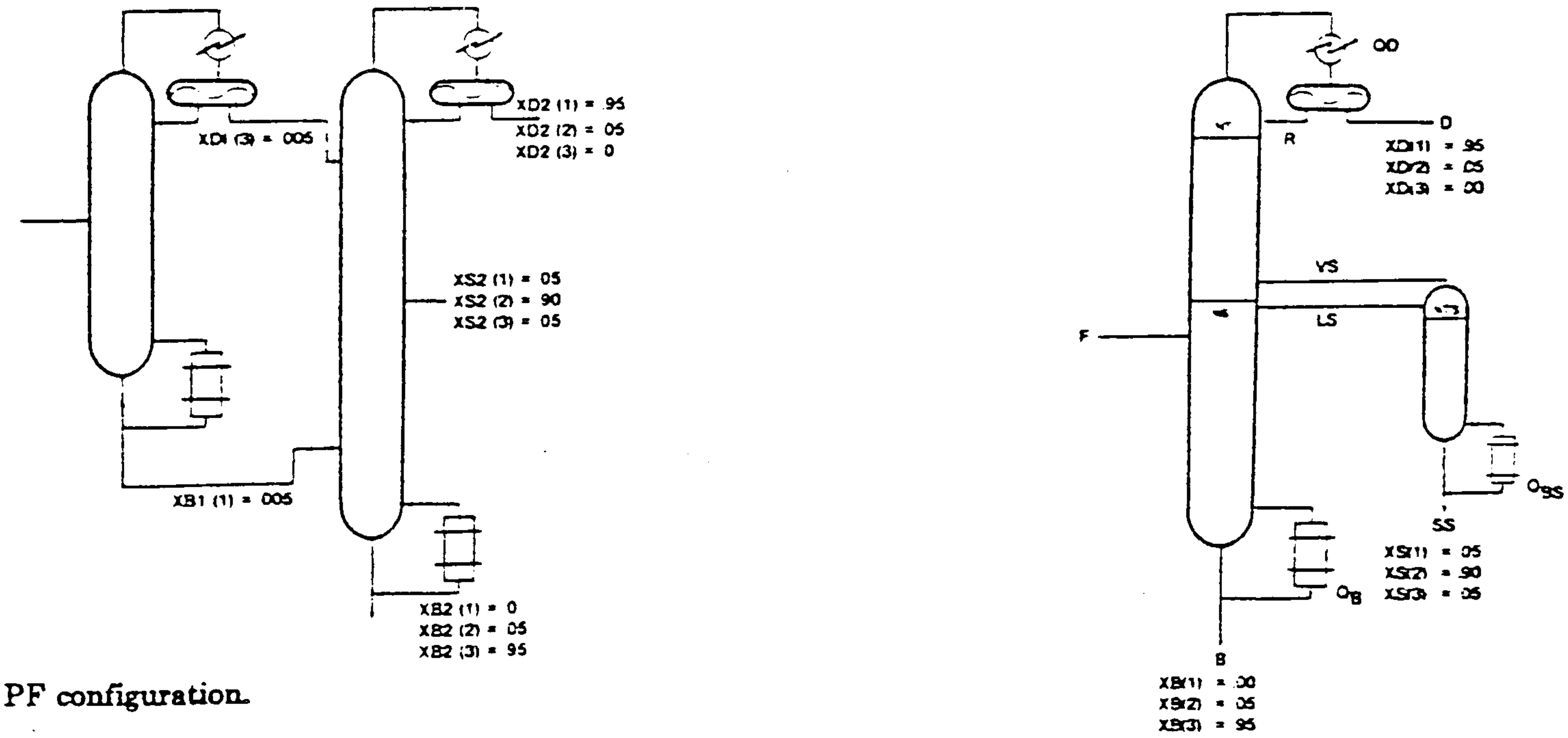
2) the SSS configuration (Figure 2.2d) consumes less energy than both the LOF (Figure 2.2a) and PF (Figure 2.2b) configurations.

Generally the results demontrated that sidestream columns are inefficient for removing small amounts of the intermediate boiling component in a ternary mixture. However, a sidestream column coupled with a sidestream stripper consumed up to 30% less energy than the conventional two - column sequence.



A: LOF configuration.

C: SS configuration.



B: PF configuration.

D: SSS configuration.

FIG. 2.2 ALTERNATIVE DISTILLATION CONFIGURATIONS USED BY ALATIQI AND LUYBEN (1985)

When the capital cost was included in the total cost, the conclusions reached above were not changed. However, the authors noted that in some processes where the capital costs are quite high, the results may be affected.

Some of the conclusions from this work and that of Doukas and Luyben(1978) could be regarded as rules of thumb but specific for the particular problem.

Tedder and Rudd (1978) carried out an analysis of eight distillation sequences separating ideally behaving three-component feed mixtures of light hydrocarbons. The objective was to discover rules of thumb for selecting one sequence in preference to another. The eight sequences included the simple direct and indirect sequences, single column with sidestream, separators with and without prefrationators and thermally coupled columns. The economic objective was the venture cost.

Two general triangular diagrams were constructed with the expected regions of optimalty for ESI <1.6 and ESI > 1.6, where

$$ESI = \frac{K_A K_C}{K_B K_B} \qquad \ldots\ldots\ldots \quad \ldots\ldots\ldots(2.2)$$

and K_A, K_B and K_C are the equilibrium K-values for components A, B and C respectively.

Each of the trangular diagrams is separated into regions where a particular distillation configuration is expected to be optimal. Based on this sort of analysis the authors came out with five rules for the case of ESI > 1.6 and another five rules for ESI < 1.60. The rules were based on the consideration of the concentration of the components in the feed.

This is a qualitative approach to develop some guiding rules (using a cost function) for the sequencing of distillation columns. Unfortunately, these rules are not general; they are specifically developed for a 3-component mixture.

However, as noted by Nishida et al (1981), such efforts should continue since they provide invaluable insights of the synthesis problem and the separations themselves.

Against the background that the solution to the problem of multicomponent separation synthesis can point the designer into the right direction but not to give him "best design", Stephanopoulos et al(1984) suggested a near-rigorous procedure of "great simplicity". On close examination of the characteristics of optimal and near-optimal unintegrated sequences using three examples, the authors concluded that the synthesis of heat-integrated sequences can probably be decomposed into two steps:

(1) using the simple well known heuristics, synthesize a small number of near-optimal unintegrated sequences.

(2) select the two or three sequences with best overall cost and heat integrate.

The heuristics used which were considered to be the most powerful were:

(1) favour the easiest separation.

(2) favour near-equimolar split.

(3) remove the most plentiful component first, and

(4) remove the lightest component first.

The above decomposition implies that "the optimal or near-optimal unintegrated distillation sequences generated by the four heuristic rules tend to offer the best potential for heat integration". We note that this same observation has been made by Freshwater and Ziogou(1976). Then Stephanopoulos et al(1984) provided a qualitative explanation to the above decomposition on the basis of the behaviour of nonkey components in a distillation system. They were of the opinion that the heuristic rules essentially minimise the flow of the nonkey components. The consequence of the low nonkey component flow rate is to narrow the temperature gaps between the profiles of T-Q diagrams; and narrower gaps in T-Q diagram gives better potential for energy integration.

Although the new decompostion principle was effective for the examples considered, more numerical trials are required before the principle can be fully justified.

Malone et al (1985) derived a quantitative approximate criterion for the selection of simple distillation sequence for ideal ternary mixtures. The objective function was the total overhead vapour rate which was obtained by a modified shortcut solution of Underwood(1948) equation. The analytical equation obtained included the relative volatilities and feed composition as variables. For the three - component mixture examples to which the equation was applied, the agreement between the total vapour load obtained and that of the Underwood was favourable. But for the case where the relative volatility between one the pair of adjacent components was in the neighbourhood of unity, the agreement was only fair. The authors indicated that in some situations the commonly accepted heuristics are incorrect. The heuristic referred to included;

1) Remove the most plentiful first
2) Make easier separation first
3) Favour equimolal split.

From their analysis, the total number of trays is insensitive to the way sequencing of the columns is made, if the fractional recoveries in all columns, are specified or if the purities are specified but the relative volatilities between the adjacent pair of components are not in the neighbourhood of unity. That would imply that if the relative volatilities are close to unity, the number of plates may effect the sequencing of the distillation columns and the method may likely fail.

Though the equation derived is useful, the major snag is that it is only applicable to a three - component system. Extending the derived procedures to higher number of components may result to an expression which "becomes undesirably complicated" [Glinos and Malone(1983)] except when lumping of the components is applied.

For the three-component mixture A, B and C, the analytical equation obtained is

$$\frac{\Delta V}{F} = \frac{R}{R_m}\left[\frac{x_B + x_C}{\alpha_B - 1} \cdot \frac{x_A x_C}{1 + x_A x_C} + \frac{1}{\alpha_A - 1}\,\frac{x_C - f.x_A + x_A x_C^2}{f(1 + x_A x_C)} - \frac{\alpha_B(x_A + x_B)}{\alpha_A - \alpha_B}\,\frac{f-1}{f}\right] - x_A \qquad \ldots\ldots(2.3)$$

where

$f = 1 + 1/(100.x_B)$

ΔV = difference in vapour flow rate between the direct and indirect sequences; F = molar feed rate; x is the mole fraction of the components; α is the relative volatility and R/R_m is the operating reflux to minimum.

We have been examining the works which deal with only the sequences of distillation columns using the heuristic rules. It is noted that the heuristics so far utilised by the various authors can sometimes contradict each other. There are one or two quantitative methods which attempt to choose between conflicting heuristics but these are inadequate. They only apply to ternary mixtures. The weighting factors used by some authors are chosen arbitrarily and this renders them very limited in applications.

Now we shall examine those works which allow the use of other separation methods in addition to distillation. This is a more complex problem as it involved the problem of selection of suitable separation method(s) in an addition to the problem of sequencing.

The earlier attempts were made by Sirola and Rudd(1971), Power(1972), and Sirola et al(1971). They all sought to develop means by which the type and order of separation operation could be determined using heuristic techniques. The heuristics employed are heuristic number 1, 2, 3, 6, 8, 12 and 13. Systematic procedures for generating separation schemes were set up as part of a general process synthesis program known as AIDES (Adaptive Initial Design Synthesizer). These procedures were based on the use of design heuristics for the selection of the most appropriate separation method for a multicomponent mixture. Application of these heuristics to the original mixture generated new (smaller) groups of components to which the heuristics were again applied. This process was carried out sequentially in this fashion until no further separations were required and the separation sequences (hopefully optimal) had been obtained. This logic is in Figure 2.3. The heuristics were assigned weighting factors. This in essence an attempt to overcome the problems associated with the use of several different heuristics for separation sequences. The separation method chosen at any point in the synthesis is the result of the combined effect of the various heuristics used. Obviously such a procedure depends heavily upon the heuristics that are included and upon the weighting factors used. According to Hendry et al(1973), it is quite likely that many optimal separation sequences could be found that would not conform to these particular heuristics.

The problems associated with selection and weighting of heuristics for the general-purpose design of separation sequences will require a great deal of further work. Their method was just scratching the surface of the problem. The various methods of separation included in the package and the systematic order in which the heuristics are applied and the way the weighting factors are assigned is not stated.

A similar approach to that above was proposed by Thompson and King(1972). The computer program was developed, and the basic approach, which had been implemented, involved evaluating and making decisions using as little information as possible. The general strategy of the method is shown in Figure 2.4.

The first step carried out by the routine PROD was to identify a feasible set of products for the plant. The next step is the generation of a separation sequence by routine SYNT. This routine shared some of the work with PICK routine which selects

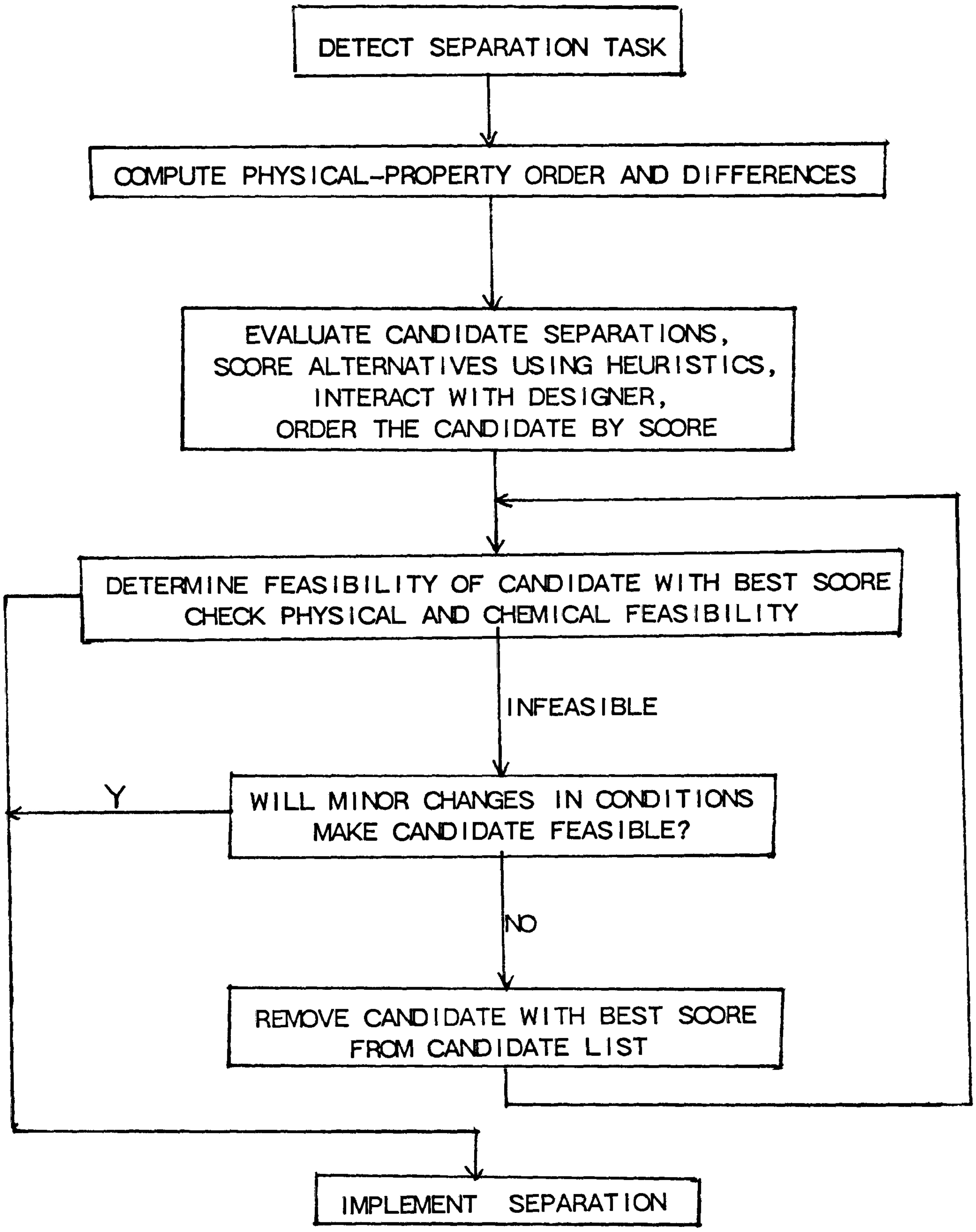


FIGURE 2.3: AIDES separation-synthesis logic [Powers(1971)].

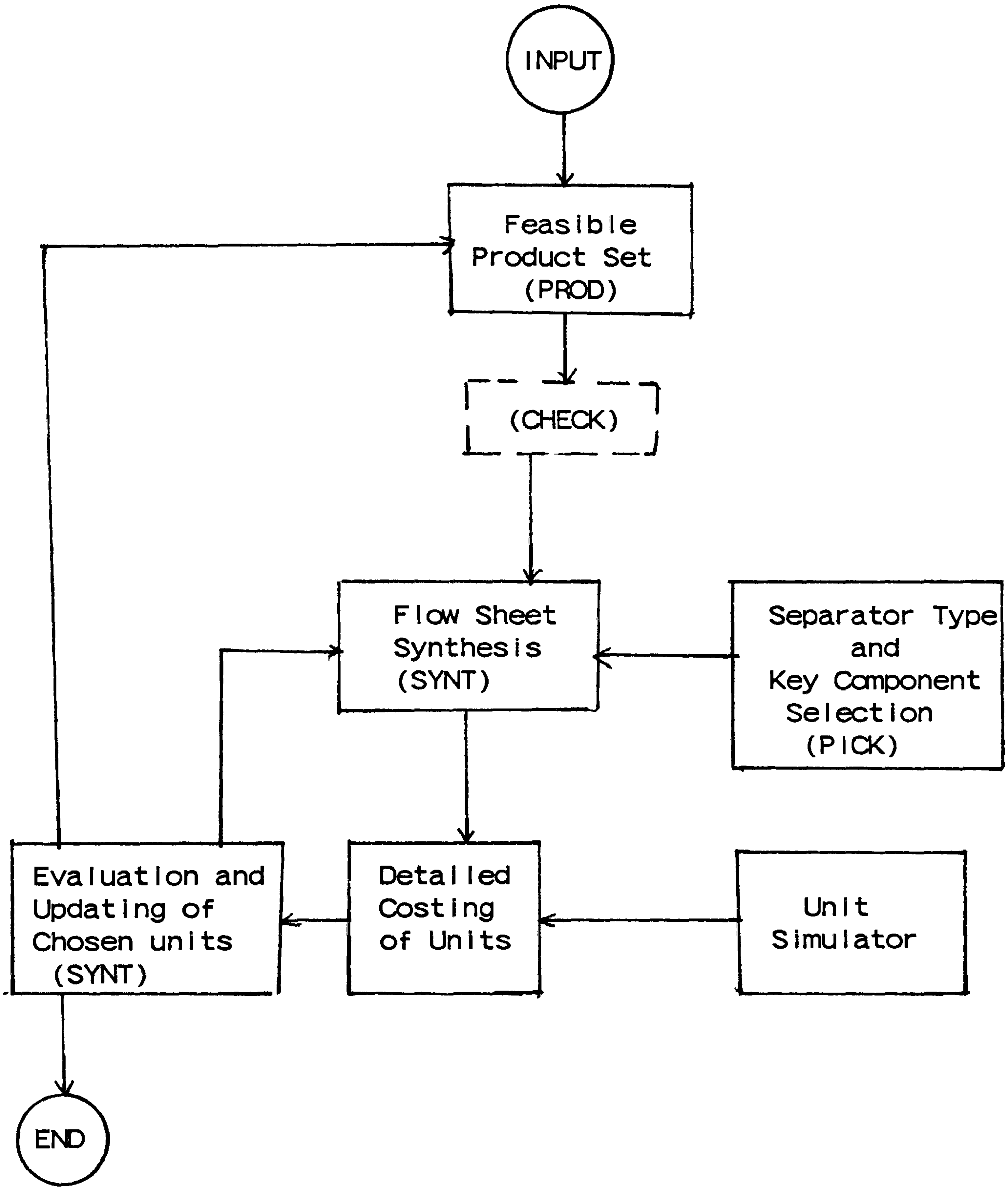


Figure 2.4: General strategy of Thompson and King(1972)

the next separator in the train on the basis of a heuristic which states that the next separation to be made is the one that can apparently be made most cheaply. For the first step, the heuristic applied is that the best process will have the least number of products. This will imply the direct sequence. In summary the heuristics employed are heuristic number 1, 2, 3, 7 and 11. After the creation of the required sequence, the routine DETAIL takes over the sizing and costing of the process.

This approach was illustrated by a six component mixture of ethane, propane, butane, pentane, propene and 1-butene from which it was desired to make four relatively pure products of 99% recovery. For this problem four separation methods were included in the package. These were ordinary distillation, extractive distillation, extraction, stripping and absorption. Only the extractive distillation was however considered feasible for the problem in addition to ordinary distillation. While the approach undoubtedly has much to recommend in it because it can apparently create reasonable processing schemes without very large consumption of computer time (reported by the authors), it can create, at best, sequences with a high probability of optimality and is unquestionably liable to complete failure when confronted with a sufficiently complex and unusual situations [Hendry et al(1973)]. Furthermore, the logic appears quite complicated and not based upon enough heuristics for a sound selection of separation methods to be made.

According to Nishida et al(1981), Hartmann(1979) and his coworkers, Hartmann and Hacker(1979) employed heuristic rules for the synthesis of the optimum separation sequence, and these heuristic rules could be divided into two groups: (1) those rules that determine the structure, i.e. the selection and sequencing of splits; (2) those that determine the operating conditions of the separation methods. The first group was based on a set of heuristics [Heuristic numbers 1, 2, 3, 6, 8 and 16] while the second which was of parametric rules includes

(1) choose operating conditions which are close to the ambient,

(2) choose operating reflux 1.2 times the minimum reflux, and

(3) choose the reflux in such a way that the maximum realizable number of trays is required.

The heuristics used are not new but all have been suggested before. The authors had assigned subjective weights to the heuristics and their goal was to synthesize the separation sequence with the maximum sum of weights. There were no guidelines given on how to weigh the various heuristics, and it was left for the designer to decide on the basis for each problem.

Nadgir and Liu(1983) proposed a "simple" heuristic method involving the sequential application of seven heuristics which have been suggested before. The authors classified the heuristics into four category: 1) method heuristic, which favour the use of certain separation methods under given problem specifications; 2) design heuristics which favour specific separation sequence with certain desirable properties; 3) species heuristics which are based on the property difference between species to be separated; 4) composition heuristics which are related to the effects of the feed and product composition on separation costs. The list of these heuristics are heuristic numbers 15, 21, 11, 8, 2, 6, 3, 1 and 10.

In the systematic use of the heuristics, they were applied one by one in the given category order. If any heuristic is not important in, or not applicable to the synthesis problem, the next one in the method category is considered. Finally, the actual initial sequences are synthesized by using composition heuristics with the help of the Coefficient of Ease of Separation (CES). This was defined as the product of the ratio of the molar flow rates of products (distillate and bottom) and the boiling point difference between the two components to be separated

The method was applied to three synthesis problems which had been solved previously using other methods. Based on the reported costs, the initial sequences obtained for these examples by their method were cheaper than those obtained by other heuristic methods. Only the extractive distillation is considered in addition to the ordinary distillation for the examples illustrated.

In general there are no clear rules for synthesizing sequences which allow the use of other separation methods other than an ordinary distillation columns. In all the works, only extractive distillation has been considered with the exception of Thompson and King(1972) who included a few other separation methods in their synthesis computer package but not utilised for any example problem.

2.2.2 Evolutionary Techniques.

Evolutionary technique is a strategy wherein one devises a processing scheme, analyses that scheme, changes the scheme in one or more ways to improve it, analyses the revised scheme, improves it again, etc. This is repeated until no further improvement on the scheme can be made. In brief, the evolutionary approach refers to the synthesis of new processes by modification of previously generated ones. With a few exception, the evolutionary technique is found to have been applied to sequences of distillation columns only.

Stephanopoulos and Westerberg(1976) classified the evolutionary technique in the synthesis of separation processes into three main subtasks:

(1) the development of an initial sequence from which to start the evolution. As in the case of optimisation, the starting point is very crucial for the success and effectiveness of a search scheme. The better the starting point (which in this case is the initial sequence), the closer we are to the optimum solution and therefore the faster we attain it.

(2) the identification of rules which govern the evolutionary steps. These rules are the guidelines needed to develop all the neighbouring sequences of the current one. Simply put, these rules are needed to generate all the permissible structural changes in the initial separation sequence.

(3) the determination of an evolutionary strategy, i.e. to decide which method to use for comparing the returns of the current and the modified structures. There are different variations that this step can follow depending largely on the search time that can be spent and the quality of solution that is desired. The general tendency, however, is to move from one structure to a neighbouring one and in particular to the most promising one.

Stephanopoulos and Westerberg(1976) illustrated the above notions of the evolutionary techniques on the sequencing of a multicomponent separation process of ABCDE. In generating the initial sequence, the separation sequence is represented as a binary tree. Every separator receives one feed and produces two product streams which either are final products or have to be treated further.

Having generated the initial sequence using heuristic number 7, the identification step of the evolutionary rules began. The aim was to make a simple modification to the initial sequence by exchanging the relative positions of the operators (separation methods) and therefore the relative position of the splits in the overall configurations. To do this systematically, three evolutionary rules were developed and used. The reader is referred to the original paper for the listing and discussions on these evolutionary rules as these are not considered necessary to be stated here.

For the evolutionary strategy, each sequence was generated using the first two of the evolutionary rules. The sequences obtained were optimally sized and costed; and the one that exhibited the lowest cost was retained while the rest were rejected. The neighbouring sequences for this new base sequence were developed and evaluated. This procedure ends when no other neighbouring sequence to the current best one has a lower cost. Then the third evolutionary rule was now applied and the same procedure as described above was carried out until no neighbouring sequence could be generated with lowest cost.

The authors illustrated this approach again with a real mixture of n-butane, Butene-1, trans-butene-2, cis-butene and pentane. Ordinary and extractive distillation methods were used.

On the whole, the authors succeeded in presenting systematic steps to organise the evolutionary sequences of separation processes. In general terms, they discussed the rules to make modifications and their desired properties, strategy to use these rules and various means to compare them. Their work gave a lot of understanding to the subject of evolutionary technique in the synthesis of separation processes.

King et al(1972) applied the evolutionary technique to the synthesis of a demethanizer column in an ethylene plant in which successive improvements were sought to reduce the loss of ethylene to the overhead tail gas. Starting with an initial feasible structure involving ordinary distillation with a refrigerated partial condenser, their technique led to a final structure with lower operating cost. No theoretical guidance or rules were given for the selection of process modifications, these were probably drawn from considerable engineering experience in the processing of this particular mixture.

The second example detailed the use of a computer in implementing the evolutionary logic for the design of a methane liquefaction process. The objective was to minimise the energy consumption per unit quantity of methane liquefied. Although the optimal structure generated was complex, it was found to represent considerable savings in energy over a simple initially assumed structure.

Seader and Westerberg(1977) presented an approach for merging heuristic and evolutionary techniques for the sequencing of simple separation sequences. The authors adopted the evolutionary views of Stephanopoulos and Westerberg(1976). Six known heuristics (all embedded in heuristic numbers 1, 2, 3, 9, 11, 12, 13 and 18) were used to aid the generation of the initial sequence and the application of the evolutionary rules. They devised techniques for executing the three basic steps (which are already outlined above) in an evolutionary approach.

Their approach was applied to two examples; the first was the problem of Hendry and Hughes(1972) and the second was that of Rodrigo and Seader(1975). One of the examples involved the use of an extractive distillation in addition to ordinary distillation columns. Although the approach as reported helped a great deal to reducing the number of sequences to be examined, it failed when applied to the second problem.

Nath and Motard(1981) presented another evolutionary procedure which consisted of two phases. In the first phase, a good initial sequence was created by combining eight known heuristic selection rules. These heuristics are those of numbers 11, 15, 10, 14, 9, 19, 17 and 20. In the second phase, the initial sequence created was successively modified using five evolutionary rules. These are:

(1) Challenge heuristic 11

(2) Examine the neighbouring sequence, if:(a) the CDS (defined below) is within 10%; and (b) refrigeration is required to condense the reflux.

(3) Challenge heuristic 15

(4) Examine neighbours to decide if the MSA removal should be delayed.

(5) Challenge heuristic 10: if (a) R_m of the immediate successor >> R_m of the unit under consideration; and (b) the cost of the immediate successor >> the cost of the unit under consideration.

Of the heuristics applied, the first five provided guidelines for the selection of the separation method and the split product for each stream starting from the feed stream. The last three provided specifications for the detailed simulation of the design of the separators of the sequence. The authors attempted to resolve conflicts in some of the heuristics by giving each split a numerical value proportional to the difficulty of separation. This function was called the Coefficient of Difficulty of Separation (CDS). The split with the smallest value of CDS is tried for detailed simulation; if it is not feasible, the split with the next larger value is tried. This procedure is followed for each stream that needs to be processed in the sequence, resulting in the creation of the initial sequence. The five evolutionary rules evolved were then applied in a hierarchical order. If a particular rule does not suggest any structural modification, the next rule is applied. The evolution stops when no more modifications are possible.

On the evolutionary strategy, the authors suggested that the first evolutionary rule should be applied before any other rule to resolve the question of the product definition. Other rules can now be applied until the sequence obtained is superior to all others.

The approach was applied to two examples in the literature; the example of Rodrigo and Seader(1975) and that of Hendry and Hughes(1972). The examples involved the use of extractive distillation in addition to ordinary distillation columns. Similar optimal sequences were obtained. And although the entire logic was programmed in the computer, the work is similar to some of the previous ones on this subject. All the same, the approach helps to mimic the problem solving procedures commonly employed for the sequencing of separation processes.

2.2.3 Algorithmic Technique

The problem of the synthesis of separation sequences is considered as that of a minimisation problem. The algorithmic technique attempts to find the best separation sequence using well-known optimisation methods developed in the area of nonlinear mathematical programming. Because all the algorithmic methods are in principle rigorous and less fallible, but at the sametime cumbersome and overwhelming in terms of computational time and efforts required, heuristic methods are normally required to reduce the size of the search space.

The earliest purely algorithmic method is credited to Hendry and Hughes(1972). Their approach made use of the dynamic programming in attempting to identify rigorously the optimal sequence without innumerable sequences. The key to the procedure was the initial identification of all separation subproblems (i.e the unique splits) which may be generated from the initial separation problem. Synthesis of the optimal separation sequence was carried out by progressively buiding up information on the minimum cost of separation for the subgroups derived. That is to say, the search for the optimal sequence is started at the binary separation subproblems and proceeds to ternary and larger separation subproblemss. For example, the optimal method for separating the ternary mixture is to determine first the optimal costs for separating the mixture into two streams (one containing one species, the other containing two). To these cost is added the previously determined optimal cost for separating the stream which contains two species. By systematically computing the optimal cost for each separation subproblem it is possible to build up the costs for all sequences in the process.

The authors applied the method to the problem of the purification of mixtures of n-butylene in two different module processes - the straight fractionation and extractive distillation modules. The components are propane, n-butane, butene-1, trans-butene-2, cis-butene-2 and pentane.

It should be noted that a key assumption in the use of the dynamic programming search method is that the information flow is serial. That is, there is no feedback of information on the system. The principle of optimality indirectly applied is based on the fact that the optimal decisions preceeding a decision can only be made if they do not depend on the later decisions. So the method cannot be applied to recyle problems. Although the method guarantee a near-optimal sequence for the examples considered, the computational time requirement would definitely be very large. As it is for a dynamic programming method, all the unique subproblems are evaluated during the sub-optimisation process. This could be a disadvantage.

In order to relax some of the inherent assumptions or limitation in dynamic programming approach, Westerberg and Stephanopoulos(1975) proposed the Branch and Bound Strategy(BBS). This, when properly used, "is capable of findind the optimal separation sequence without having to search over the entire space of all possible separators." The approach is explained thus. Consider a three component mixture A,B and C to be separated using separation methods β_1 and β_2. Let the ranked list (RL) for the components (ranked according to relative volatility, highest first) for both methods are shown below:

RL(β_1): ABC

RL(β_2): ACB

Figure 2.5 shown below is the tree of all possible sequences that can be found by following the branches of the tree. Consider the sequence of separators 1 and 5. Let the cost of this sequence be C_u . This value is an upper bound to the optimal cost of the sequence that can be generated for this problem. If C_l be a lower bound of the cost of the unknown optimal sequence, then

C_l < C(optimal sequence) < C_u

If any sequence has $C_l > C_u$, it is clear that that sequence cannot be optimal since it is being attempted to minimise the cost. This approach results in fewer sequences which are further examined by the designer.

This approach was applied to examples already considered by Hendry and Hughes(1972) and Thompson and King(1972). The optimal sequence obtained in each case was similar to that obtained in the literature cited.

This approach has some advantages over the dynamic programming approach. The approach helps to eliminate unoptimal separation sequences before they have been completed; and

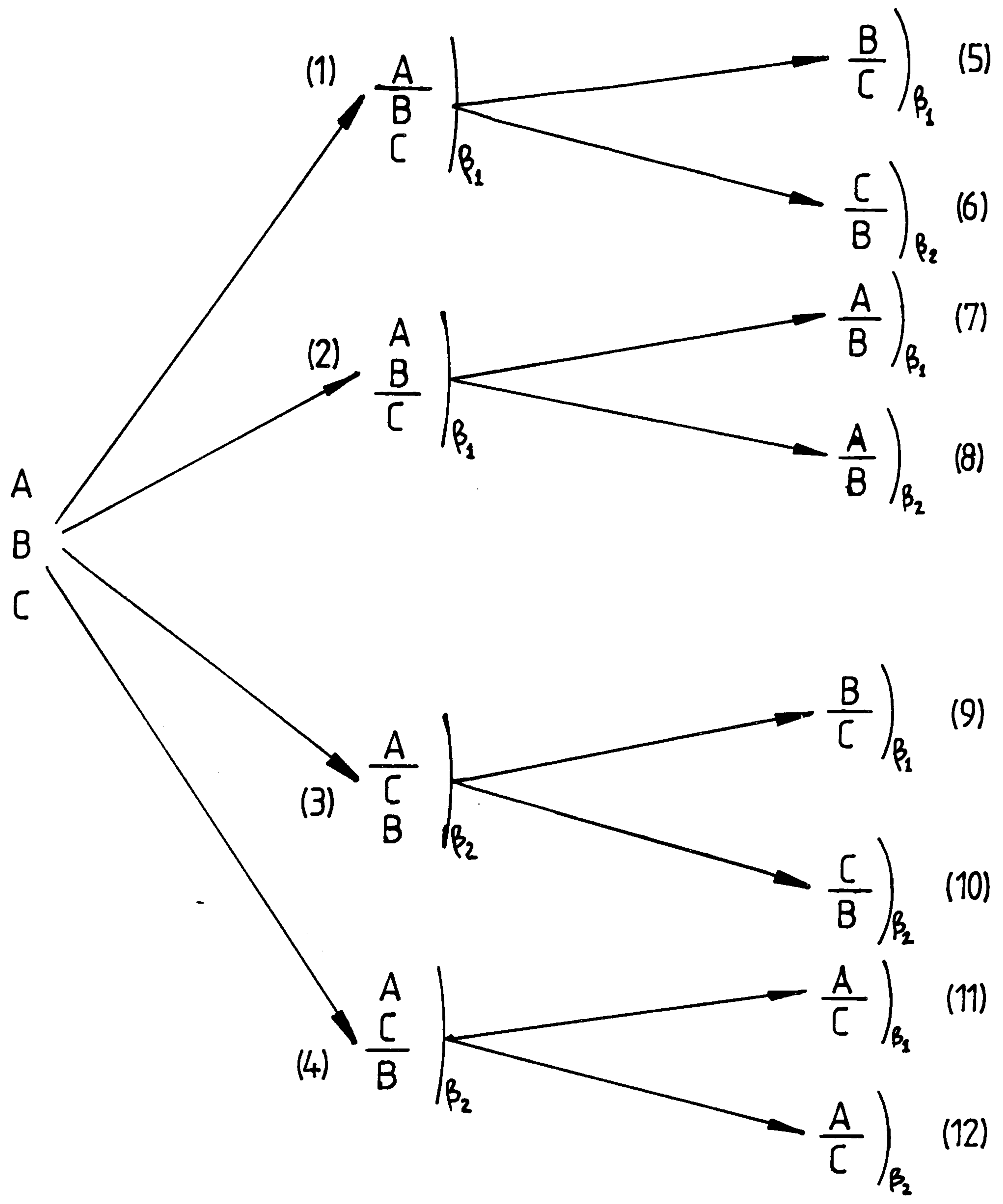


FIG. 2.5 A TREE OF ALL POSSIBLE SEPARATORS WITH A THREE-COMPONENT MIXTURE A, B AND C TO BE SEPARATED USING METHODS β_1 AND β_2 (NISHIDA ET AL, 1981).

therefore the computational time required by the new method may be reduced. No major assumptions concerning the serial nature of the separation sequences are made as is the case with dynamic programming. However, the choice of the basic sequence and the values of the dual and primal (upper and lower) bounds for the initial basic sequence are crucial; neither of which is a trivial problem.

Rodrigo and Seader(1975) regarded the method of Westerberg and Stephanopoulos(1975) as much more complex than the previous ones. They then developed a new approach which in principle was similar to that of Westerberg and Stephanopoulos(1975). This approach was referred to as Ordered Branch Search (OBS) approach and it involves the list processing of the possible separation subproblems followed by an ordered branch search to find the optimal sequence with respect to the system structure. Two simplification rules were employed to reduce the search space: 1) identify multiplicate separators and analyse them no more than once; 2) identify certain forbidden separations thus eliminating other separators which stem from those forbidden splits.

Then the ordered branch search is begun using other three known heuristic rules [Heuristic numbers 1, 3 and 7] to aid the search. The search proceeds in first and subsequent stages. In the first stage, the search proceeds by branching with the aid of the heuristics until all products are produced, thus completing the development of the initial sequence. The cost of this sequence obtained during its development by accumulating costs of subproblems contained in the sequence as the subproblem are being analysed, is selected as the upper bound to the cost of the optimal sequence. The second and subsequent stages involve backtracking and the branching to seek subsequent and perhaps lower cost sequences. If a lower cost is found, it becomes the new and current upper bound. Branching is discontinued and a new phase is begun by backtracking whenever the cost of a partially completed sequence exceeds the current upper bound.

This method was illustrated using component mixture of n-hexane, Benzene and Cyclohexane by ordinary and/or extractive distillation with phenol as solvent. Reduction of search space was observed as compared with the method of Westerberg and Stephanopoulos(1975). The five-component example by Rathore et el(1974) was also used to illustrate the authors' method. This involved only the ordinary distillation columns. They observed that the distribution of sequence costs was relatively narrow for this case. In this case a relatively high percentage of all possible sequences may be near optimal resulting in a search over most of the space of possible separation sequences. This will negate the advantage of the method in reducing the search space for a separation problem.

In a later paper, Gomez and Seader(1976) further refined the search procedure of Rodrigo and Seader(1975). They developed a Predictor Ordered Search procedure which was used to scan the graph representing all possible separation sequences for a given separation problem. As shown in Figure 2.6 each node in the graph represents a step towards the development of complete sequence. The beginning node B is the initial feed mixture and terminal node T is the set of the desired product. The lower bound associated with node i denoted by $g_i^*(B,T)$ is given by

$$g_i^*(B,T) = g(B,i) + C(i,j) + C^*(j,T) \quad .... (2.4)$$

where $g_i^*(B,T)$ is the estimated cost of the complete sequence going from B to T and passing through node i; g(B,i) is the actual cost of the partially completed sequence from node B to node i; C(i,j) is the minimum actual cost from node i to node j by an appropriate separation method, evaluated for every successor j; $C^*(j,T)$ is the estimated cost of the separators involved from node j to node T i.e, the cost of remaining binary subproblems evaluated in the absence of nonkeys. A node i can only be developed if the values of the lower bound $g_i^*(B,T)$ and the actual cost g(B,i) of the partial sequence ending at node i are both less than the current upper bound; otherwise the expansion of the node i is stopped.

The procedure was applied to some problems already considered by previous workers and the results were promising. For example, the problem of Rathore et al(1974) led to the optimal solution after analysizing 13 of the 20 unique separation subproblems. Extractive distillation was included in one of the examples.

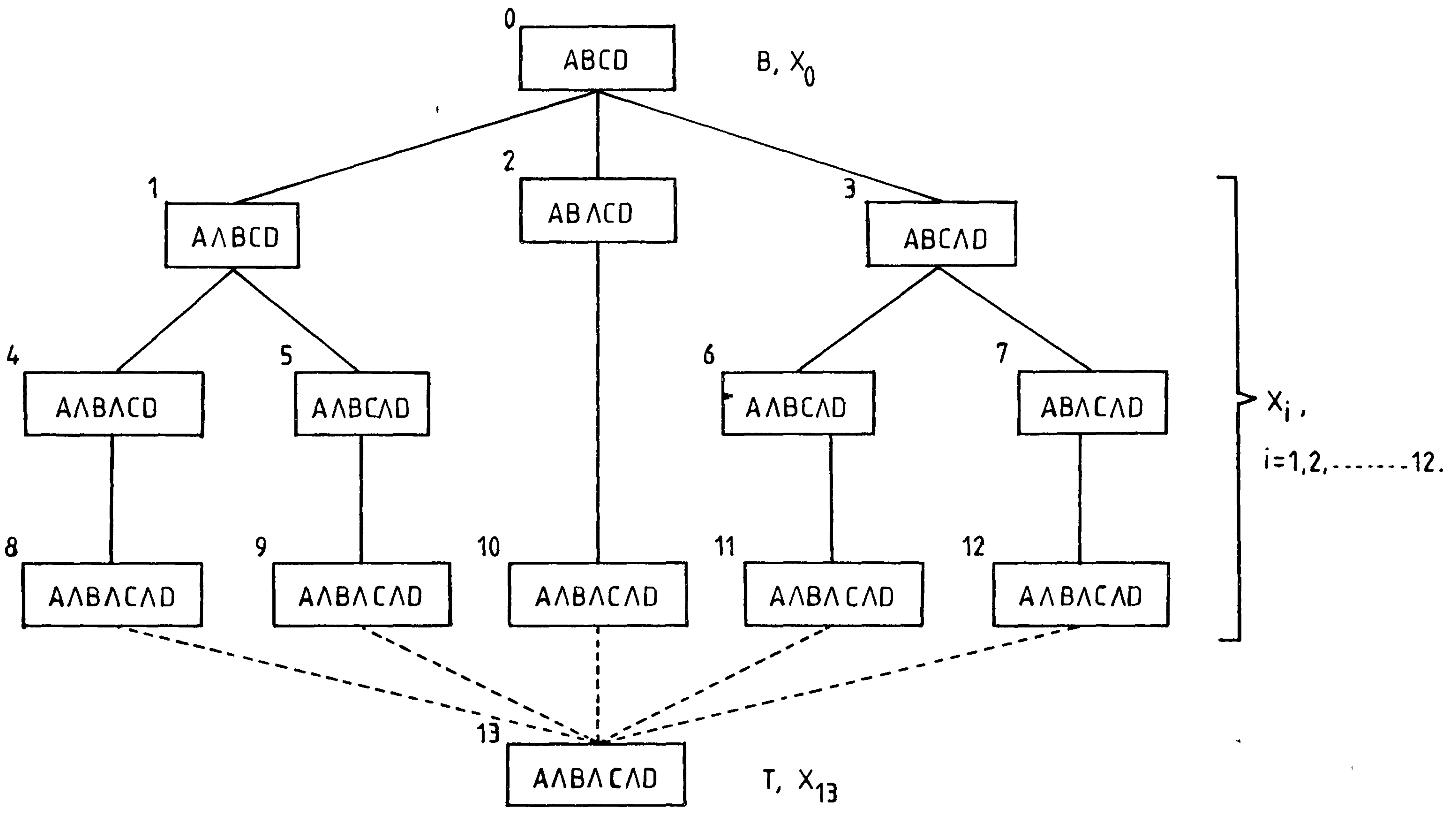


FIG. 2.6 EXAMPLE OF SEQUENCE GRAPH FOR USE OF ONE TYPE OF SEPARATOR [Gomez and Seader (1976)]

Pibouleau et al(1983) deveoped almost the same procedure as Gomez and Seader(1976). The method like most others was used to scan the search space of the type shown in Figure 2.7. The algorithm can find the distillation column optimal sequence (i.e the sequence with the minimum cost C) and a set of near optimal sequences of cost, C_N such that

$$C_N < (1 + \beta)C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.5)$$

where β is a given positive scalar.

At any step of the search procedure, the upper bound was taken to be the lowest cost of complete sequence found since the start of the search multiplied by the factor $(1 + \beta)$. The lower bound is the heuristic function of equation (2.4) developed by Gomez and seader(1976)

An example of 6-component mixture of ethane, propylene, propane, isobutane, n-butane and pentane) showed that the ratio of the number of explored sequence to the total number of possible sequence was always small (less than 25% in some cases) and that similar operating conditions (operating pressure and reflux ratio) usually gave the same optimal sequence. The method is purely for ordinary distillation sequences.

Recently, Gomez-Munoz and Seader(1985) addressed the synthesis problem by means of thermodynamic objective functions. The paper was divided into three main parts. First, all

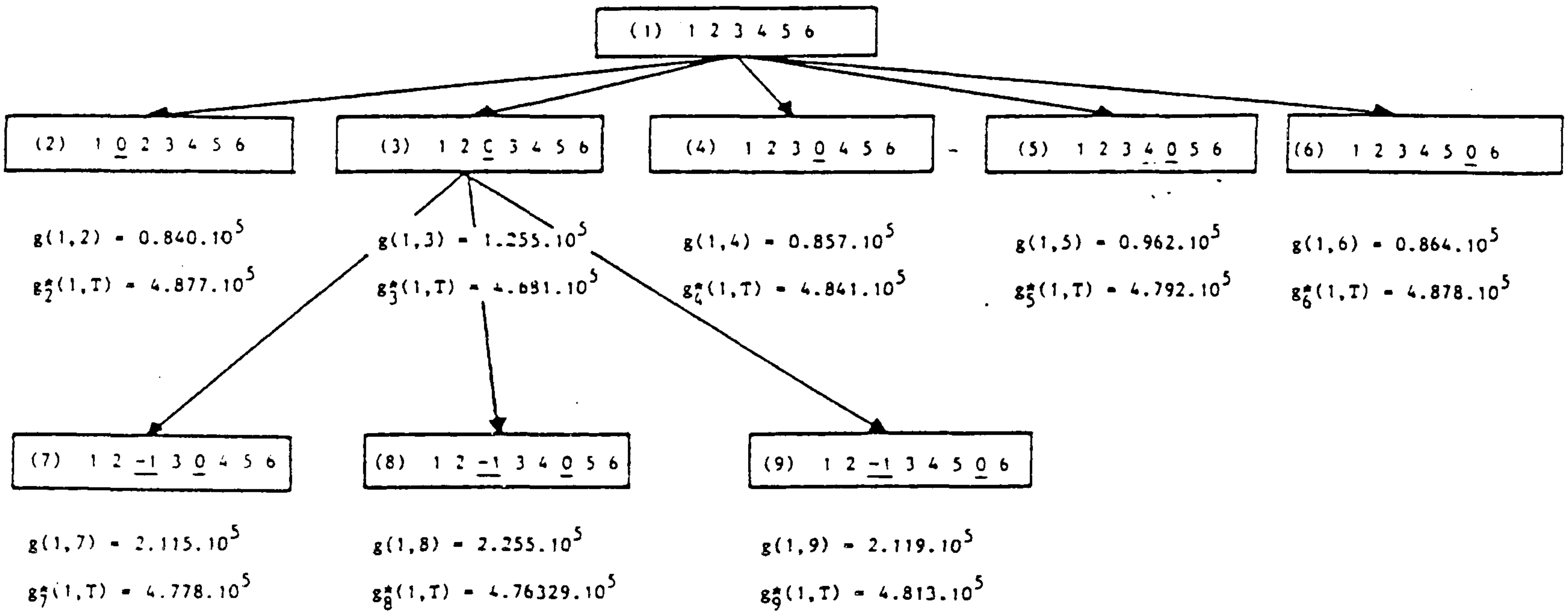


FIG. 2.7 AN EXAMPLE OF HOW TO CARRY OUT THE BRANCH AND BOUND PROCEDURE [PIBOULEAU ET AL (1983)]

thermodynamic functions were derived (not new!). Second, the parametric studied of ternary mixtures were presented. Third, a thermodynamic search (TS) algorithm was proposed for the synthesis of separation sequences including simple and complex types.

The thermodynamic functions derived were for

(1) the dimensionless minimum isothermal work for reversible separations of ideal gas and liquid mixtures.

(2) the Carnot equivalent work; and

(3) the irreversible separations and lost work

These three thermodynamic functions derived were next applied to the sequencing of ordinary distillation sequences for a mixture of 3-components. Four different sequences were considered and these include the simple direct(I), indirect sequence(II) and two complex sequences with prefractionators (III & IV). The criterion of comparison was that the best sequence is the one that minimises the total amount of unit feeds for the process. The regions of optimality found for the sequences I & II were the same using any of the thermodynamic functions.

From the results, the authors noted that when the purity of the products and the optimal conditions are specified, the selection of the optimal sequence is less influenced by the relative volatilities between the components except for complex configurations. And that the feed and product compositions appeared to exhibit a more important role. These observations are not wholly true even from their results.

On the use of the TS algorithm to provide an evolutionary technique for improving the sequences, the results obtained showed that the TS was more efficient than previous methods. Although tedious calculations may not have been necessary in applying the TS algorithm, the procedure to be followed is quite involving. On the whole the values of their work lies in exploring the synthesis of separation processes using thermodynamic objective functions. This is an area that little attention has been given.

2.3 Sequences of Separation Processes with Heat Integration.

So far we have been dealing with sequences of separation processes in which energy/heat matching was not taken into consideration. In distillation and other separation equipments, costs associated with supplying and removing energy are very important. Hence, the cost of energy can have a large effect on the size and sequence of distillation columns used in multicomponent separation problem.

In recent years the design of complex plant with extensive energy matching has become commonplace. In particular, the heat integration of two distillation columns is possible because there are heat sources (overhead vapour) and heat sinks (reboiler steam). Although our focus is not in energy integration it is wise we mention briefly the various authors that have included energy integration in their synthesis.

The first systematic effort for the synthesis of distillation sequence with heat integration was undertaken by Rathore et al(1974a,b) in two separate papers. They utilised the dynamic programming techniques already proposed by Hendry and Hughes(1972) to generate feasible matches between separation sub-problems of a five-component mixture. This was illustrated with an ordinary distillation sequences of Propane, i-Butane, n-Butane, i-Pentane and n-Pentane.

Freshwater and Zioguo(1976) expanded the work of Rathore et al(1974) to a range of component mixtures. They noted that (though not very evident from their results) that the sequence which gives the greatest energy saving is often that which has the lowest energy use without integration. And that when this is not so, the difference between the optimal sequence with energy re-use and that without energy re-use is often a few percentage.

Umeda et al(1979) presented an evolutionary approach based on the available energy concept for energy integration systems. They illustrated the idea by developing an improved heat-integrated sequence for a five-component distillation problem already studied by Rathore et al(1974).

Morari and Faith also developed an algorithmic technique based on Lagrangian method to optimise the problem of Rathore etal(1974). He used heat availability diagrams to improve the heat integration for the specific problem but did not extend the work to propose a general separation sequencing problem.

Naka et al(1982) showed how to develop a heat-integrated distillation sequence which minimizes the losses of available energy. Their method considered sequences based on distillation columns and permits multiple heat sources and sinks which may be either utility or process streams.

Minderman and Tedder(1982) made a comparison between some published energy integrated sequences (Rathore et al(1974), Umeda et al(1979), Morari and Faith(1980)) and the authors' state optimised sequences generated by simple synthesis scheme utilising the rules suggested by Tedder and Rudd(1978) and the applying a rigorous branch and bound search over the unintegrated solution space using the heuristic generated sequence cost as an upper bound to the optimum cost. By comparing an extensively optimised distillation sequence with published extensively integrated sequence, the cost savings due to such complex energy integration was seen to be small for new facility designs.

Andrecovich and Westerberg(1985a,b), Westerberg and Andrecovich(1985) and Westerberg(1985) presented a method of heat-integration of distillation systems based on the concept of $Q\Delta T$, (the product of the condenser or reboiler heat duty and the temperature difference between the reboiler and condenser). This permits them to develop utility bounds for distillation sequences. They observed that the heuristics that suggest using the sequence having the minimum sum of $Q\Delta T$ areas appeared sensible.

Consequent to the work of Andrecovich and Westerberg(1985a), Glinos et al(1985) provided a simple algebraic equation for the evaluation of ΔT and $Q\Delta T$ based on some simplifying assumptions;

$$T = RT_F^2 \, \mathrm{Ln}\left[\frac{\sigma_D}{\sigma_B}\right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.5)$$

$$Q\Delta T = RVT_F \, \mathrm{Ln}\left[\frac{\sigma_D}{\sigma_B}\right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.6)$$

and $T_F^2 = T_D T_B$; V is the vapour rate; R is the gas constant and is a weighted parameter by the mole fractions (x) average of the relative volatilities (α), and is defined as

$$\sigma_k = \Sigma \alpha_i x_{i,k}$$

Kattan and Douglas(1986) also described a four-step approach for synthesizing heat-integrated distillation sequences. The procedures involved in the four-step approach are not new.

Another related synthesis problem with heat integration involves thermally coupled distillation systems, distillation with sidestreams, and prefractionators. Some of these have however been mentioned.

Petlyuk et al(1965) were among the first to study complex sequences of this nature. They presented five different sequences for a ternary mixture. Their analysis did not go very far.

Stupin and Lockhart(1972) discussed one of the sequences proposed by Petlyuk et al(1965) for a ternary mixture with high relative volatilities of 9:3:1, equimolar feed of the three components and 90% product purity.

Chiang and Luyben(1983) compared five different sequences of two-column heat-integrated distillation columns on the basis of energy consumption with a conventional distillation column. A binary mixture of methanol and water was studied over a feed composition ranging from 30% to 80%.

Cheng and Luyben(1985) extended the work of Doukas and Luyben(1978)to include heat-integration in complex sequences of distillation. Eleven sequences were studied using a ternary mixture of Benzene, Toulene and M-Xylene. Without heat-integration, configuration 4 (prefractionator/sidestream column at low pressure) showed the minimum energy consumption. The result also showed that a conventional sequence with lower operating pressure may be better than a complex configuration with a higher operating pressure.

With heat-integration, configuration 8 (prefractionator with reversed heat integration) was found to be the best, consuming 45% less energy than the best conventional configuration. And in general, complex sequences with heat integration were found to be more energy-efficient than conventional sequences with heat integration. We note that this observation appears to contradict the work of Minderman and Tedder(1982).

It is worth noting that all the work relating to energy integration are based on distillation column sequences only.

2.4 Summary of the review of the literature on sequencing of separation processes

The review covered in details up-to-date literature on the optimum sequencing of separation processes without heat integration. However, a brief mention was made of works in the area of heat-integrated sequences. An attempt has been made at a critical analysis of each of the works so as to lead to a better understanding of its contents in relation to sequencing of separation processes.

The techniques for determining the optimal separation sequence were classified into three main categories:

(1)Heuristic Techniques

(2)Evolutionary Techniques, and

(3)Algorithmic Techniques.

The heuristic methods being not mathematical in nature may not always guarantee optimality. Nevertheless, the development of heuristic rules has provided a first breakthrough towards the solution of the problem of sequencing. The evolutionary and the algorithmic techniques employed these rules to reduce the number of searches to be made thus reducing computational time and computer space; and to generate an initial sequence(s) for further improvements. The algorithmic techniques are usually very rigorous and require a lot of mathematical skills from the users. Therefore, it means that the heuristic rules will continue to play a prominent role in the sequencing of separation problems. Quantitative expressions representing the heuristic rules will be valuable in strenthening the applications of the rules to separation sequencing problems.

Although significant progress has been made in these few years, much still remain to be done. Some areas worth further attention may be cited:

(1) Most of the existing works have dealt with ideal multicomponent mixtures of ordinary distillation sequences. There is not much on the alternative methods of separation. Furthermore, there are no clear heuristic rules for the general-purpose sequences of separation processes.

(2) Nonsharp separation processes and the nonideal mixtures are another areas that may deserve some attention in future.

(3) Further work is needed on the synthesis with heat-integration. The algorithms so far developed are complex and require large computational efforts. More rules of thumb and decomposition principles are required to reduce the complexity of the problem. So far only distillation columns are being considered.

With a few exceptions all the works make use of the shortcut design method of sizing the columns and heat exhangers.

In conclusion, the optimal sequencing of separation processes is no doubt a complex problem. It cannot be said to have reached an advanced stage. Conflicting results are sometimes found in the literature. And most of the work are on the sequences of ordinary distillation columns. This is not surprising as distillation is the most widely used separation method in the process industry. The methods of finding the optimum distillation column sequence have reached such a complex state that it seems unlikely that the introduction of other separation methods into the sequence will be an easy problem to solve. It has been noted that the techniques developed for the optimal solution of the sequencing problem, apart from the heuristics, are complex and time consuming. This is even with simplifying assumptions that are usually made. It would seem appropriate, even as noted by some workers [e.g. Stephanopoulos et al(1982)] to develop simple procedures which are less rigorous but that would simplify the problem without a significant loss in accuracy. Such simple procedures will provide greater understanding of the problem which can lead to further modifications. Particularly valuable would be the development of quantitative equations that will represent and supplement the heuristic techniques.

The optimum sequence produced by such simplifying methods may have to be compared with that produced by the total annual cost (TAC) analysis of the sequences. This TAC is usually considered as the final arbiter on any conflict over which method of separation is to be used and/or which sequence is the best (i.e. optimum). Usually, the TAC may be sensitive to some column parameters. In the next chapter, we investigate the concept of energy flow per unit area of distillation column. This energy flow per unit area is found to affect the capital and energy cost relationship in a distillation columm and thus the optimum reflux ratio of the distillation column.

CHAPTER THREE

PARAMETRIC STUDIES IN OPTIMUM REFLUX RATIO AND COST OF A DISTILLATION COLUMN OPERATION.

3.1 Introduction

In a distillation column, an increase in operating pressure results in an increase in the vapour throughput along the column. Hence, the energy flow per unit area of column increases. Pressure changes are related to the Flow Parameter (FP) which in turn is used to correlate the maximum capacity of trayed and packed columns. In fact, high values of the Flow Parameters are associated with the high pressure distillation of low molecular weight materials, and low values with low pressure distillation of high molecular weight materials. It is interesting to observe below that the energy flow per unit area of column may be correlated against the flow parameter with more energy flow per unit area of column at high values of Flow Parameters than at low values. Therefore, for each additional plate at high pressure operation, more energy is saved than at low pressure operation. That is, each incremental additional tray cost produces bigger incremental energy savings at high pressure than at low pressure. These changes in the operating pressure are sure to affect the balance between the capital costs and the energy costs of a distillation column operation. This balance between the capital costs and the energy costs of the column dictates the optimum reflux ratio to be used for the operation of the column. Thus, the examination of the energy flow per unit area of distillation column is shown in this chapter to result in a simple equation for determining the optimum reflux ratio and the cost of distillation columns.

And because of the importance of this ratio in design, it is pertinent to understand the effects of operating and system variables on its value and how all these effects correlate against the Flow Parameters (or the operating pressure) and in effect against each other. The variables considered apart from the operating pressure includes the feed composition, the recovery fraction, the relative volatility and the materials of construction. These variables are crucial to the relationship between the capital and energy costs of a distillation column; and would therefore be important in determining the optimum sequences of distillation colums.

In the context of the thesis as a whole, the results from this chapter give credence to and explanations for some of the simplifications employed and results obtained in the next few chapters; Also the results may be found useful in the design of sequences of distillation columns with and without heat integration.

First, we discuss briefly some of the previous work done on the determination of the optimum reflux ratio.

3.2 Previous Work

Typically, the determination and choice of the optimum reflux ratio is done by cost evaluations. These are always displayed in the cost versus reflux ratio curves from which the optimum reflux ratio is picked as the ratio corresponding to the minimum cost. This is the trend in the literature.

Robinson and Gilliland(1950) carried out cost estimates for the fractional distillation of a methanol-water mixture and the results were presented in a graphical plot of cost against reflux ratio. It was observed that the curve passed through a minimum at operating reflux to minimum of less than 1.10.

Peters and Timmerhaus(1980) gave an example of the determination of the optimum reflux ratio for a benzene-toluene mixture with set feed conditions, set pressure and a set product specification. The sum of costs for piping, insulation, and instrumentaion were estimated to be 60 percent of the cost for the installed equipment. The optimum reflux ratio obtained (in a graph similar to that of Robinson and Gilliland(1950)) is 1.10 times the minimum. This is, however not apparent from the graph presented.

As reported by King(1980), Heaven(1969) used typical economic condition for the 1960's to find the optimum reflux ratio to minimum for 70 different hydrocarbon distillations carried out at atmospheric pressure and above. Except for two columns with the minimu reflux ratio under 0.2, he found the optimum to be between 1.11 and 1.24 times the minimum in all cases.

Fair and Bolles(1968) presented graphical results for three cases which covered (as coolant) a -125 °F refrigerant; a -40°F refrigerant and +85°F cooling water. In all the three cases, the optimun reflux ratio obtained is approximately 1.05 times the minimum.

Other workers who have developed correlations for obtaining approximate value of optimum reflux ratio are mentioned below. These correlations are mainly graphical which may not be easily utilised.

Neretniek(1970) developed a global search procedure to find where the optimum reflux ratio lies in the optimisation of a distillation sieve tray columns.

Liddle(1968) presented an equation to correlate the Gilliland plot for estimating the theoretical number of plates. He then extended the shortcut design method for a distillation column to the estimation of approximate optimum reflux ratio. Applying the developed equation to a sample problem gave R/R_m equal to 1.04. As usual, the low value was attributed to the high cost of steam used for the sample problem.

Madsen(1971) combined the correlation of Gilliland for estimating the actual number of plates with the equation of Liddle(1968) to estiamte the optimum reflux ratio. He represented the Gilliland equation in the form

$$N/N_m = 1 + b(R_m/R) \qquad \ldots\ldots\ldots\ldots(3.1)$$

where

b = -0.6915 and N, N_m are the actual and minimum number of plates) from which, in combination with Liddle(1968)'s work, an expression for the optimum reflux ratio was obtained. It is important to note that the cost equations both from this work and that of Liddle(1968) do not take into account the cost of condensing the overhead vapour and the capital costs of condenser and reboiler.

Happel and Jordan(1975) presented an equation and graphs for obtaining the optimum number of plates and reflux ratio of a distillation column. Although the correlation involved many assumptions it is useful in finding an approximate value of R/R_m.

The work of Winkle and Todd(1971,1972), however, attempted to analyse the effects of some variables on the total annual costs of a distillation operation. Their results were presented in various graphical forms. In most of the cases, the energy costs were not considered in the calculations. In the sample calculation shown, as low value as 1.06 was obtained for R/R_m.

Oluji(1981) translated one of the graphical correlations of Winkle and Todd(1972) into an analytical form suitable for computer program. The analytical equation is

$$R/R_m = \frac{(1.6 - Y)}{6.5}(X - 7.5) + 1.6 \qquad \text{......(3.2)}$$

where

$$Y = \frac{\alpha_{LK}}{1.0614\,\alpha_{LK} - 0.4175}$$

$$X = \mathrm{Log}_{10}\left[(x_{LK}/x_{HK})_D(x_{HK}/x_{LK})_B(x_{LK}/x_{HK})_F^{0.55\,\alpha_{LK}}\right]$$

where

x is the mole fraction; LK and HK are the Light and Heavy Keys respectively; D ,B and F are the molar rates for distillate, botttom and feed streams; and α is the relative volatility between the components.

In summary, none of the authors have demonstrated clearly the effects of pressure and other variables on the optimum reflux ratio and the cost of distillation. In most of the work, the costs of condensing the overhead products and that of heating the bottom products are not taken into account in the optimisation thereby making the equations or graphs obtained inaccurate in the determination of the optimum reflux ratio.

3.3 Basis and Method

It is a common observation that for the conditions of practical distillation the major determinant of both physical properties and throughput is the operating pressure. The high pressure systems are always low surface tension, high vapour density and high throughput; and low pressure systems high surface tension, low vapour density and low throughput. Porter and Jenkins(1979) provided an explanation for this observation by showing that for a distillation operation, all of the physical properties, as well as the economic design flow rates may be approximately correlated against the total reflux Flow Parameter (FP), X_∞ , and thus in effect against each other. Flow Parameter, $X = \{L/V(\rho_V/\rho_L)^{0.5}\}$ and $X_\infty = (\rho_V/\rho_L)^{0.5}$ are a group of parameters widely used for correlating the maximum capacity of packed and trayed columns. Therefore, it would be possible, they observed, to show which combinations of flow rates and physical properties are found together in practical situations. The justification for this approach was as follows:

For most distillation operations (particularly difficult ones) the mass or molar flow of liquid down the column is frequently similar to the mass or molar flow of vapour up the column. At total reflux, these are the same. So is the composition of the vapour at any point in the column similar to that of liquid. These observations permit the authors to derive a simple theoretical justification for classifying practical combinations of flow rates (i.e. mass velocities) and the physical properties by means of the flow parameter.

At total reflux, and assuming the vapour and liquid compositions to be equal, one may write

$$X_\infty = \frac{L}{V}\left[\frac{\rho_V}{\rho_L}\right]^{0.5} = \left[\frac{\rho_V}{\rho_L}\right]^{0.5} = \left[\frac{V_L}{V_V}\right]^{0.5} \text{ or } \left[\frac{V_{RL}}{V_{RV}}\right]^{0.5} \quad ..(3.3)$$

where L,V are the mass velocities of the vapour and liquid respectively, assumed to be equal.

ρ_V, ρ_L the vapour and liquid densities

V_V, V_L the molar volumes of vapour and liquid, and

V_{RV}, V_{RL} the reduced molar volumes of vapour and liquid respectively.

As the authors point out, these relationships depend on the mean molecular weights and critical volume of the vapour both being equal to those of the liquid. When this is a reasonable approximation, (e.g. when composition of liquid similar to that of vapour) it follows that

$$X = f(P_R, T_R, C_1, C_2 \ldots\ldots) \qquad \ldots\ldots\ldots(3.4)$$

where P_R and T_R are the reduced pressure, temperature, and C_1, C_2, ... are the characteristic parameters for the particular compounds involved. It then follows from the general theory of corresponding states that since all the physical properties of the vapour and liquid may also be correlated by other equations in P_R, T_R, and C_1, C_2... ,that all the physical properties may be correlated against the Flow Parameter. This is shown in Figures 3.1a and 3.1b which are reproduced from Porter and Jenkins(1979). Although one may expect that differences in physical properties of a particular value of X will exist for different materials, the authors (Porter and Jenkins) found that these differences are not large enough to invalidate the principles introduced above.

In this work, we first extended the principle to thermal properties as shown in Table 3.1 and Figure 3.2. The values of the various properties are obtained as described in section 9.3.2 and Appendix D

The figure and the accompanying table show the values of the various properties for a range of organic compounds at their usual practical operating pressures. The properties are found to correlate well with the flow parameters.

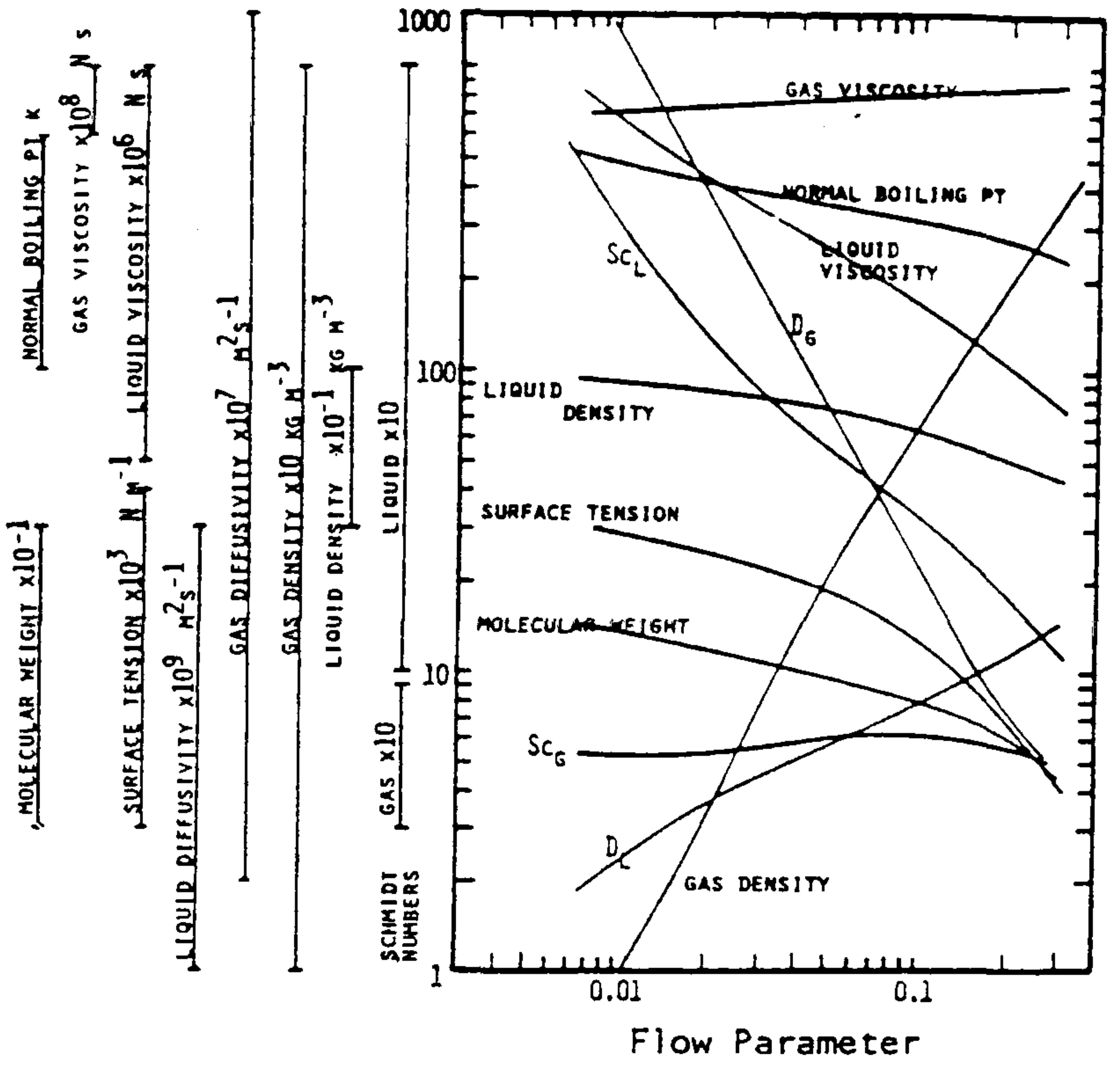
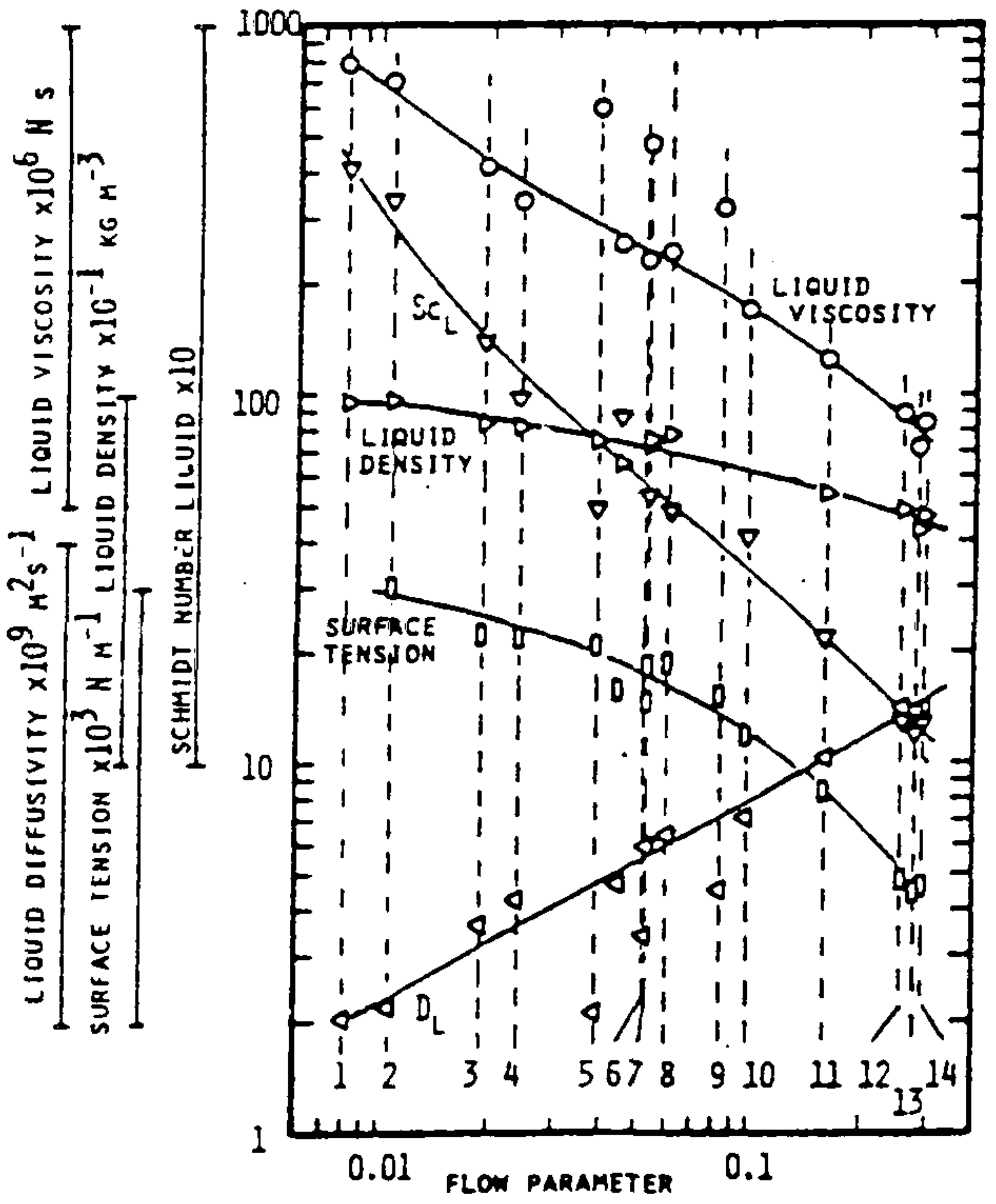


FIG. 3.1a PLOT OF PHYSICAL PROPERTIES AGAINST FLOW PARAMETERS [PORTER AND JENKINS (1979)]



KEY

	Compound	Pressure atm
1	Diphenyl	0.0132
2	Naphthalene	0.0263
3	Ethylbenzene	0.0790
4	p-Xylene	0.132
5	n-Heptane	0.352
6	Cyclohexane	0.352
7	Acetone	1.0
8	Toluene	1.0
9	Cyclohexane	1.69
10	n-Pentane	2.0
11	n-Pentane	5.0
12	isoButane	11.6
13	Ethane	17.8
14	Propane	15.9

FIG. 3.1b PLOT OF LIQUID PHASE PHYSICAL PROPERTIES AGAINST FLOW PARAMETER FOR A NUMBER OF COMPOUNDS [PORTER AND JENKINS (1979)]

Based on the above classification and principles, we next carried out a study of a sieve tray distillation operation using seven different binary mixtures normally distillable at different operating pressures using a water-cooled condenser.

The binary component mixtures used, most of which are taken from the work of Sakata and Yanagi(1979) are shown in Table 3.2 which also gives the pressures, total reflux flow parameters and the average molecular weights at the top of the column. The flow parameters are calculated using equation (3.3) i.e $X_{\infty} = \{ \rho_V / \rho_L \}^{0.5}$

It is known that the maximum flooding capacity may be correlated against the Flow Parameters [Fair(1961)] so that (for total reflux and near L/V = 1.0), the vapour mass velocity (i.e flow per unit area) may be correlated against total reflux flow parameters. And therefore, the energy flow per unit area of column may also be correlated against the total reflux flow parameter.

TABLE 3.1: Physical and Thermal properties against the Flow Parameter (FP) for a number of compounds.

Component*	P Atm.	F.P	ρ_L	λ	ρ_V	C_{pL}	C_{pV}	k_L	k_V
Diphenyl	0.0132	0.008	992	347.5	0.063	1.884	1.403	0.134	0.0105
Naphthalene	0.0263	0.011	960	389.4	0.110	1.758	1.340	0.135	0.0125
Ethylbenzen	0.0790	0.190	840	376.8	0.310	1.758	1.361	0.120	0.0210
p-Xylene	0.132	0.025	800	389.4	0.49	1.884	1.465	0.121	0.0151
n-Heptane	0.352	0.043	680	339.1	1.270	2.386	1.842	0.109	0.0150
Cyclohexane	0.352	0.039	750	376.8	1.12	1.926	1.465	0.117	0.0125
Acetone	1.00	0.052	790	501.6	2.15	2.303	1.382	0.148	0.0138
Toluene	1.00	0.060	780	368.4	2.93	1.884	1.424	0.113	0.0320
Cyclohexane	1.690	0.080	720	343.3	4.65	2.093	1.717	0.108	0.0188
n-Pentane	2.00	0.092	626	337.9	5.31	2.470	1.800	0.101	0.0170
n-Pentane	5.00	0.140	626	302.7	12.01	2.680	1.968	0.091	0.0120
I-Butane	11.60	0.210	557	261.3	23.60	2.554	1.926	0.080	0.0220
Propane	15.9	0.243	450	289.0	26.60	2.847	1.758	0.084	0.0200
Ethane	17.80	0.240	430	326.6	24.80	3.035	1.591	0.096	0.0210

* Taken from Porter and Jenkins(1979)

F.P Flow Parameter defined by Eqn. (3.3)

ρ_L = Liquid density, KG/M^3

ρ_V = Gaseous density, KG/M^3

λ = Heat of vaporisation, KJ/KG

C_{pL} = Liquid specific heat capacity, KJ/KG K

C_{pV} = Gaseous specific heat capacity, KJ/KG K

k_L = Liquid thermal conductivity, W/M K

k_V = Gaseous thermal conductivity, W/M K

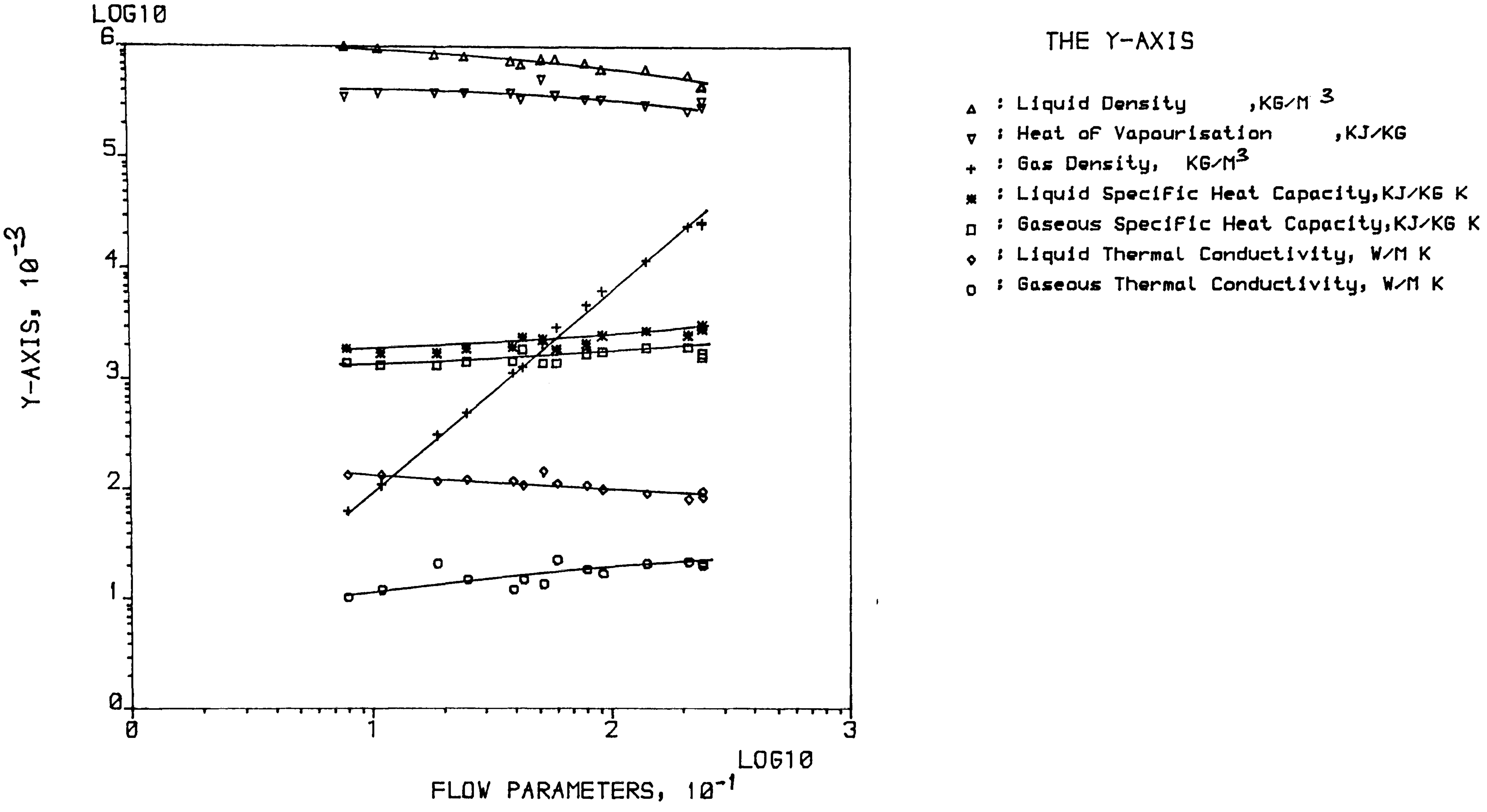


FIG. 3.2 PHYSICAL AND THERMAL PROPERTIES AGAINST FLOW PARAMETER

Note also that as well as the direct cost of energy, there are related proportional costs of heat exchangers. Even at zero energy costs, the optimisation will be related to the vapour flow per unit area because reboiler and condenser costs are proportional to the vapour flows. The idea of zero energy costs would be very important when considering the energy integration of the total system where it is necessary to utilise energy from other parts of the system (say, waste heat, reactor heat, etc.) for the separation of components in the distillation columns. The question of what the optimum reflux ratio should be in such cases is not yet being tackled. Although we do not attempt to tackle the total problem here, the results obtained may throw some light on this complex problem.

For the analysis, the operating pressure levels considered are shown in the table (Table 3.2). This fixes flow rates and physical properties typical of that pressure. However, relative volatility is considered as a variable parameter and is set at values of 1.05, 1.10, 1.20, 1.50, 2.25 and 3.0 of component A to B. The feed composition cases are 10/90, 25/75/ 75/25 and 90/10 molar mass of component A to B. The recovery fractions at the top of the column are 0.90, 0.95, and 0.99; and the materials of construction being carbon steel and stainless steel. The base material is the carbon steel. The cost factors of stainless steel are taken as four times that of carbon steel material (Peters and Timmerhaus(1980))

TABLE 3.2: Binary component mixtures.

No.	Mixture	P, Atm.	F.P	A.M.W
1	Ethylbenzene - Styrene	0.066	0.0168	106.15
2	Cyclohexane - n-Heptane	0.352	0.0376	84.18
3	Benzene - Toluene	1.000	0.0556	78.25
4	Cyclohexane - n-Heptane	1.690	0.0828	84.18
5	n-Butane - i-Pentane	5.000	0.1360	58.26
6	i-Butane - n-Butane	11.60	0.2005	58.12
7	Propane - n-Butane	15.50	0.2162	44.24
8	Propylene - Propane	20.00	0.2306	42.10

P = Usual practical operating pressure, Atm.
F.P = Flow Parameter as defined by Eqn. (3.3)
A.M.W = Average molecular weight at top of column.

For each of the binary mixtures, the column is designed and costed in a shortcut design procedure. The steps may be given as follows:

(1) composition and quantities of the bottom and top products specified.

(2) for each operating pressure P, the bubble point temperature of the top and that of the bottom products obtained.

(3) for each value of the α , the minimum reflux ratio, the minimum number of plates and the actual number of plates are obtained by the Fenske(1932)-Underwood(1948)-and Erbar-Maddox(1961) equations.

(4) then the costs are evaluated using equations obtained below. These costs include:

(i) the capital cost of column, condenser, and reboiler.

(ii) the cooling water cost for the condenser, and

(iii) the steam cost for heating the bottom products.

(5) the optimum reflux ratio to minimum is then obtained from equation (3.35) which is solved by Newton-Raphson iteration method.

[Appendix B contains all the information and equations used in the various steps of design and costing.]

3.4 Rapid Estimation Method for the Determination of the Optimum Reflux Ratio, R.

Here, the objective is to develop a shortcut equation which permits rapid estimation of the optimum reflux ratio and consequently the optimum cost of separation by the distillation process for any operating pressure. The development of the equation involves all the major parameters contributing to the total annual cost. This equation is then differentiated with respect to reflux ratio; and the differential equated to zero in order to obtain the optimum reflux ratio.

3.4.1 Derivation

The various costs involved in a distillation operation are:

1) Cost of Column, $C\,C_p$

$$C\,C_p = \frac{k_1 N A_p}{E_o} \qquad \ldots\ldots\ldots(3.5)$$

But $A_p = V/G_a$ ....(3.6)

$$C\,C_p = \frac{k_1 N V}{E_o G_a} \qquad \text{..........(3.7)}$$

where

K_1 = unit cost factor in dollars/(plate)(area)

N = number of theoretical plates

A_p = cross-sectional area of column, m^2

V = molar vapour rate, Kmol/hr

G_a = molar velocity of vapour, Kmol/m^2hr

= $u\,\rho_V/M$

u = superficial velocity, m/hr,

M = molecular weight

E_o = overall fractional column efficiency.

ρ_V = vapour density, Kg/m^3

2) Cost of Condenser, C_c

$$C_c = k_2 A_c \qquad \text{..........(3.8)}$$

But $$A_c = \frac{Q_c}{U_c \Delta T_{Ln,c}} = \frac{V\lambda}{U_c \Delta T_{Ln,c}} = \frac{V}{G_c} \qquad \text{.....(3.9)}$$

$$C_c = k_2 V/G_c \qquad \text{..............(3.10)}$$

where

Q_c = the condenser heat load, KJ/hr

$G_c = U_c \Delta T_{Ln,c}/\lambda$,the molar rate vapour capacity of condenser, Kmol/m^2hr; U_c , the overall heat transfer coefficient in the condenser, KJ/m^2sec K; and $\Delta T_{Ln,c}$ is the logmean temperature difference in the condenser.

k_2 = unit cost factor in dollars/heat transfer area, A_c, S/m^2

λ = molar latent heat of vapourisation, KJ/Kmol

3) Cost of Reboiler, C_r

Following the same approach as in (2) above

$$C_r = k_3 V/G_r \qquad \text{.........................(3.11)}$$

where

$G_r = U_r \, \Delta T_{Ln,r}/\lambda$, the molar rate vapour capacity of reboiler, Kmol/m^{2}hr; U_r , the overall heat transfer coefficient in the reboiler, KJ/m^{2}sec K; and $\Delta T_{Ln,r}$ is the logmean temperature difference in the reboiler.

k_3 = unit cost factor in dollars/heat transfer area, A_r, S/m^2

4) Cost of cooling water, C_w

$$C_w = \frac{Q_c C_1 h}{\rho_w C_{pw} \Delta t} \qquad \text{..............(3.12)}$$

$$= \lambda V k_4 \qquad \text{................(3.13)}$$

where

$$k_4 = \frac{C_1 h}{\rho_w C_{pw} \Delta t} \qquad \text{............(3.14)}$$

C_1 = unit cost of cooling water, S/m^2

ρ_w = density of water, Kg/m^3

Δt = temperature rise of water

h = number of hours of operation per year

C_{pw} = heat capacity of water, KJ/Kg K

5) Cost of Steam, C_s

$$C_s = \frac{Q_r C_2 h}{\lambda s} \qquad \text{..........(3.15)}$$

$$= \lambda V k_5 \qquad \text{...........(3.16)}$$

where

Q_r = the reboiler heat load, KJ/hr.

$$k_5 = C_2 h / \lambda_s \qquad \text{............(3.17)}$$

C_2 = unit cost of steam, S/Kg

λ_s = heat of condensation of steam, KJ/Kg or KJ/Kmol

[The λ^s at the top and bottom of the column may not necessarily be equal.]

Combining Equations (3.7),(3.10), (3.11), (3.13) and (3.16) gives the total annual cost of the distillation operation.

$$TAC = \mu \; k \left[\frac{K_1 N \; V}{E_o G_a} + \frac{k_2 V}{G_c} + \frac{k_3 V}{G_r} \right] + \lambda V k_4 + \lambda V k_5 \qquad \text{......(3.18)}$$

where

k = a factor converting the capital cost of equipments to an annual cost or k^{-1} (the payout time)

μ = installation costs and other charges

[All the data involved in the above equation are given in Appendix B-11]

For a binary distillation column optimisation two possible strategies may be used but require fixing the product purities. The first possible strategy (Case I) is to keep the column diameter constant, thus allowing the distillate product, D, to vary with the reflux ratio. The second case II is to keep the rate of distillate product, D, constant while the diameter of the column varies as the reflux ratio varies. In each of these cases, the pressure of the column is fixed and hence the logmean temperature differences in the condenser and reboiler will be constant for a constant column pressure.

CASE I

Dividing Equation (3.18) by D, we have

$$TAC = (1/D)[f_1N + f_2 + f_3 + f_4 + f_5] \qquad \ldots\ldots\ldots(3.19)$$

where

$$f_1 = \mu kk_1V/E_oG_a$$
$$f_2 = \mu kk_2V/G_c$$
$$f_3 = \mu kk_3V/G_r$$
$$f_4 = \lambda Vk_4$$
$$f_5 = \lambda Vk_5$$

For this case (it is a reasonable assumption that the maximum vapour velocity varies with vapour density but is independent of the liquid flow rate over the range considered) it means that V is constant since the diameter is not changing.

For minimum cost of production per distillate,

$d(TAC)/dR = 0$

$$\frac{d(TAC)}{dR} = (1/D^2)\left[f_1 D\frac{dN}{dR} - \frac{dD}{dR}(f_1N + f_2 + f_3 + f_4 + f_5)\right] = 0 \qquad \text{........... ..(3.20)}$$

But $D = V/(1 + R)$ ....(3.21)

$$\frac{dD}{dR} = -V/(1 + R)^2 \qquad \text{................(3.22)}$$

Then the Equation (3.20) becomes,

$$f_1\frac{dN}{dR} + (1/(1+R))(f_1N + f_2 + f_3 + f_4 + f_5) = 0$$

$$1 + R = \left[N + \frac{f_2 + f_3}{f_1} + \frac{f_4 + f_5}{f_1}\right]/[-\,dN/dR]$$

$$1 + R = [N + Y_1 + Y_2]/[-dN/dR] \qquad \text{.....(3.23)}$$

where

$$Y_1 = [k_2/G_c + k_3/G_r]/[k_1/(E_oG_a)] \qquad \text{.....(3.24)}$$

$$Y_2 = [\lambda k_4 + \lambda k_5]/[\mu k\ k_1/(E_oG_a)] \qquad \text{.....(3.25)}$$

$$1 + R = [N + Y]/[-dN/dR] \qquad \text{.......(3.26)}$$

where,

The Total Cost Factor, $Y = Y_1 + Y_2$

$$=[k_2G_c + k_3G_r + (\lambda/\mu\ k)(k_4+k_5)][E_oG_a/k_1] \qquad \text{......(3.27)}$$

This is the equation that introduces the concept of energy flow per unit area of column. The Y_2 equation is a function of the energy flow per unit area of column. The Y_1 equation is a function of the heat transfer areas per unit area of column; and this in turn is related to the energy flow per unit area of column. Since the energy flow per unit area is shown in Figures 3.3 and 3.4 below to correlate against the operating pressure or flow parameter, then the optimum reflux ratio and consequently, cost of distillation per moles of distillate may be shown to correlate against the flow parameter. The values of Q/A, Y_2 and Y_1 given in Table 3.3 are those computed for the relative volatility value of 1.05.

CASE II

The alternative derivation strategy is to keep the distillate product rate constant while the diameter varies.

With

$r_1 = \mu k k_1/(E_o G_a)$

$r_2 = \mu k k_2/G_c$

$r_3 = \mu k k_3/G_r$

$r_4 = \lambda k_4$

$r_5 = \lambda k_5$

Equation (3.18) becomes,

$$TAC = (r_1 N + r_2 + r_3 + r_4 + r_5)V \qquad ......(3.28)$$

For minimum cost of production, $d(TAC)/dR = 0$

$$\frac{d(TAC)}{dR} = r_1 N \frac{dV}{dR} + r_1 V \frac{dN}{dR} + \frac{dV}{dR}(r_2 + r_3 + r_4 + r_5) = 0$$

$$............(3.29)$$

From equation (3.21)

$$\frac{dV}{dR} = D \qquad ....(3.30)$$

TABLE 3.3: Energy Flow per Unit area of distillation column (Q/A) against the operating pressure (P) and the flow parameters (F.P)

F.P	P, Atm.	Q/A, KJ $m^{-2}hr^{-1}$	Y_2	Y_1
0.0168	0.066	309396.67	71.48	4.23
0.0376	0.352	514278.94	118.95	6.95
0.0556	1.000	868445.01	213.50	8.17
0.0828	1.690	942824.30	243.19	8.66
0.1360	5.000	1128381.78	267.29	12.37
0.2005	11.60	1335322.21	317.78	14.28
0.2162	15.50	1454974.56	346.96	18.35
0.2306	20.00	1657780.49	379.92	26.93

Y_1 and Y_2 are as defined in Equations (3.24) and (3.25) respectively.

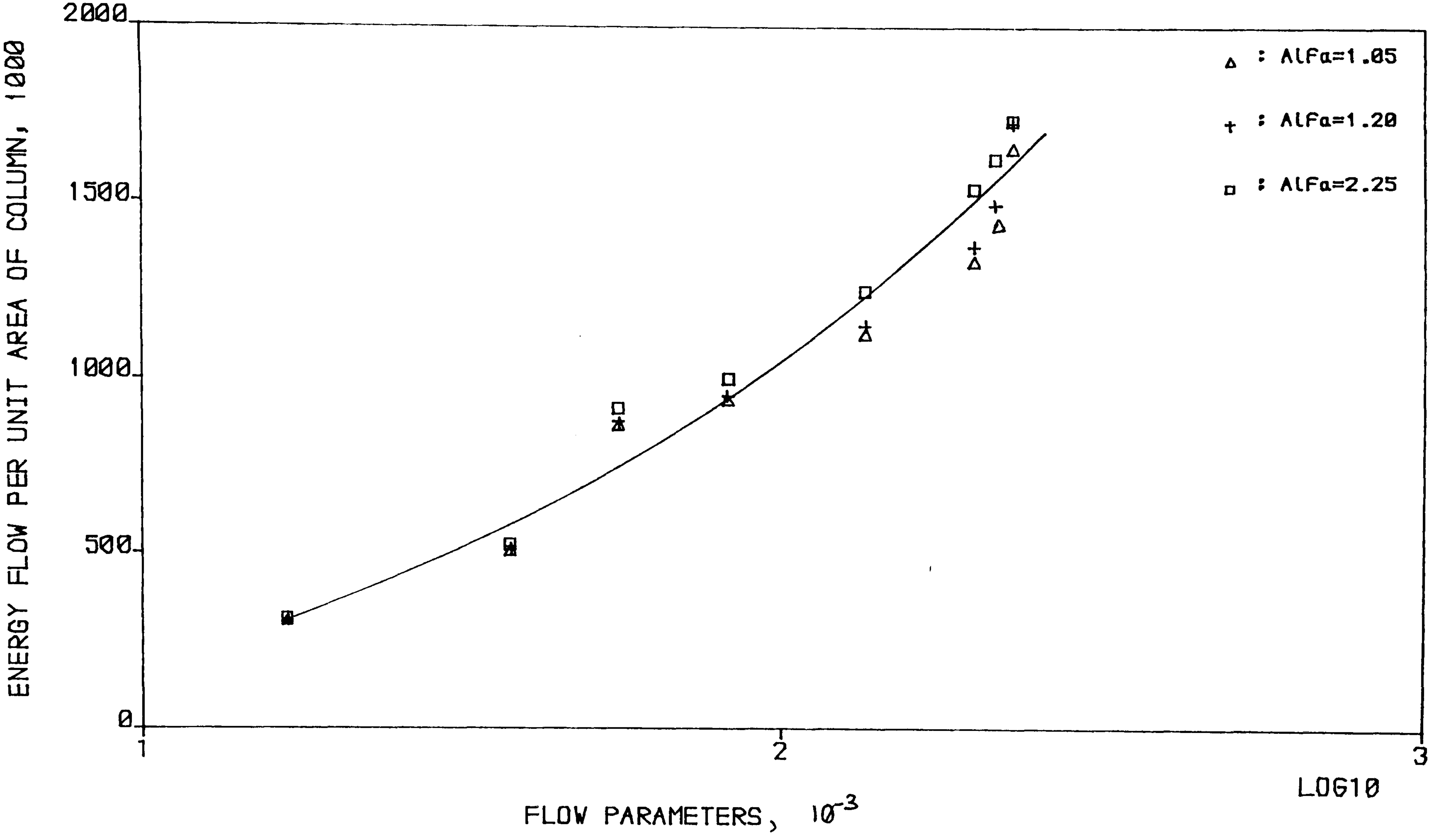


FIG. 3.3 ENERGY FLOW PER UNIT AREA OF COLUMN AGAINST THE FLOW PARAMETERS

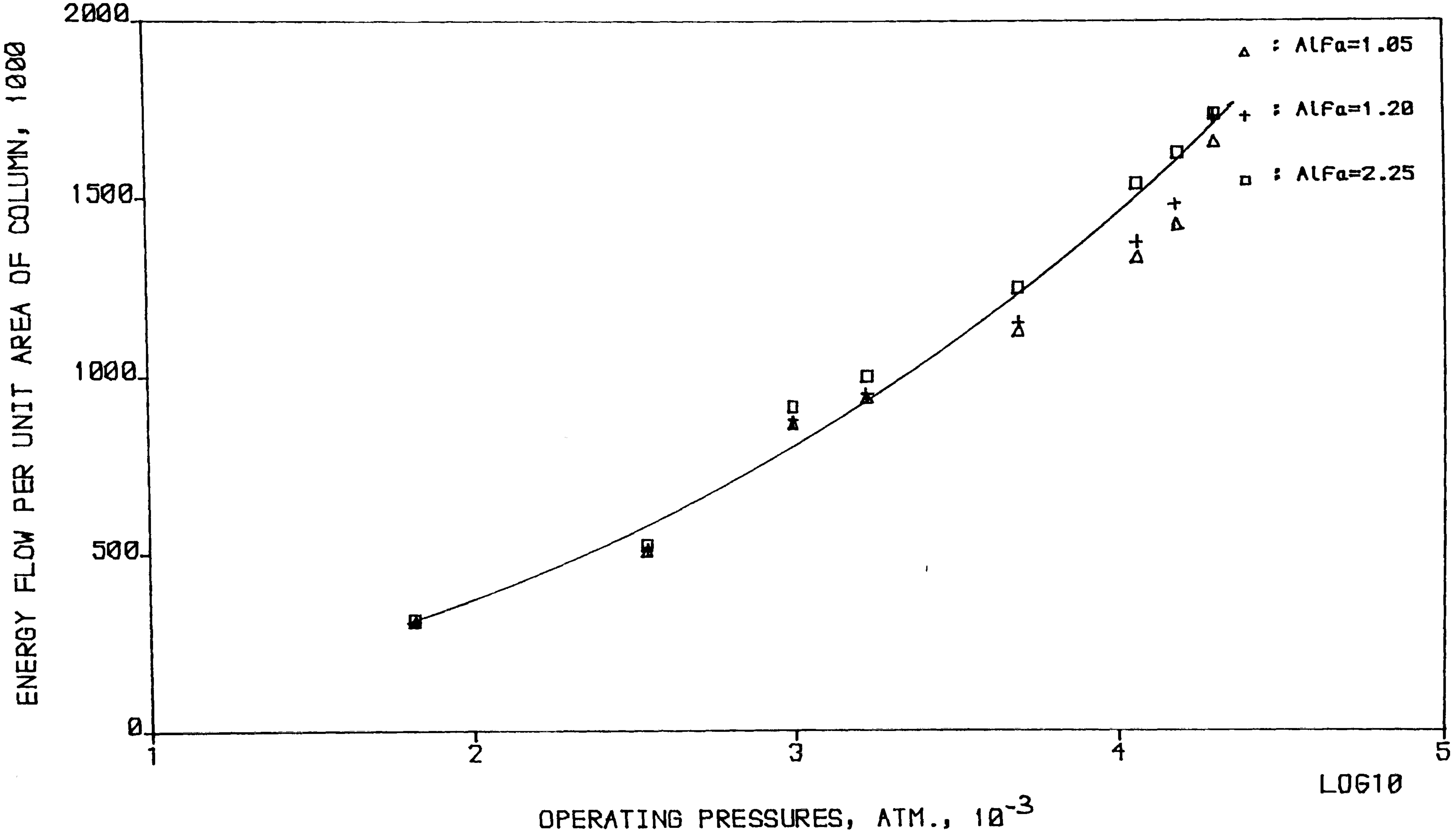


FIG. 3.4 ENERGY FLOW PER UNIT AREA OF COLUMN AGAINST THE OPERATING PRESSURES

Therefore

$$r_1 N + r_1(1+R)\frac{dN}{dR} + (r_2 + r_3 + r_4 + r_5) = 0$$

$$1 + R = [N + \frac{r_2 + r_3}{r_1} + \frac{r_4 + r_5}{r_1}]/[-dN/dR]$$

$$1 + R = [N + Y_1 + Y_2]/[-dN/dR]$$

$$1 + R = [N + Y]/[-dN/dR] \qquad ....(3.31)$$

It is noted that Equations (3.26) and (3.31) are the same. All the parameters are of the same definitions. Thus, the optimisations of cases I and II are identical

These derivations are similar in principle but not in detail to that undertaken by Happel and Jordan(1975). The derivation here relaxes some of the assumptions involved in that of Happel and Jordan(1975) and thereby incorporates more parameters in the derivation. The systematic usage of these parameters resulting from the concept of energy flow per unit area permits a calculation of many systems versus the total reflux flow parameter which covers a wide pressure range. Therefore, the equations derived here are more useful. In the derivation of Happel and Jordan(1975), the costs of steam and coolant were lumped together and considered to be the same. This is an assumption that cannot be justified. Furthermore, the allowable molar vapour capacities and the overall temperature differences in the condenser and reboiler were assumed to be the same.

With these equations, it was possible to obtain the effects of feed compositions, relative volatilities, etc. as presented in the tables on the optimum reflux ratio and cost of distillation per moles of distillate.

To continue the derivation of the optimum reflux ratio, it is necessary to introduce a correlation which relates reflux ratio, R, to the number of plates. [The first example of this is the well known graphical correlation of Gilliland(1940)]. The equation used here is that which has been considered [Barna and Ginn(1985)] to provide a satisfactory combination of N and R in terms of R_m (minimum reflux ratio) and N_m (minimum number of plates). This is the Erbar-Maddox(1961) graphical correlation [Figure 9.1]. This is translated into an analytical form suitable for computations.

$$\mathrm{Ln}(N-N_m) = \beta \, \mathrm{Ln}[(R-R_m)/(N_m^{1.25} R_m^{0.96})] + 0.796 \qquad \ldots\ldots(3.32)$$

where $\beta = -0.37866$

From Equation (3.32)

$$\frac{dN}{dR} = \frac{\beta(N - N_m)}{(R - R_m)} \qquad \ldots\ldots\ldots\ldots(3.33)$$

Substituting Equation (3.33) into equation (3.26), we have

$$\frac{1 + R}{R - R_m} = \frac{N + Y}{-\beta\,(N - N_m)} \qquad \ldots\ldots\ldots(3.34)$$

or

$$\frac{R_f + 1/R_m}{R_f - 1} = \frac{N + Y}{-\beta\,(N - N_m)} \qquad \ldots\ldots\ldots\ldots(3.35)$$

where $R_f = R/R_m$.

Equation (3.35) can be solved for R_f to obtain the optimum reflux ratio by a trial-and-error method. In this work, it is decided to employ a numerical method of finding real roots of a non-linear equation. The Newton Raphson method is found very useful here.

Rewriting the equation in a functional form,

$$f(R_f) = \frac{(R_f + 1/R_m)}{R_f - 1} + \frac{N + Y}{\beta\,(N - N_m)} \qquad \ldots.(3.36)$$

the procedure then reduces to finding R_f such that $f(R_f) = 0$. By Newton-Raphson method, we shall have

$$R_{f,n+1} = R_{f,n} - \frac{f(R_{f,n})}{f'(R_{f,n})} \qquad \ldots\ldots\ldots\ldots(3.37)$$

where

$R_{f,n}$ = operating reflux ratio to minimum for trial n

$R_{f,n+1}$ = operating reflux ratio to minimum for trial (n+1)

$f'(R_{f,n})$ = the derivative of the functional equation (3.35)

3.5 Results and Discussions

As has been mentioned, the Appendix B contains all the information, calculations and necessary data used in the various steps of design outlined in Section 3.3. For example, capital cost factors for the column, condensers and reboilers are taken from Happel and Jordan(1975), the condensing temperature is fixed at 322 K, etc.

The results on this chapter are given in Tables A3.1 to A3.13 (in Appendix A) and in Figures 3.5 to 3.21 which are placed at the end of the chapter.

[Except where indicated, the results shown in the tables and figures are for 50/50 molar composition of the binary mixtures involved, and the top and bottom purities are respectively 0.99 and 0.01 of the light component. And the results are for the carbon steel material except where indicated otherwise.]

Table A3.1 gives the sample results of the variation of the total annual cost cost, TAC, per mole of distillate with reflux ratio for all the operating pressure levels considered and for three levels of relative volatilities, $\alpha = 1.05$, 1.20 and 2.25. The minimum values of the total annual cost per moles of distillate are indicated by a star sign in the table. These results are also shown in Figure 3.5 - 3.7.

The entire results for the optimum reflux ratio to minimum, R/R_m, are presented in Tables A3.2 and A3.3. Table A3.2 gives the tabulation of the optimum values of R/R_m for the various operating pressures, feed compositions and relative volatilities. Table A3.3 gives the optimum values of R/R_m as a function of the recovery fraction of the more volatile component in the distillate, x_R. And Tables A3.4 and A3.5 give the R/R_m for the carbon steel and stainless steel materials respectively at x_F=0.5.

All these results are obtained using the Equation (3.35) which is solved numerically by Newton-Raphson's method. When compared with those obtained from the graphical solution of the form of Figure 3.5, there was good agreement. It should however be noted that the numerical method cannot with great accurancy take into account the flat optimum which is always apparent in the figures such as those of Figure 3.5-3.7. Therefore, the values of R/R_m read from these sort of graphs may in some cases be higher than that obtained by a numerical method.

The important observations and/or conclusions that can be drawn from the results include:

(1) That the optimum reflux ratio to the minimum, R/R_m, varies with the operating pressure or the total reflux flow parameter with its value decreasing as the operating pressure or the total reflux flow parameter increases. So do the total annual cost of distillation operation per mole of distillate. The value of the optimum reflux ratio in recent years' energy cost lies

between 1.05 and 1.10 times the minimum reflux ratio. This is in accordance with what have been reported in the literature. For the condition of zero-energy cost, a much higher value is obtained.

(2) The energy cost dominates the cost of distillation operation in the ranges of relative volatilities equal or greater than 1.50. However, for the lower values of relative volatilities this is not so. The contribution of capital cost to the total annual cost of distillation becomes significantly increased. In this case the energy cost cannot be said to dominate the cost of distillation anymore.

It is necessary to comment below on these and few other observations.

3.5.1 Optimum Reflux Ratio

(i) The optimum reflux ratio to minimum varies with changes in operating pressures or flow parameters with the value of R/R_m decreasing as the operating pressure increases [Figures 3.8 - 3.9]. This is due to to the increased energy flow per unit area of column [Table 3.3] as the operating pressure or the flow parameter increases. In other words, one now pays more for energy per unit area of the column. However at normal energy cost, the variation in the optimum values of R/R_m is between 1.05 and 1.10.

(ii) There is a decrease in the optimum values of R/R_m as the relative volatilities between the components increases. A decrease in the total capital cost (due to a decrease in the number of plates) as the relative volatility increases will account for this variation. At low pressure levels, however, the reverse of the above trend is observed. This may be difficult to pin down to one particular factor. Changes in the molar latent heat of vaporisation which may be quite significant as the operating pressure of the column changes is very likely to account for this observation.

(iii) For most cases, there are only very slight changes in the optimum values of R/R_m as the feed composition changes except for low pressure and high relative volatilities where there are significant increases in R/R_m as the feed composition increases [Table A3.2].

(iv) For the recovery fractions, x_R, there are no significant changes in the optimum values of R/R_m as the recovery fraction increases [Table A3.3].

(v) For the zero-energy cost, the optimum values of R/R_m obtained lie between 1.20 and 1.34 [Table A3.6 and Figures 3.10 to 3.11]. Although there are small variations, the optimum values of R/R_m do not change much because for all cases the capital cost of the column is relatively independent of pressure. The small variations are due to the heat exchanger costs which are effected by changes in pressure. In general, increase in pressure results in an increase in the costs of the heat exchangers because of increased column throughput.

3.5.2 Cost of Distillation per mole of distillate.

In order to explore further the relations between the operating pressure or the flow parameter and the optimum reflux ratio and cost of distillation per moles of distillate, various analysis are undertaken. These are presented in Fgures 3.12 - 3.22. The TAC per mole of distillate decreases as the operating pressure increases [Table A3.7 and Figures 3.12 and 3.13], and this is due to the larger quantities of distillate product resulting from increased throughput for the same size of column.

An important observation can be made from the results shown in Figure 3.14 or 3.15 and in Table A3.9. The percentage ratio of capital cost to the total annual cost lies between 10 and 21 percent for the atmospheric pressure and above and in the ranges of relative volatilities equal or greater then 1.50 (i.e $\alpha >$ 1.50). In most cases, this is within this range of α's that the ordinary distillation operation is considered viable for the separation of component mixtures. This demonstrates the dominant contribution of the energy cost to the total annual cost of a distillation operation for this range of relative volatilities. But for very low relative volatilities, this is not so. The rapid increase in the capital cost resulting from increase in the number of plates (as the relative volatility moves nearer to 1.0) makes the capital cost contribution to the total annual cost significantly increased; so that at a relative volatility of 1.05, the capital cost (for atmospheric pressure and above) contribution to the total annual cost is between 40 and 56 percent [Table 3.12]. Under vacuum, at a pressure of 0.066 atmospheres, the contribution, is unusually, as high as 78% for α =1.05. These observations show that the usual assumption of a distillation operation being dominated by energy cost may not be true at very low relative volatilities which are close to 1.0, particularly for low pressures. These observations resurface again in some of the results shown in some of the following chapters on sequencing of distillation columns. Discussion will be made as and when necessary.

3.5.3 Other Comments

The analysis also indicates a correlation between the optimum values of R/R_m and the average molecular weight of the components at the top of the column [Figure 3.16] on one hand; and the TAC per energy cost and the average molecular weight on the other hand [Figure 3.17]. The higher molecular weight materials correspond to lower pressure molecules and therefore higher optimum values of R/R_m and TAC per energy cost.

A situation of using a different material of construction other than a carbon steel may arise if one of the components to be separated is corrosive. In this analysis, a stainless steel material, for example, is considered at different operating pressures.

Figures 3.18 and 3.19 [Table A3.8] indicate the correction factors on R/R_m to be introduced into the values for the carbon steel if stainless steel material is to be used as materials of construction. A factor ranging between 1.015 and 1.09 is obtained. This is surprisingly low. Similarly, Figures 3.20 and 3.21 [Table A3.9] indicate the correction factor on the optimum total annual cost per energy cost to be used if stainless steel material is being considered as a material of construction. A factor lying between 1.313 and 3.30 is obtained for the various operating pressures or total reflux flow parameters and relative volatilities.

The usefulness of these results can be seen when distillation sequences with or without heat integration is considered. One of the methods employed in energy integration is to change the operating pressure of some of the columns in the sequence thereby altering the temperature of the condenser/reboiler to such an extent that it is possible to heat integrate it with the reboiler/condender of other columns. Though the usual procedure is to rely on fixing the optimum R/R_m to be 1.1 or 1.25 for all columns following the traditional rule of thumb, the optimum R/R_m

in practice may differ from one column to another. A similar observation is made by Linnhoff et al(1983) who noted that in energy integration the range of reflux ratios of the actual to minimum usually considered is 1.03 - 1.3. From the sort of work presented here, it would be very easy to pick the ratio of operating reflux to minimum once the operating pressure of the column is known. This operating pressure may be approximately estimated for any real mixture being used since this is also correlated against the molecular weight of a range of hydrocarbons [Figure 3.22, Table 3.4]. Not only may pressure be taken into account but also the changing cost of energy due to the integration.

TABLE 3.4: Molecular weight of a range of organic compounds against the operating pressures.

Components	Molecular Weight	Operating Pressure at condenser temperature of 322 K
Propane	44.097	16.195
i-Butane	58.124	6.472
n-Butane	58.124	5.180
i-Pentane	72.151	1.955
n-Pentane	72.151	1.518
neo-Pentane	72.151	3.388
2-Methyl Pentane	86.178	0.685
n-Octane	84.162	0.343
n-Hexane	86.178	0.512
n-Heptane	100.205	0.178
Ethane	30.000	58.692
Propylene	42.081	19.293
1-Butene	56.108	5.701
Ethylene benzene	106.168	0.044
Styrene	104.152	0.033
Aniline	78.114	0.342
Tetrahydrofuran	92.141	0.115
Cyclohexane	84.162	0.343

Even for a full scale optimisatin of sequences of distillation columns, some of the authors [Minderman and Tedder(1982), Pibouleau et al(1983)] have found it necessary to vary the pressure from column to column in the sequence. The results from this chapter are equally going to be helpful in obtaining with ease the optimum reflux ratio corresponding to a particular column operating pressure.

3.5.4 Optimum Number of Plates.

Some results are also presented for the optimum number of plates to the minimum number of plate, N/N_m at various pressures, relative volatilities, feed compositions and recovery fractions. These are given in Tables A3.10 - A3.13 and in Figures 3.23 and 3.24. The pattern of the results is the reverse of that of the optimum reflux ratio. For instance, the optimum values of N/N_m increases as the operating pressure increases; also increases as the relative volatility increases. Like the optimum reflux ratio, there are no significant changes in the optimum values of N/N_m as the feed composition changes (particularly at low 's). The optimum values of N/N_m decreases as the recovery fraction increases. Of course the number of plates increases as the recovery fraction increases.

In general apart from the pressure changes, the optimum values of N/N_m appear to be more sensitive to changes in the parameters considered than the optimum reflux ratio. These N/N_m calculations are potentially valuable in the design of distillation columns.

3.6 Concluding Remarks

It has been shown that the energy flow per unit area of column correlates against the total reflux flow parameter. So do the optimum reflux ratio and cost of distillation per mole of distillate. The feed composition and the recovery fraction have no significant effects on the optimum reflux ratio. The examination of the relations between the flow parameter and the operating pressure results in a simple equation which permits the determination of the optimum reflux ratio and cost of distillation per mole of distillate.

It is observed that the energy cost dominates the cost of distillation column when the relative volatility of the components being separated are about equal or greater than 1.50. This is the range of relative volatilities where distillation operation is considered viable for the separation of component mixtures. But when the relative volatility is close to 1.0, the capital cost forms a significant proportion of the total annual cost of the column.

The results would be useful in calculations for distillation sequences with or without energy integration where it may be necessary to operate the columns within the sequence at different operating pressure and at the sametime calculating the optimum R/R_m for each of the columns.

The low values of the optimum R/R_m obtained are not surprising since over the years the percentage increase in steam cost is substantially greater than the percentage increase in capital cost of the column. Even lower values than these have been reported in the literature. Because of uncertainty in the vapour-liquid-equilibrium data, it is always best to design for a reflux ratio somewhat higher than the economic optimum found by this sort of analyses done here. One may suggest an addition of 0.1 to the values of R/R_m obtained here for some practical purposes.

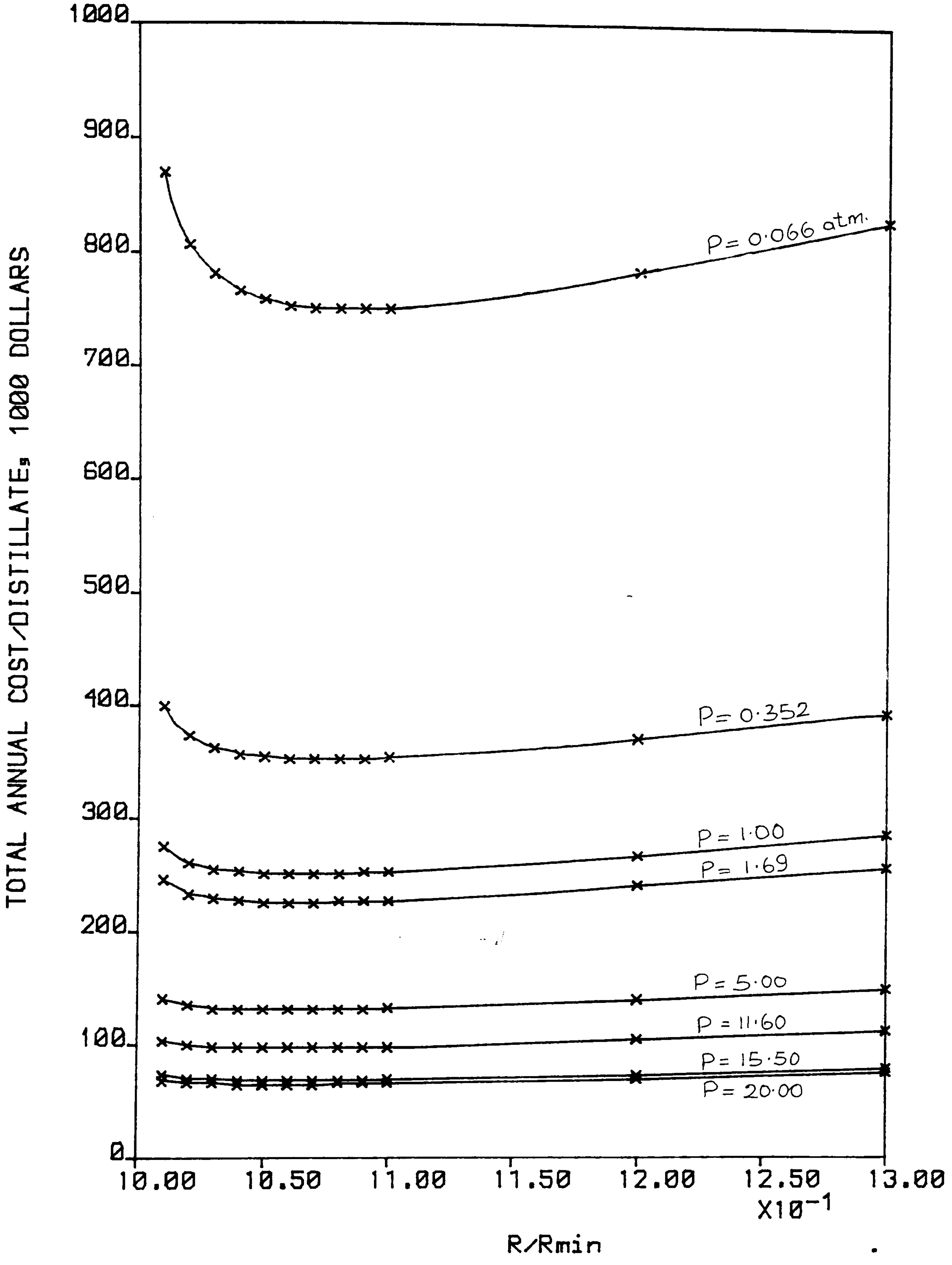


FIG. 3.5 : VARIATIONS OF TOTAL ANNUAL COST WITH R/Rmin AT VARIOUS OPERATING PRESSURES FOR $\alpha = 1.05$

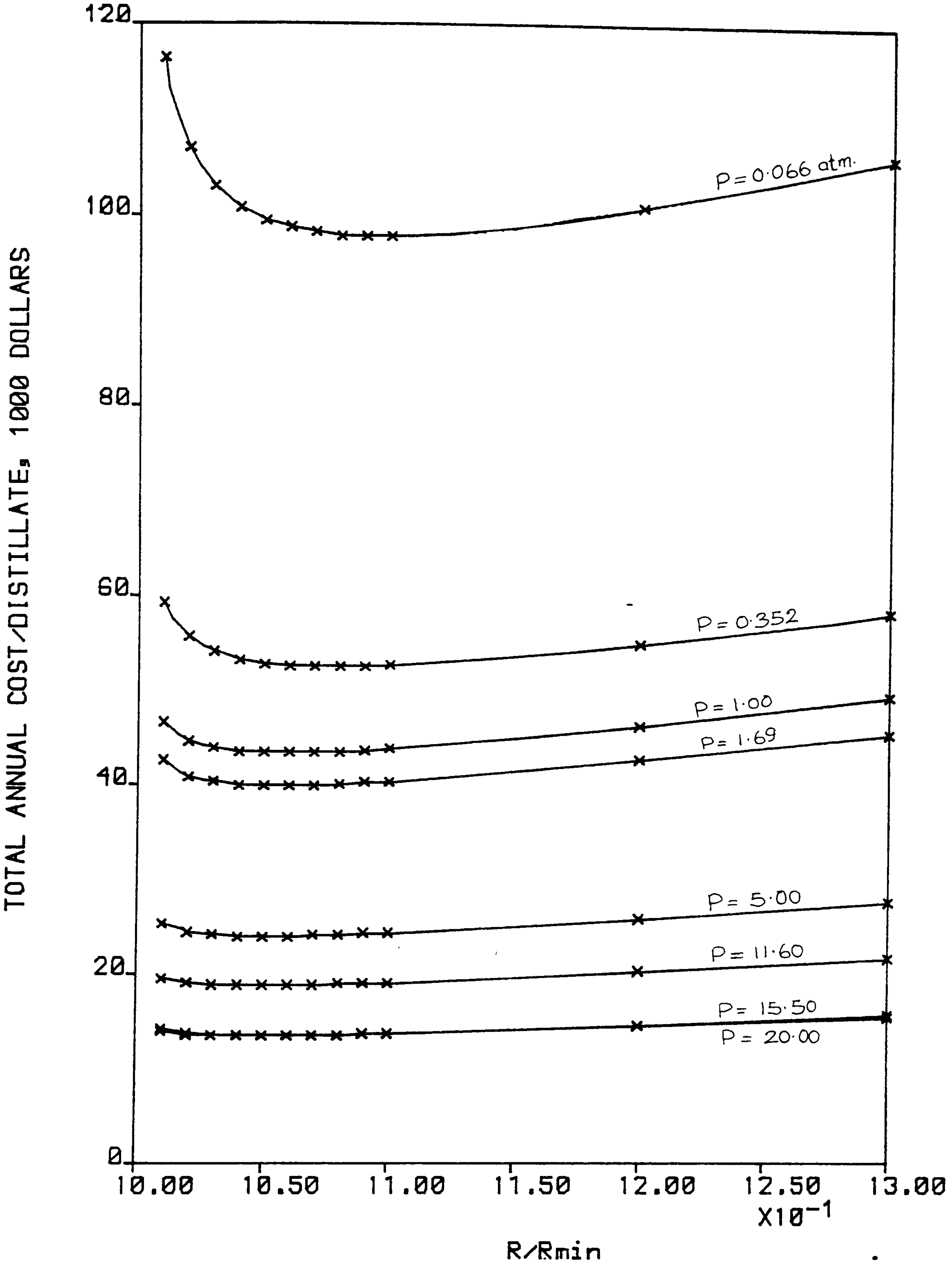


FIG. 3.6 : VARIATIONS OF TOTAL ANNUAL COST WITH R/Rmin AT VARIOUS OPERATING PRESSURES FOR α = 1.20

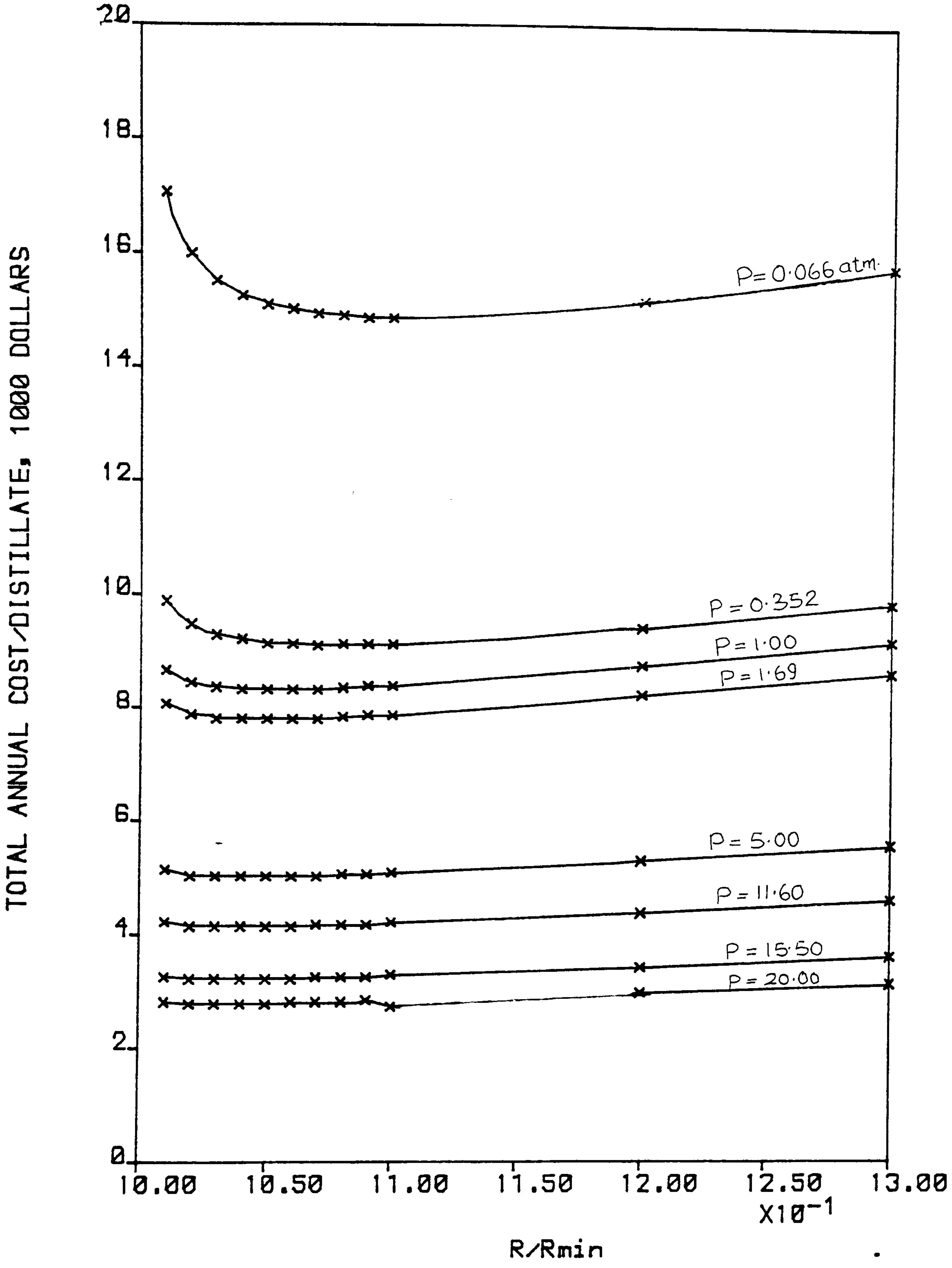


FIG. 3.7 : VARIATIONS OF TOTAL ANNUAL COST WITH R/Rmin AT VARIOUS OPERATING PRESSURES FOR $\alpha = 2.25$

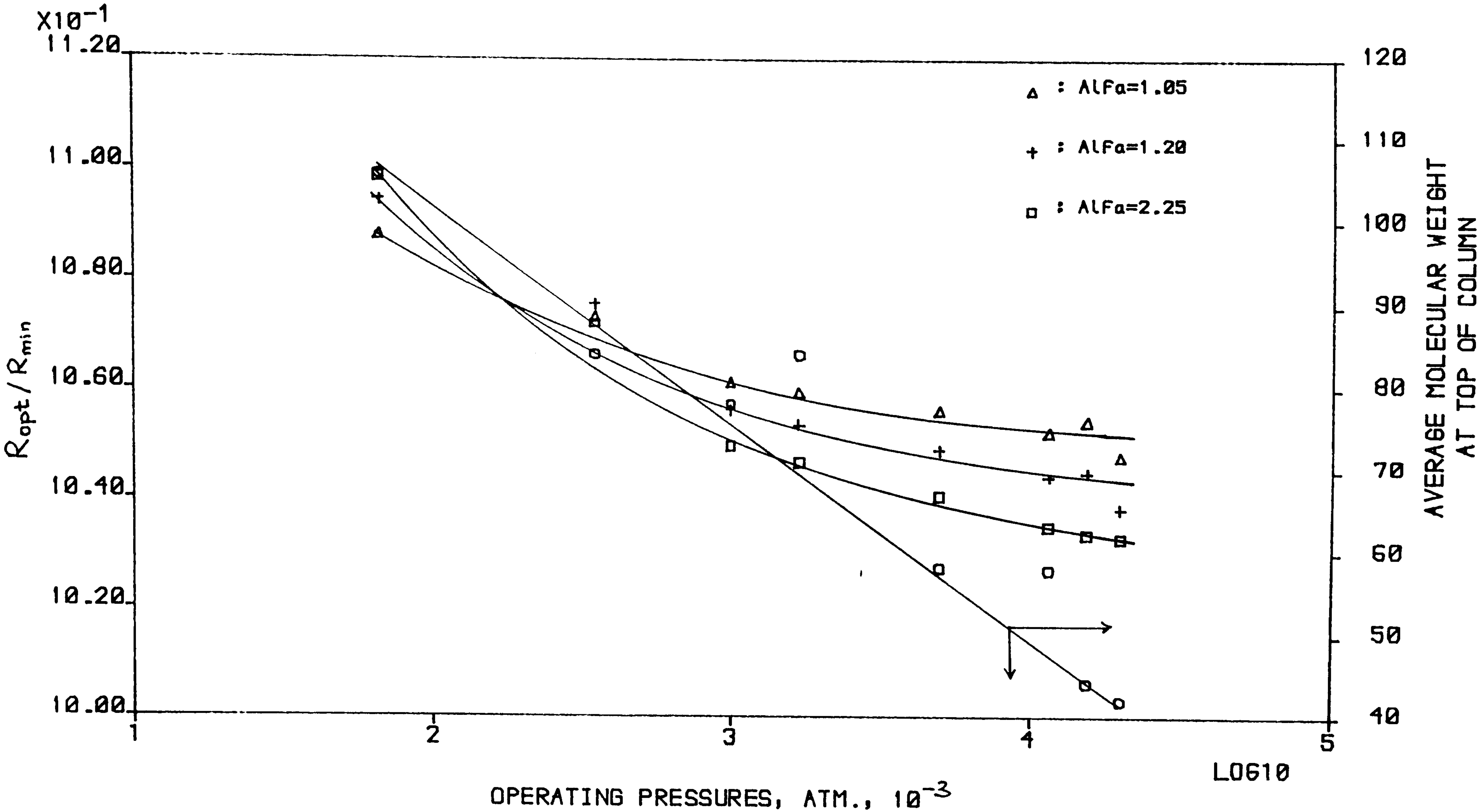


FIG. 2.8 Ropt/Rmin AND MOLECULAR WEIGHT AGAINST THE OPERATING PRESSURES

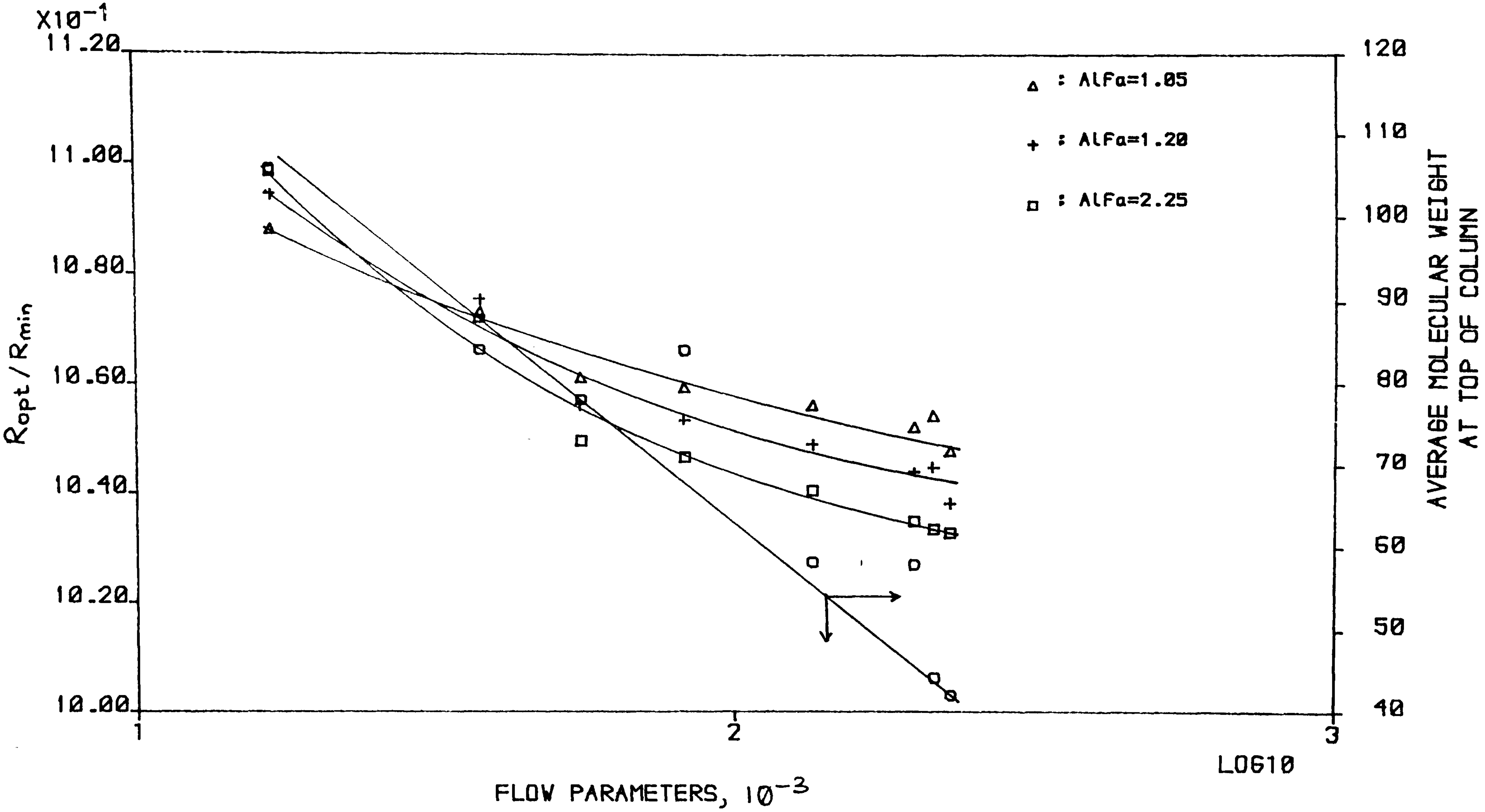


FIG. 3.9 Ropt/Rmin AND MOLECULAR WEIGHT AGAINST FLOW PARAMETERS

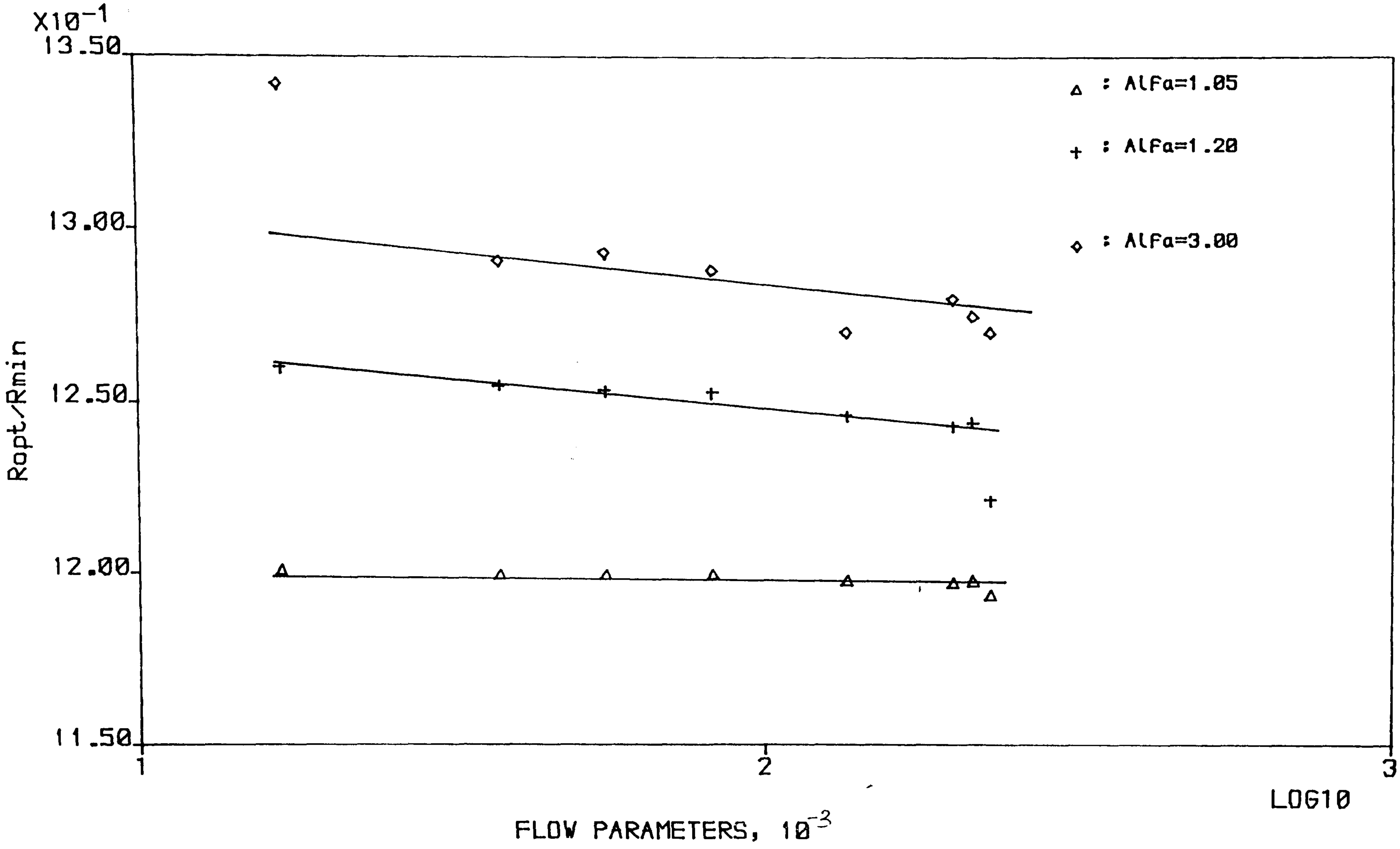


FIG. 3.10 Ropt/Rmin AT ZERO-ENERGY COST AGAINST THE FLOW PARAMETERS

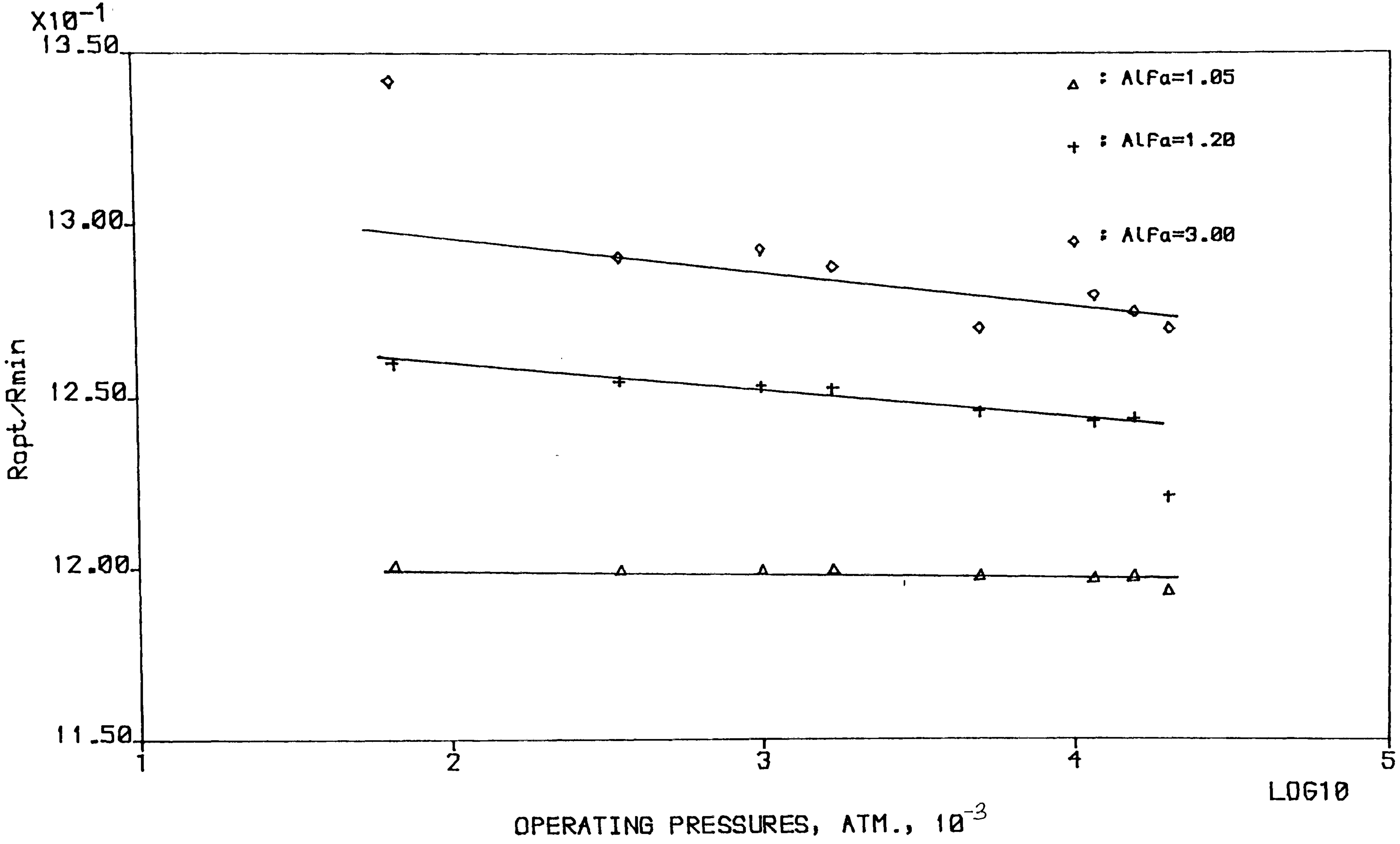


FIG. 3.11 Ropt/Rmin AT ZERO-ENERGY COST AGAINST THE OPERATING PRESSURES

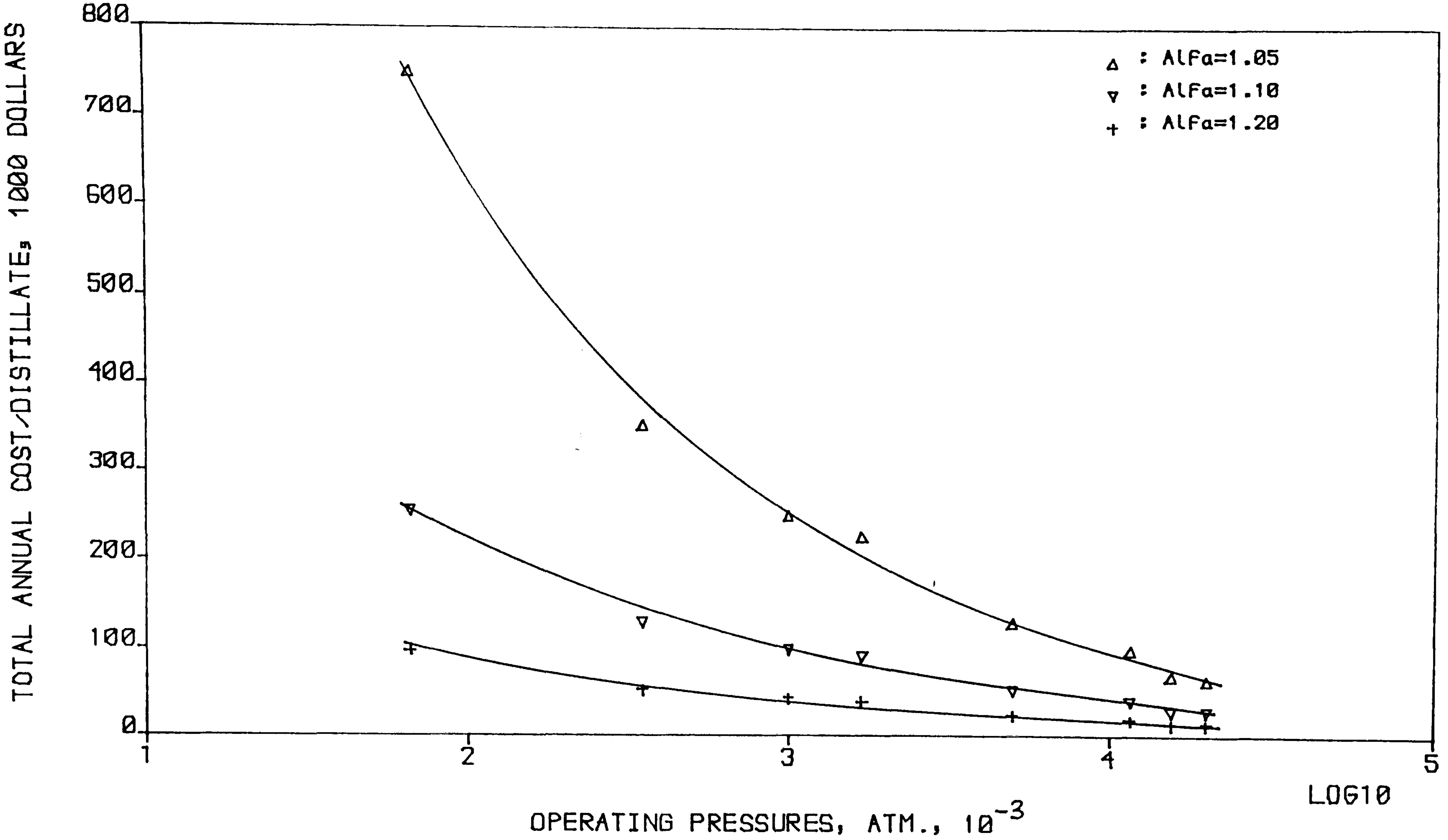


FIG. 3.12 TOTAL ANNUAL COST AGAINST THE OPERATING PRESSURES

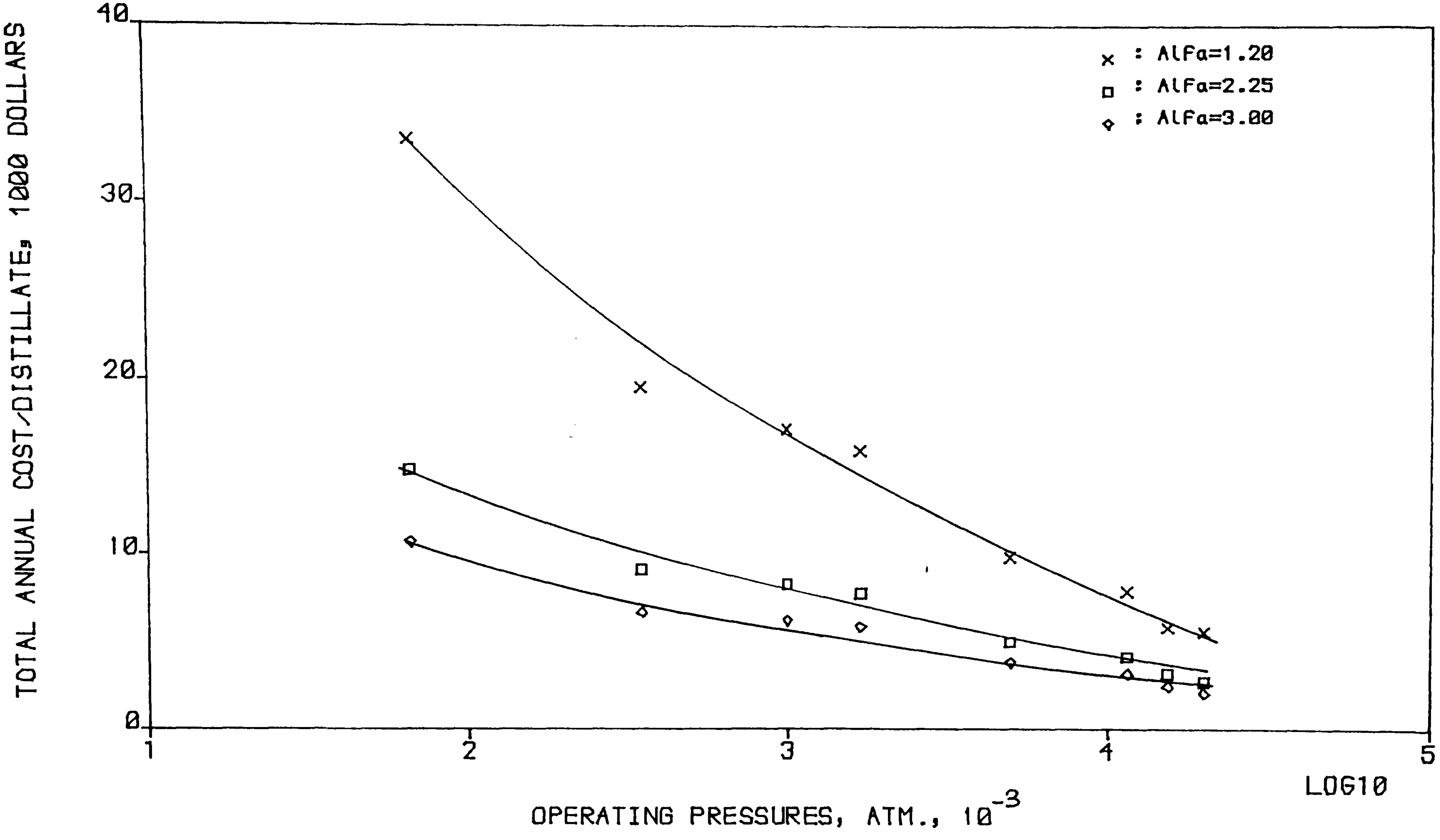


FIG. 3.12b TOTAL ANNUAL COST AGAINST THE OPERATING PRESSURES

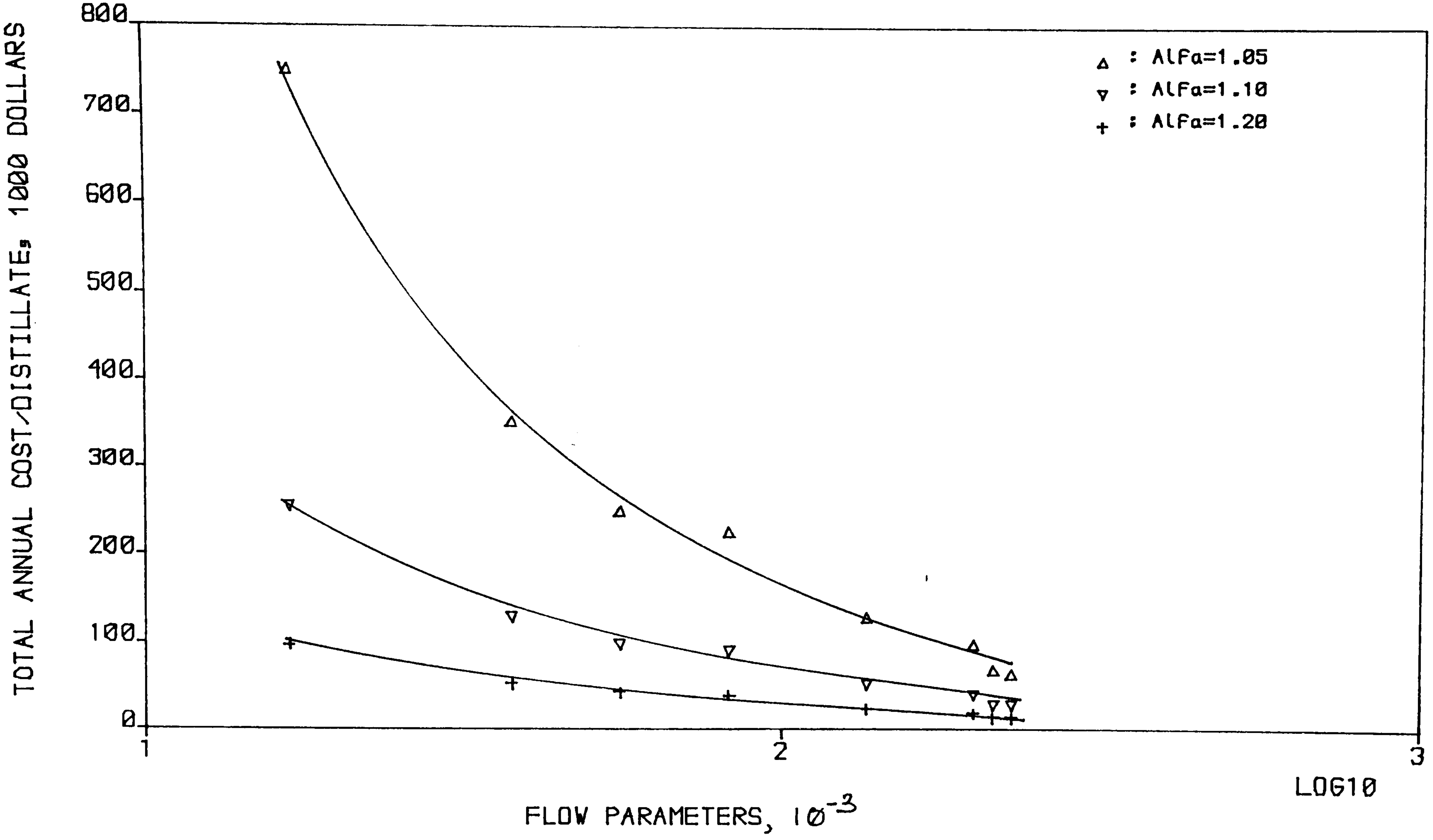


FIG. 3.13a TOTAL ANNUAL COST AGAINST THE FLOW PARAMETERS

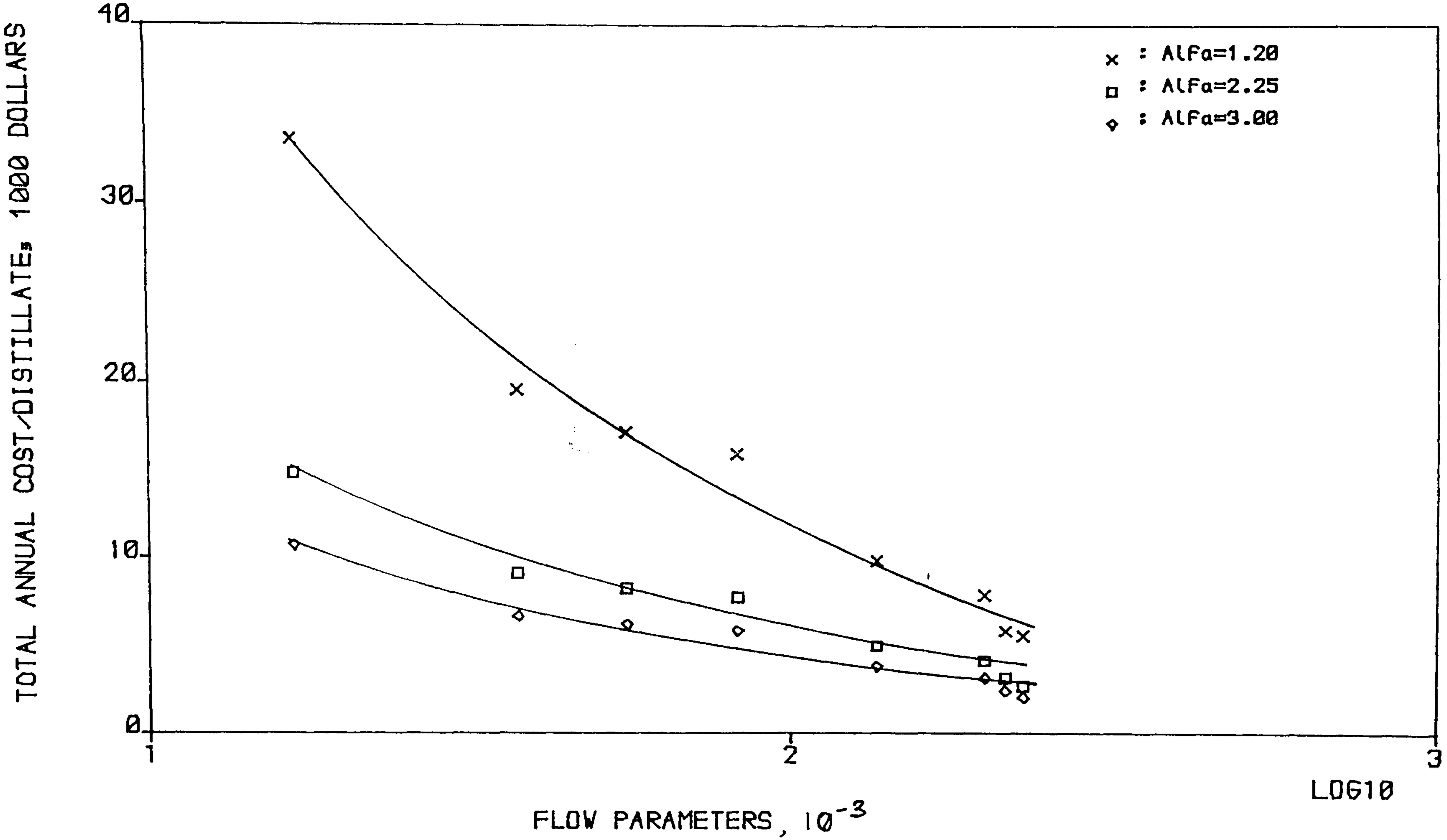


FIG. 3.13b TOTAL ANNUAL COST AGAINST THE FLOW PARAMETERS

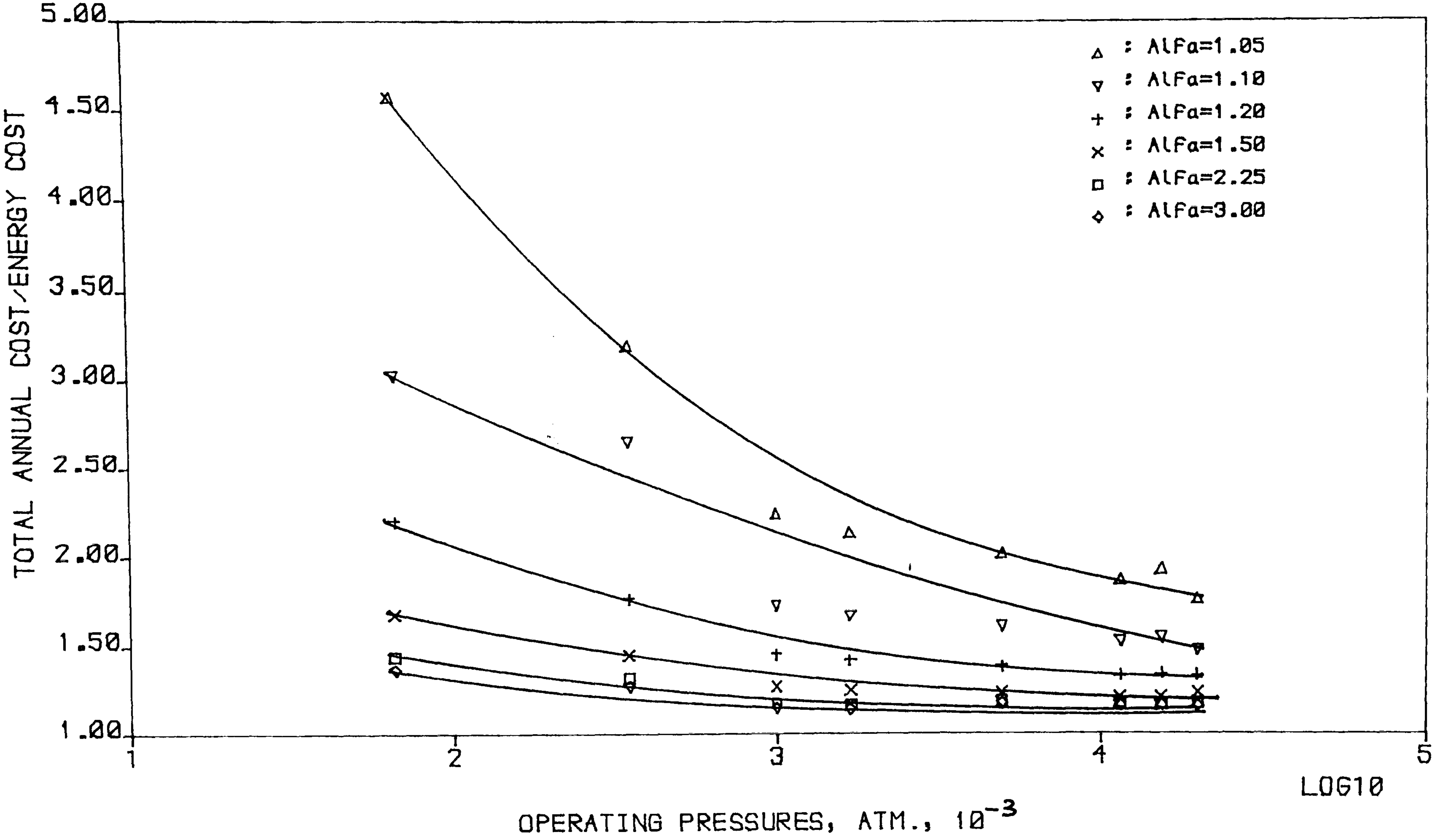


FIG. 3.14 TOTAL ANNUAL COST PER ENERGY COST AGAINST THE OPERATING PRESSURES

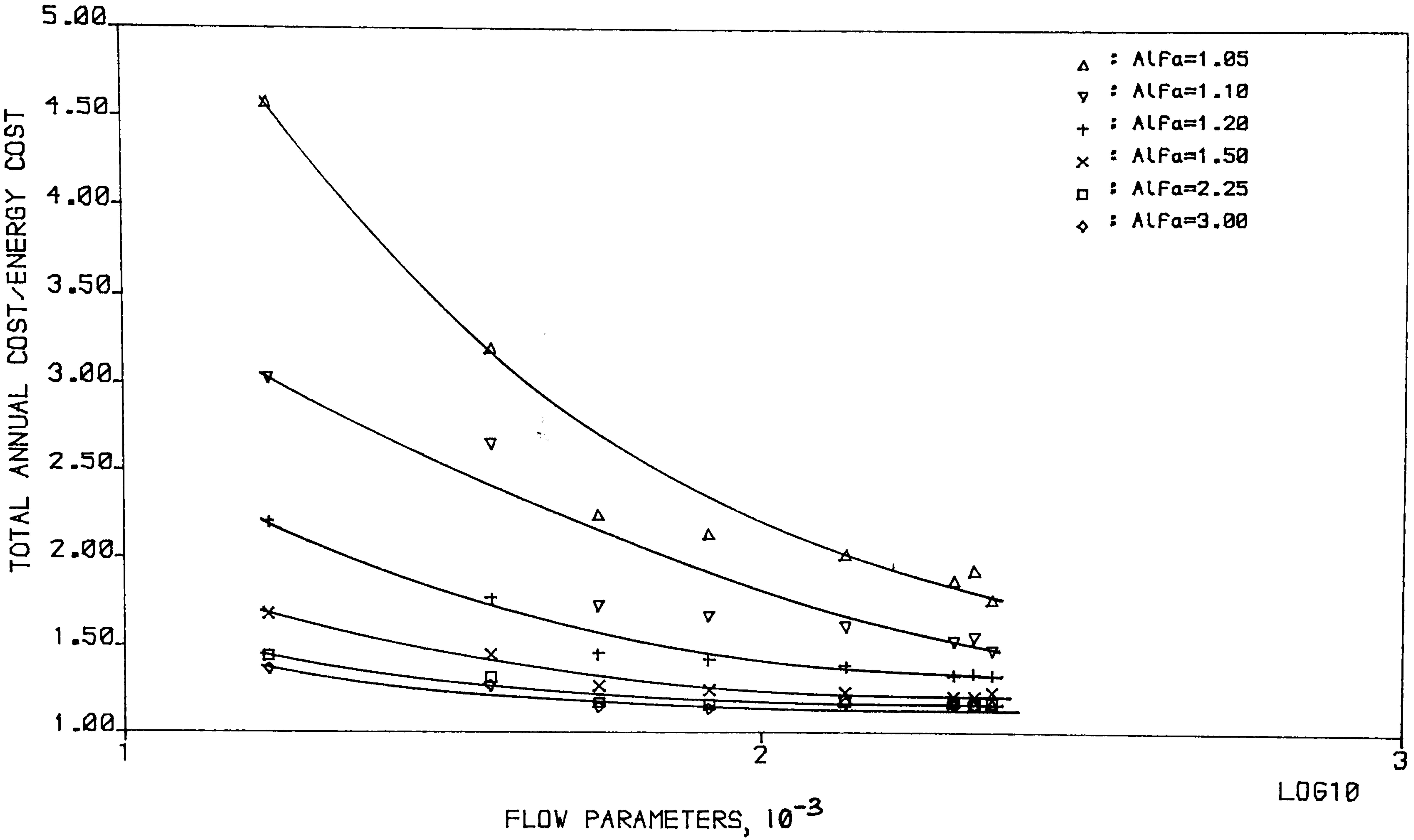


FIG. 3.15 TOTAL ANNUAL COST PER ENERGY COST AGAINST THE FLOW PARAMETERS

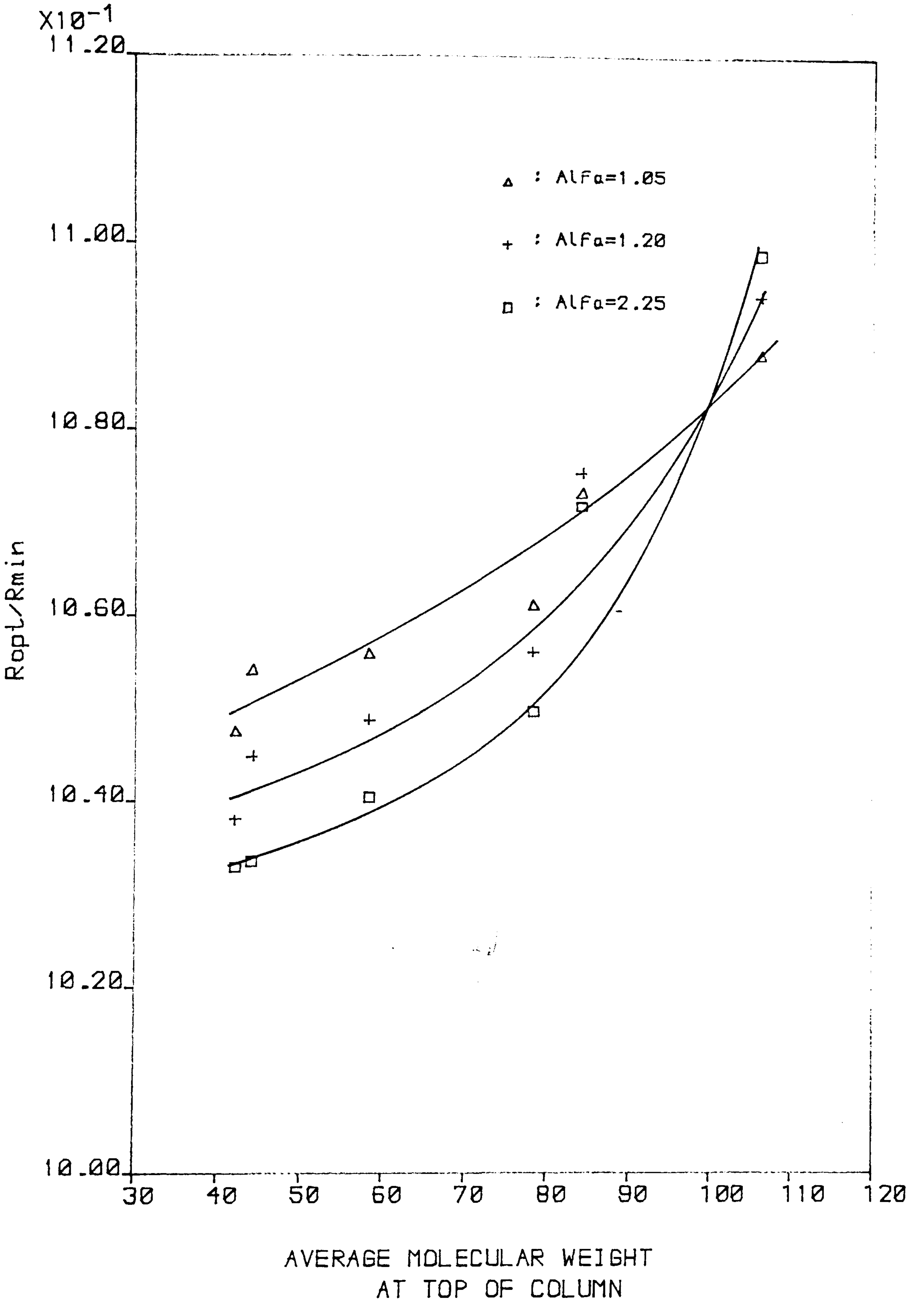


FIG. 3.16 Ropt/Rmin AGAINST THE MOLECULAR WEIGHT

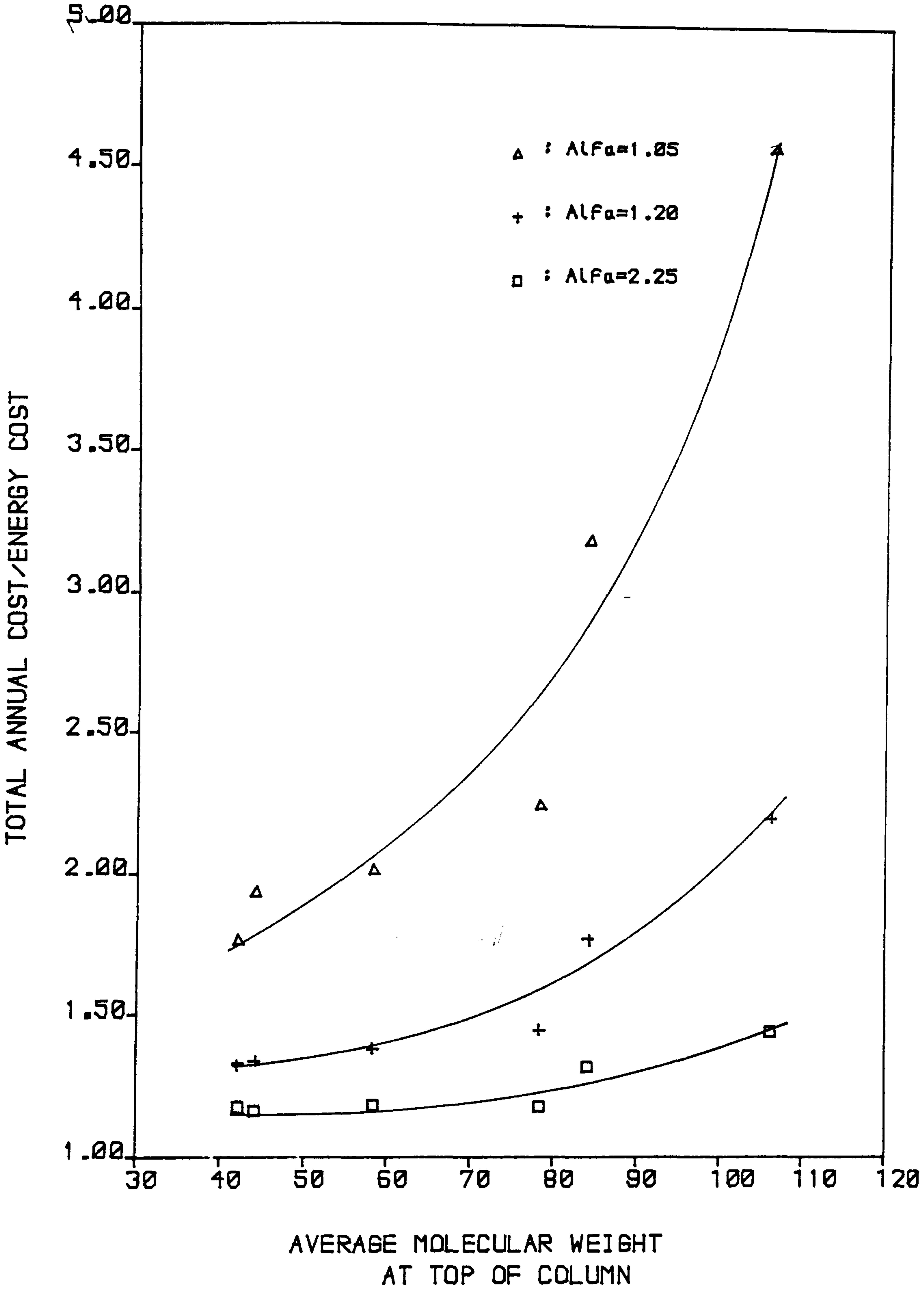


FIG. 3.17 TOTAL ANNUAL COST PER ENERGY COST AGAINST THE MOLECULAR WEIGHT

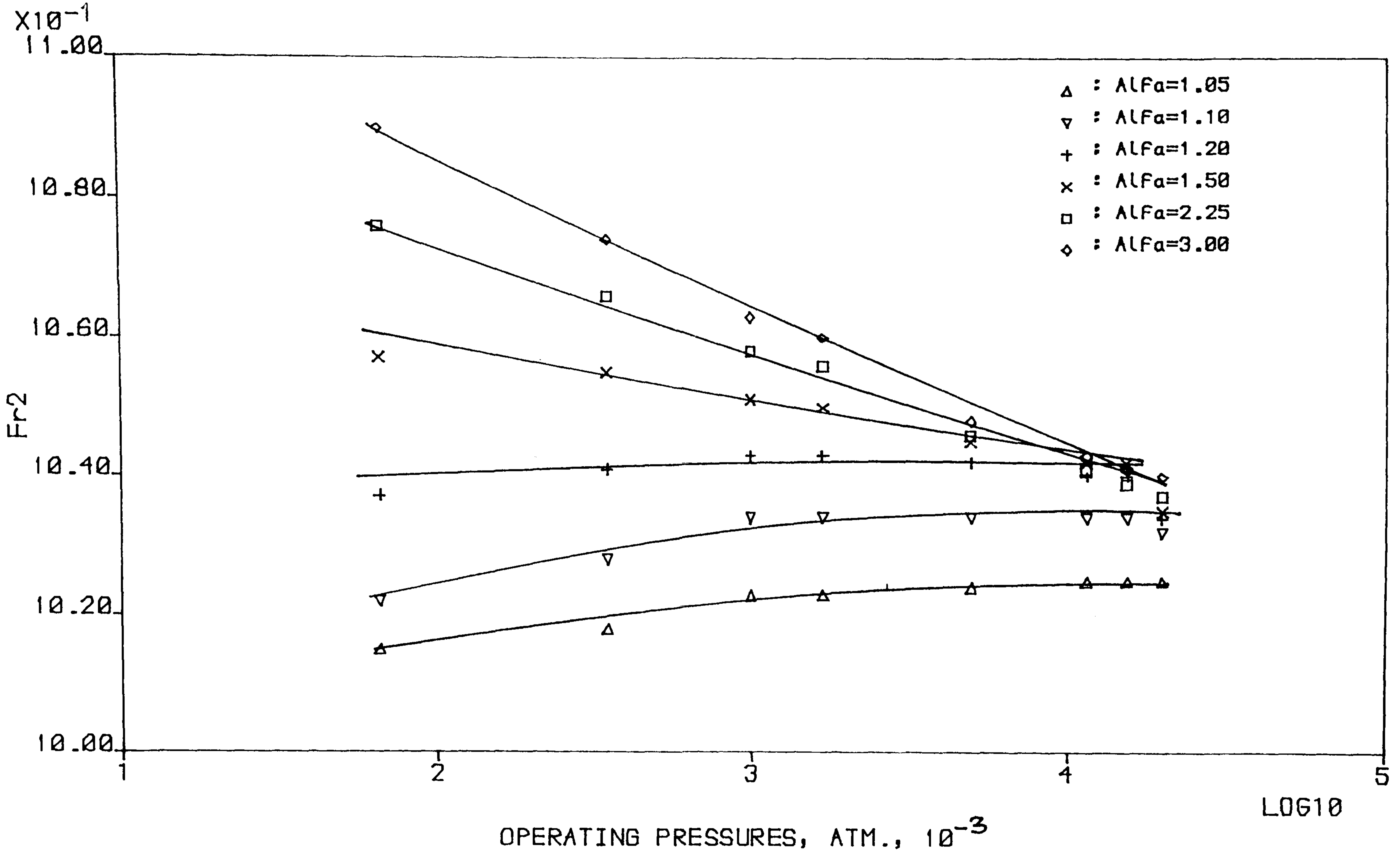


FIG. 3.18 CORRECTION FACTOR ON THE Ropt/Rmin FOR STAINLESS-STEEL MATERIAL AT VARIOUS OPERATING PRESSURES

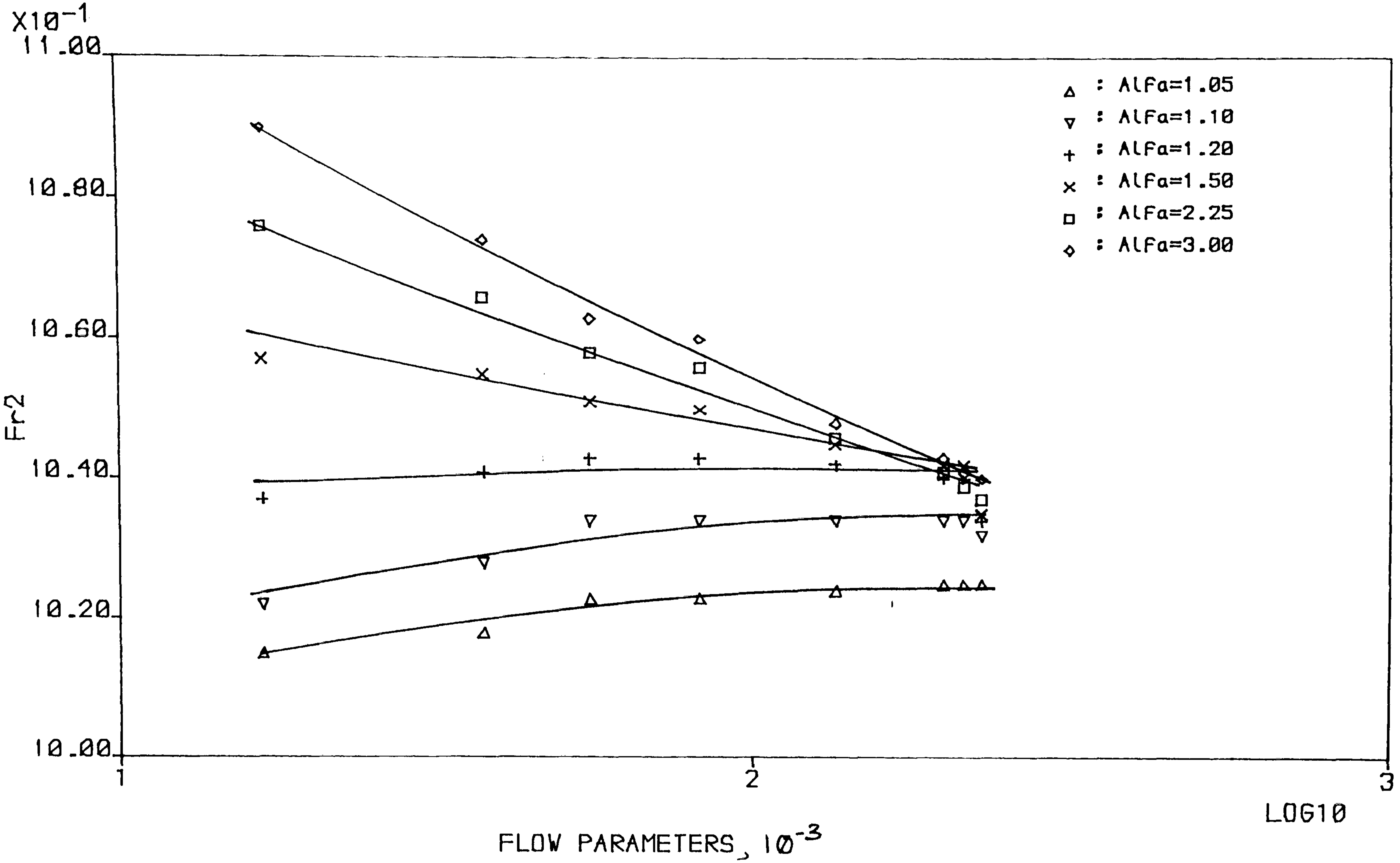


FIG. 3.19 CORRECTION FACTOR ON THE Ropt/Rmin FOR STAINLESS-STEEL MATERIAL AT VARIOUS FLOW PARAMETERS

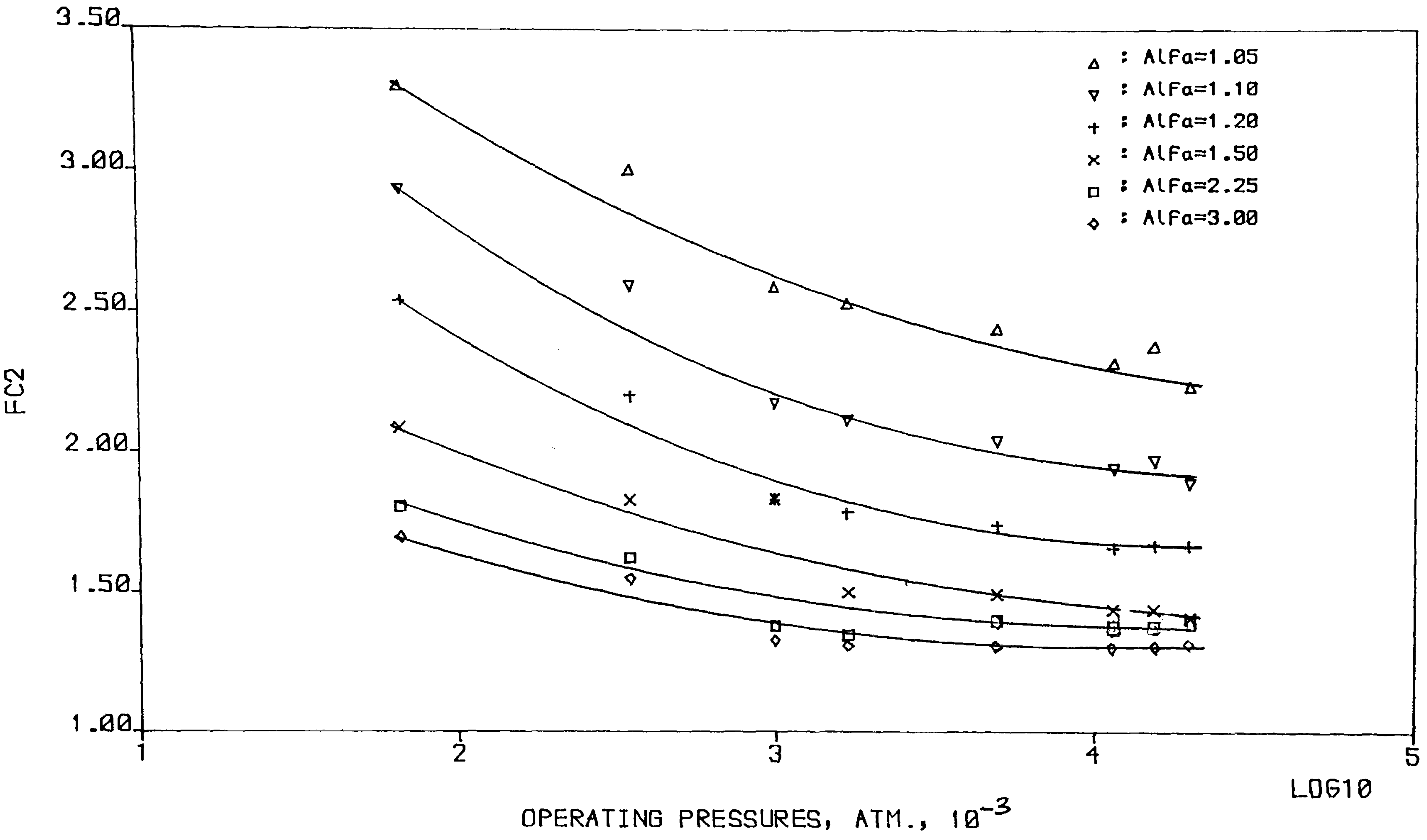


FIG. 3.20 CORRECTION FACTOR ON THE TOTAL ANNUAL COST/ENERGY COST FOR STAINLESS STEEL MATERIAL AT VARIOUS OPERATING PRESSURES

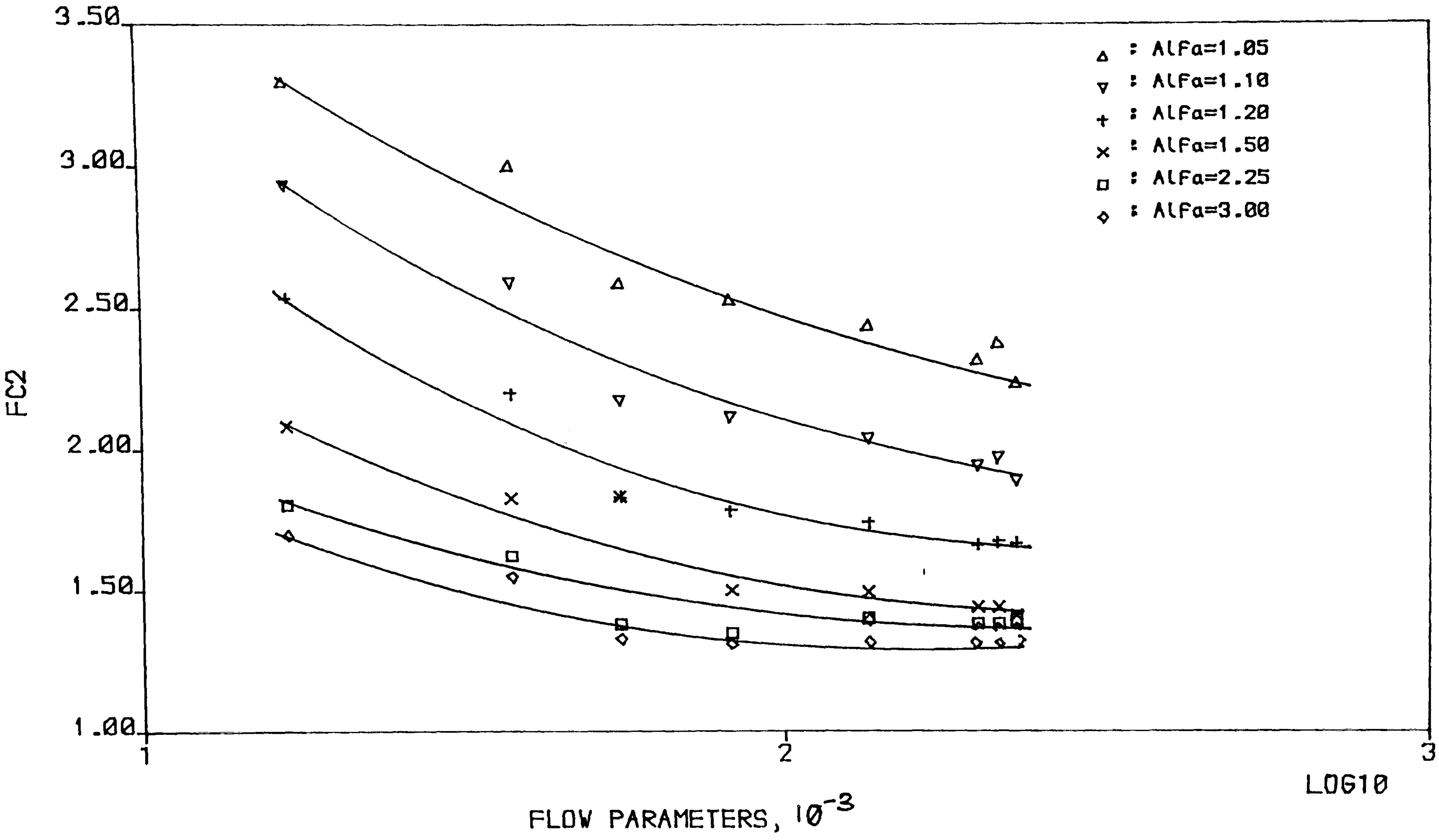


FIG. 3.21 CORRECTION FACTOR ON THE TOTAL ANNUAL COST/ENERGY COST FOR STAINLESS STEEL MATERIAL AT VARIOUS FLOW PARAMETERS

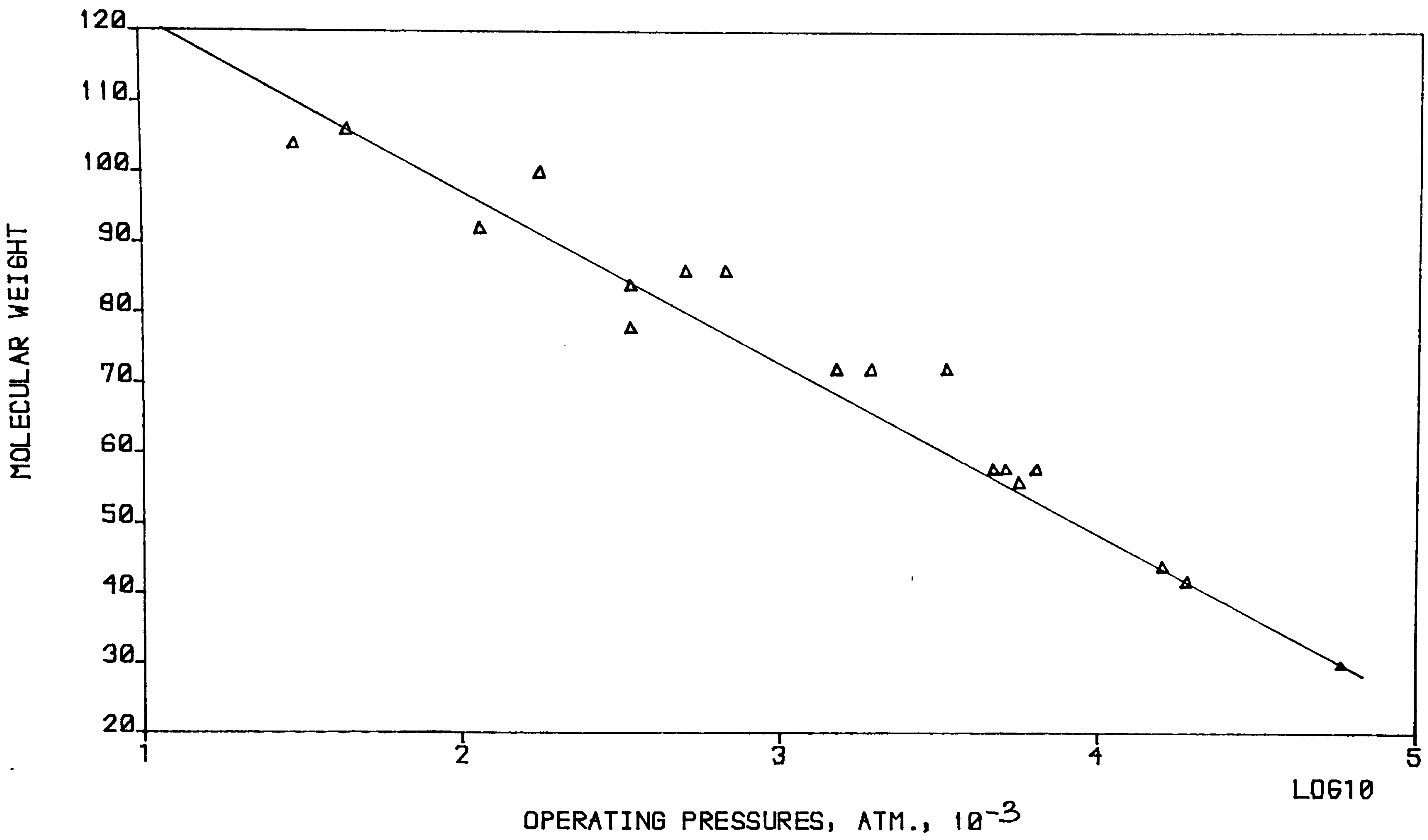


FIG. 3.22 MOLECULAR WEIGHT OF SOME COMPOUNDS AGAINST THE OPERATING PRESSURE

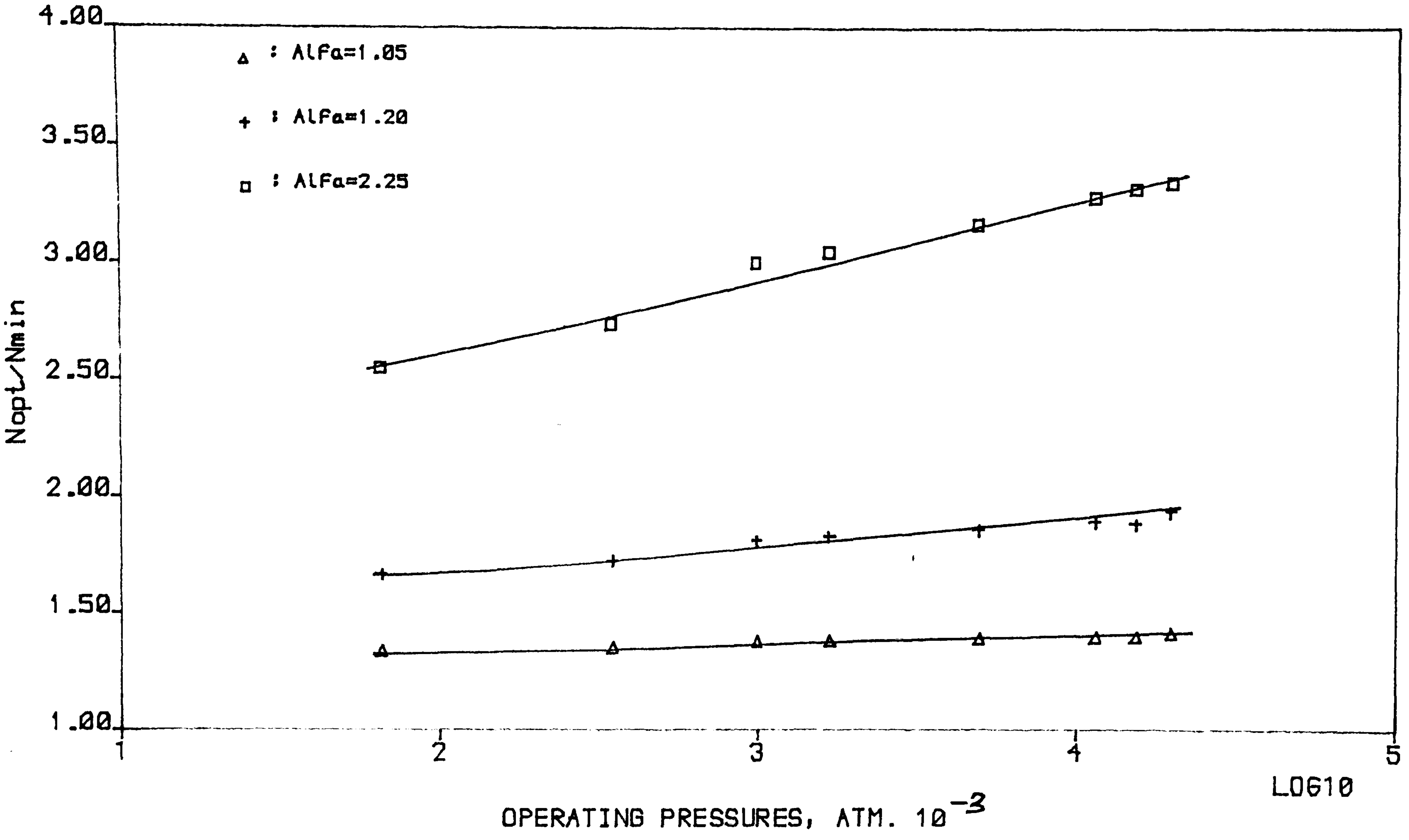


FIG. 3.23 Nopt/Nmin AGAINST THE OPERATING PRESSURES

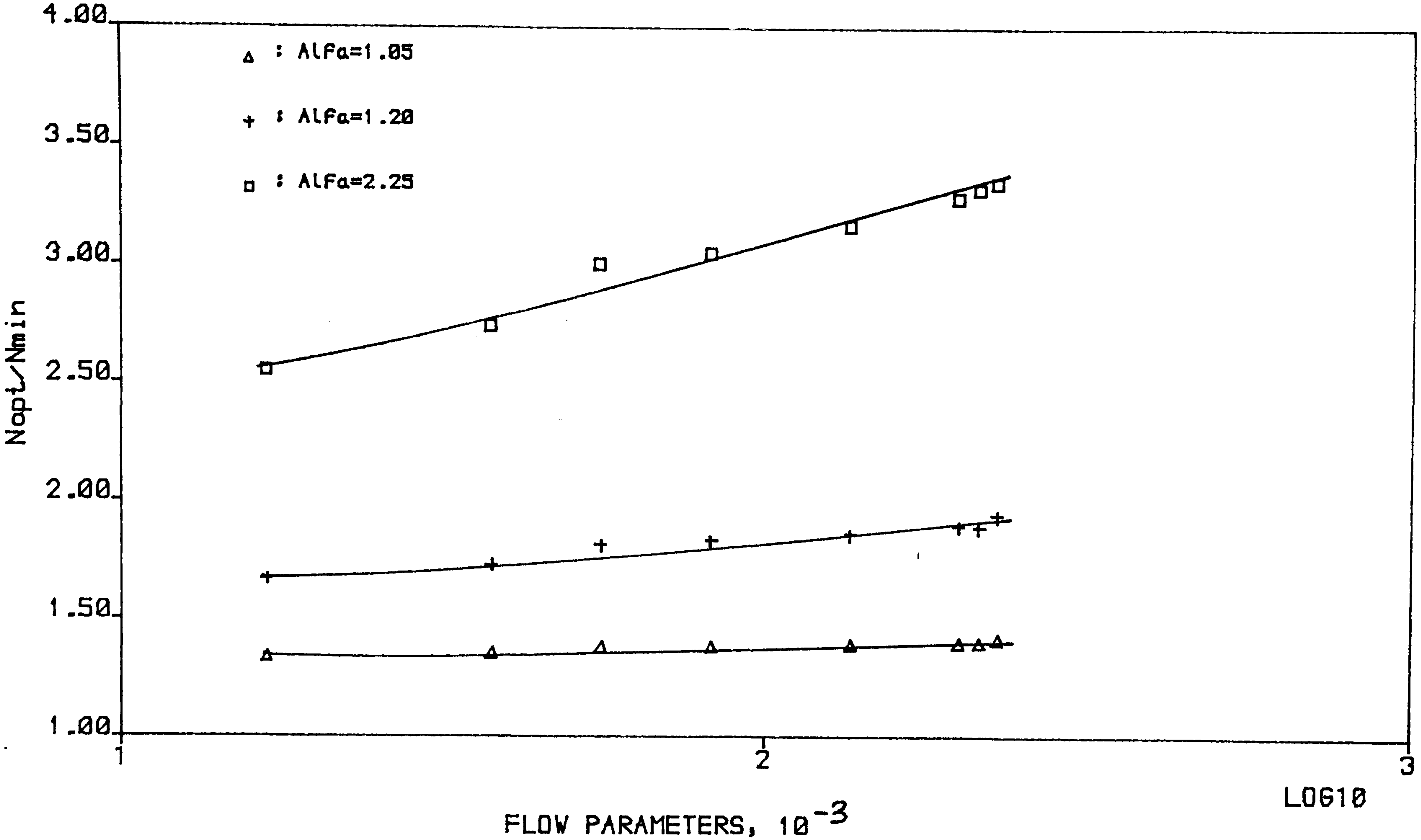


FIG. 3.24 Nopt/Nmin AGAINST THE FLOW PARAMETERS

CHAPTER FOUR

PARAMETRIC STUDIES IN OPTIMUM SEQUENCING OF DISTILLATION COLUMNS.

4.1 Introduction

In the last chapter, we studied the effects of system and operating variables on the optimum reflux ratio and the optimum cost of a single distillation column. But when a separation involves more than two components which are to be separated in a relatively pure form, more than one column is usually required. In general, processes for separating multicomponent mixtures into pure multiple products often consist of a sequence of two or more separators, each of which produces generally two, but sometimes more than two, product or intermediate streams.

For many years now, design engineers have had to face the problem of selecting the least expensive separation sequence for a given multicomponent mixture. As mentioned in the literature review, the techniques for determining the optimum sequence of separation processes can be classified into Heuristics, Evolutionary and Algorithmic methods. Irrespective of the approach adopted, it has been observed from works in the field of sequencing of distillation columns [Freshwater and Henry(1975), Tedder and Rudd(1978), Doukas and Luyben(1978)] that the optimum sequence is sensitive to some operating and system parameters used. Paramount amongst these parameters are the volatility of the component concerned and their feed compositions. In fact, the use of heuristics in the synthesis of distillation sequencing is based mainly on these two parameters.

In this chapter,

(1) we investigate how the optimum sequence varies with

- (i) the feed composition
- (ii) the volatilities of the feed components.
- (iii) the ratio of operating reflux to minimum
- (iv) the recovery fraction, and
- (v) the feed vaporisation

and

(2) Then use the results obtained to validate the use of heuristics as a technique for determining the optimum sequence of distillation columns.

Similar investigations have been attempted by some previous workers [Freshwater and Henry(1975), Doukas and Luyben(1978), Nishimura and Hiraizumi(1971), Tedder and Rudd(1978), Elaahi and Luyben(1983)]. However, these works are limited by the following reasons:

(1) Most of the works consider only one feedstock, usually a three-component mixture.

(2) Many of the workers consider the variation of the optimum sequence with only the feed composition. It was only the work of Freshwater and Henry(1975) that added the consideration of the recovery fraction and relative volatility and more than one set of feedstock mixtures.

(3) Where relative volatilities are considered, they are arbitrarily selected.

(4) Hypothetical components are normally employed. For example, Elaahi and Luyben(1983) employed hypothetical components ABCD and arbitrary volatility values of 8:4:2:1 in their studies, and considered the variation of the optimum sequences with only the feed composition.

(5) In most of the cases, only the shortcut methods are utilized in the design and costing of the columns.

Furthermore, the relative volatilities of most of the components employed in the previous studies do not vary very widely. As a result of these limitations, there is the need to examine a wide spectrum of three-, four-, five-components with varied relative volatilities and dealing with many variable that do affect the cost of distillation sequences. This is what is done here. In particular, investigations of mixtures whose relative volatility values are close to 1.0 are necessary since their investigation tells much about the validity of the use of heuristic rules in sequencing of distillation columns. A rigorous column design is employed.

4.2 Distillation Column Process Topology

Figures E-1 to E-4 in Appendix E show the distillation column process topology. This is the interconnection of process streams with sequences for three-, four-, five- and six-component mixtures. The process topologies are drawn on the assumption of a sharp separation. As defined before, a sharp separation unit is the one where each entering component exists in only one product stream. This presupposes pure component products.

The number of sequences increases rapidly as the number of components in the feed increases. The number of possible sequences (as given by Equation 2.1) for various numbers of components is shown in Table E1-1 of Appendix E.

4.3 Basis and Method of Analysis.

For this analysis, different feedstocks of three, four and five component mixture are considered. The feedstocks and their relative volatilities are shown in Tables 4.1, 4.2 and 4.3 respectively. The range of feed compositions (denoted by Feed Type) for each type of the three, four and five component feedstocks is given in Table 4.4.

For the investigation of the effects of the feed composition and volatilities of the feed components, 13 feedstocks and 67 cases (i.e. sum of the number of feedstocks and the number of feed composition types) are considered. This gives 353 number of sequences and 1167 number of distillation columns. Three of the four-component feedstocks are used in the investigation of the ratio of optimum reflux to minimum, the recovery fraction and the feed vaporisation. This gives an additional 22 cases, 110 number of sequences and 330 number of columns. Thus, 13 feedstocks and 99 cases are considered. On the whole, this gives 463 number of sequences and 1497 number of distillation columns that have been evaluated.

The feedstocks are chosen so as to allow variations in the relative volatilities between each pair of adjacent components. For example, in the first feedstock of the 3-component mixture, the first split between A and B is easier than that between B and C. Similarly, for the second feedstock, the relative volatility between A and B is about the same as between B and C. For the third feedstock, the first split between A and B is a difficult one compared with the split B and C. The same idea is used in selecting the four and five-component feedstocks. The relative volatilities quoted are those calculated at the conditions of the feed to the first column in the sequence. The relative volatilities between the pair of adjacent components may vary from column to column within the sequence.

TABLE 4.1: Feedstocks and Relative volatilities for the 3-component Mixture.

Feedstock Number	Components		Relative Volatility
1	N-Butane	A	2.4140
	I-Pentane	B	1.2872
	N-Pentane	C	
2	I-Butane	A	1.3714
	N-Butane	B	1.3929
	Neo-Pentane	C	
3	I-Butane	A	1.3714
	N-Butane	B	3.1073
	N-Pentane	C	
4	N-Pentane	A	2.9678
	N-Hexane	B	2.8736
	N-Heptane	C	
5	Trans-2-Butene	A	1.0776
	Cis-2-Butene	B	8.3300
	Hexane	C	
6	Prapane	A	3.5254
	Trans-2-Butene	B	1.0776
	Cis-2-Butene	C	

TABLE 4.2: Feedstocks and Relative Volatilities for the 4-component Mixture.

Feedstock Number	Components		Relative Volatility
1	I-Butane	A	3.3104
	I-Pentane	B	3.8201
	N-Hexane	C	2.8736
	N-Heptane	D	
2	I-Butane	A	1.3714
	N-Butane	B	3.1073
	N-Pentane	C	2.9678
	N-Hexane	D	
3	1-Butene	A	3.0955
	1-Pentene	B	1.2126
	N-Pentane	C	2.9678
	N-Hexane	D	
4	Trans-2-Butene	A	1.0776
	Cis-2-Butene	B	2.8068
	N-Pentane	C	2.9678
	N-Hexane	D	
5	Propane	A	3.5254
	Trans-2-Butene	B	1.0776
	Cis-2-Butene	C	2.8068
	N-Pentane	D	

TABLE 4.3: Feedstocks and Relative Volatilities for the 5-component Mixture.

Feedstock Number	Components		Relative Volatility
1	Propane	A	2.5024
	I-Butane	B	1.3714
	N-Butane	C	2.4140
	I-Pentane	D	1.2872
	N-Pentane	E	
2	I-Butane	A	1.9102
	Neo-Pentane	B	2.2308
	N-Pentane	C	2.2166
	2-Methyl Pentane	D	1.9992
	Cylohexane	E	

TABLE 4.4: Feed Composition Types.

Component	Feed Type (composition in mole fraction)					
	1	2	3	4	5	6
3-Component						
A	0.33	0.80	0.10	0.10	0.01	
B	0.33	0.10	0.80	0.10	0.10	
C	0.34	0.10	0.10	0.80	0.89	
4-Component						
A	0.25	0.70	0.10	0.10	0.10	
B	0.25	0.10	0.70	0.10	0.10	
C	0.25	0.10	0.10	0.70	0.10	
D	0.25	0.10	0.10	0.10	0.70	
5-Component						
A	0.20	0.60	0.10	0.10	0.10	0.10
B	0.20	0.10	0.60	0.10	0.10	0.10
C	0.20	0.10	0.10	0.60	0.10	0.10
D	0.20	0.10	0.10	0.10	0.60	0.10
E	0.20	0.10	0.10	0.10	0.10	0.60

4.3.1 Design Procedures.

Although chapter nine is devoted to the computer programs developed and the methods of design employed in this thesis, suffice to mention few basic points in this section.

The procedure adopted in the design of each column in each sequence is identical. The following specifications for a given column are made:

1) degree of recovery of the components to be separated.

2) operating reflux ratio to minimum.

3) feed composition desired.

4) the overhead condenser temperature thus fixing the column pressure.

5) the process topology for all the possible sequences for the given number of components.

6) condenser and column pressure drops, and

7) saturated liquid feed, except where indicated otherwise.

[The necessary values are listed in Appendix B-11].

The other specifications which could be considered as the assumptions made are listed in Appendix B-11. These are in line with the ones used by several authors[e.g Chiang and Luyben(1983), Cheng and Luyben(1985)] and found in standard textbooks [Henley and Seader(1981), Coulson et al(1983), Peter and Timmerhaus(1980)].

A rigorous method of column design taking into acount material and enthalpy balances is employed using the model developed by Naphtali and Sandholm(1971). The advantages of this method over most others are enumerated in chapter nine of this thesis which also feature the design equations and procedures followed. All these, including the output process data for all columns and heat exchangers required for a given sequence are generated by the computer program package developed as part of this study.

The minimum and actual number of plates and the minimum reflux ratio are determined from the Fenske(1932)-Underwood(1948)-Erbar-Maddox(1961) shortcut procedures. These shortcut procedures generated the data needed for the rigorous method instead of using arbitrarily fixed data. 80% flooding design is employed at the plate spacing of 61cm (24 ins). The rigorous steady-state simulation is then used to get precise values for the energy consumptions and the total annual costs of each column; this is summed up to obtain the total annual cost for a given sequence.

This total annual cost (TAC) is used as the economic objective function for comparing the sequences. The TAC consists of the depreciated annual capital costs of the column, condenser and reboiler; and the energy costs of condenser cooling water and reboiler boiling steam. All the costs are based on a feed rate of 100 Kmol/hr.

4.3.2 Validating our design and cost procedures.

The data generally found in the literature as to the cost of sequences are not always enough with which to compare results. When available, the annual cost given would be for only the optimum sequence obtained in that work. The absolute value of the cost of any given sequence often differs from one author to another, depending on the cost equations, factors and assumptions made. In most cases these are not stated.

The work of Morari and Faith(1980), however, reported the relative cost values for the twenty possible separation subproblems (i.e the unique splits) for a five-component mixture of Propane, i-Butane, n-Butane, i-Pentane and n-Pentane. This same problem is solved using our design and cost equations' computer program. The cost factors and some of the equations used in the work of Morari and Faith(1980) are different from those used in this thesis. But there should be a reasonable agreement of the relative cost of one sequence (or most probably one separation subproblem) to another between two different workers irrespective of the cost equation and factors used.

Table 4.5 and Figure 4.1 to 4.3 show respectively the comparison of our column operating pressures set by the condenser temperature of 322 K, column heat loads and the relative costs of the twenty separation subproblems with the results of Morari and Faith(1980). [Shortcut design procedures were however used by the authors]. There is a good agreement between the results obtained in this work and that of Morari and Faith(1980). As can be observed, the operating pressure and heat loads in particular are identical for each of the separation subproblems.

All these results confirm the validity of not only the design and cost equations employed but also the usefulness of the computer programs developed.

TABLE 4.5: Operating Conditions for the 20 Separation Subproblems in a five-component mixture.

Serial No.	Column Split	Pressure* (10^6Pa)	Pressure** (10^6Pa)	Heat Load* (10^9J/hr)	Heat Load**	Relative cost to minimum*	Relative cost to minimum**
1	B/C	0.71	0.66	23.90	21.55	4.57	5.62
2	D/E	0.21	0.21	49.27	48.96	8.59	13.52
3	A/B	1.95	1.71	3.35	3.90	1.00$^+$	1.00$^+$
4	A/BC	1.95	1.71	5.23	5.82	1.50	1.43
5	C/D	0.56	0.48	12.01	10.42	2.70	2.65
6	CD/E	0.37	0.36	53.25	50.00	10.38	13.63
7	BC/D	0.65	0.55	16.03	12.84	3.56	3.29
8	BCD/E	0.43	0.43	55.00	50.42	11.22	13.74
9	B/CDE	0.70	0.66	28.26	26.31	6.06	7.00
10	A/BCD	1.95	1.71	5.86	7.98	1.73	1.96
11	ABC/D	0.75	0.67	16.91	13.65	3.91	3.50
12	BC/DE	0.61	0.55	18.88	16.81	4.25	4.30
13	AB/CDE	0.95	0.91	28.84	26.67	6.63	7.10
14	ABCD/E	0.52	0.52	55.59	50.02	11.83	13.86
15	B/CD	0.72	0.66	26.12	23.26	5.29	6.15
16	A/BCDE	1.69	1.71	6.49	12.67	2.00	3.10
17	ABC/DE	0.75	0.67	19.67	17.89	4.60	4.58
18	AB/CD	0.97	0.91	26.83	23.16	5.84	6.13
19	AB/C	0.98	0.91	24.82	21.35	5.07	5.58
20	C/DE	0.54	0.49	15.36	14.70	3.45	3.74

* Morari and Faith(1980)

** This work

\+ The minimum cost separation subproblem.

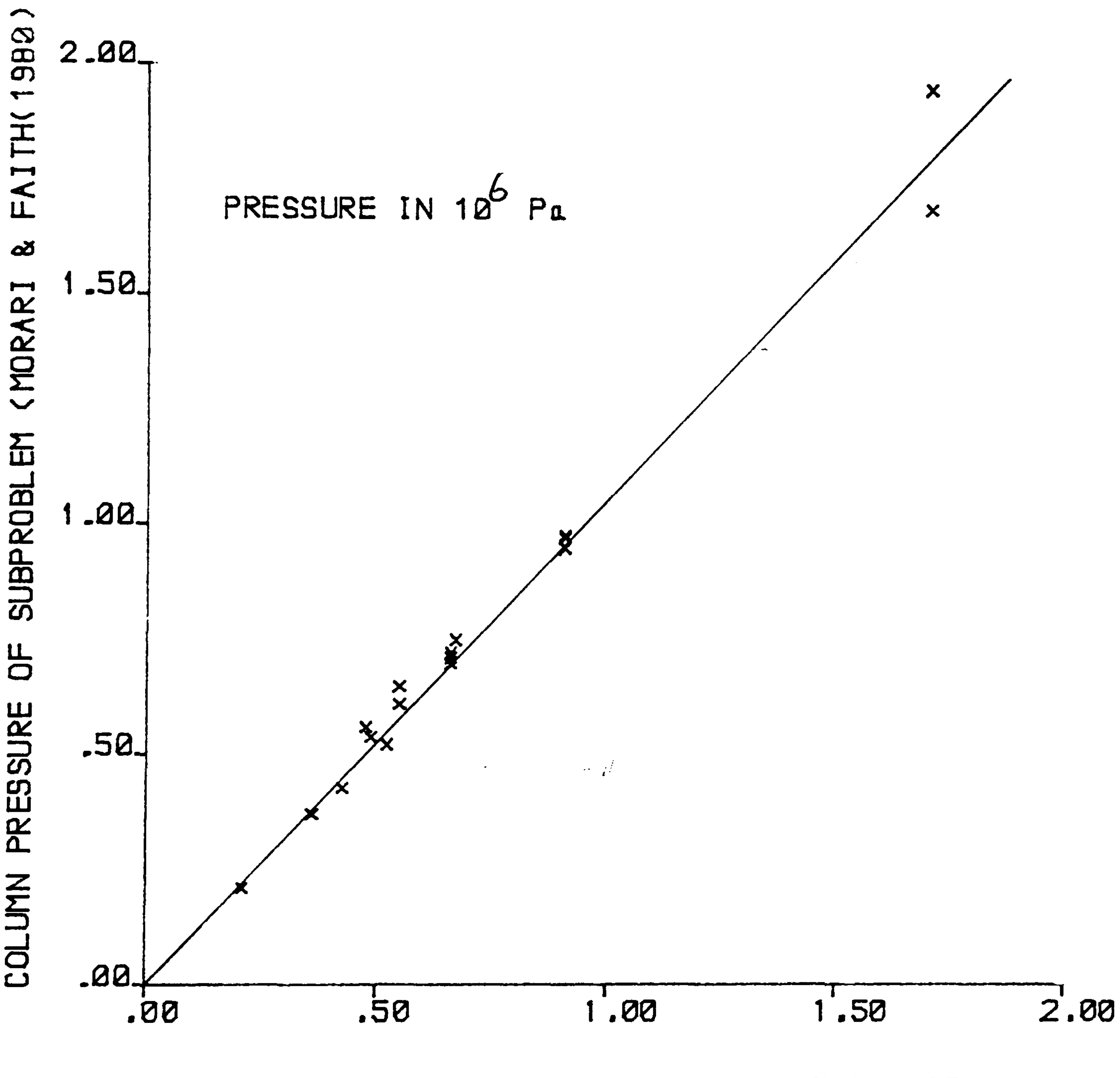


FIG. 4.1 COLUMN PRESSURE OF SEPARATION SUBPROBLEMSOF THIS WORK COMPARED WITH MORARI & FAITH(1980)

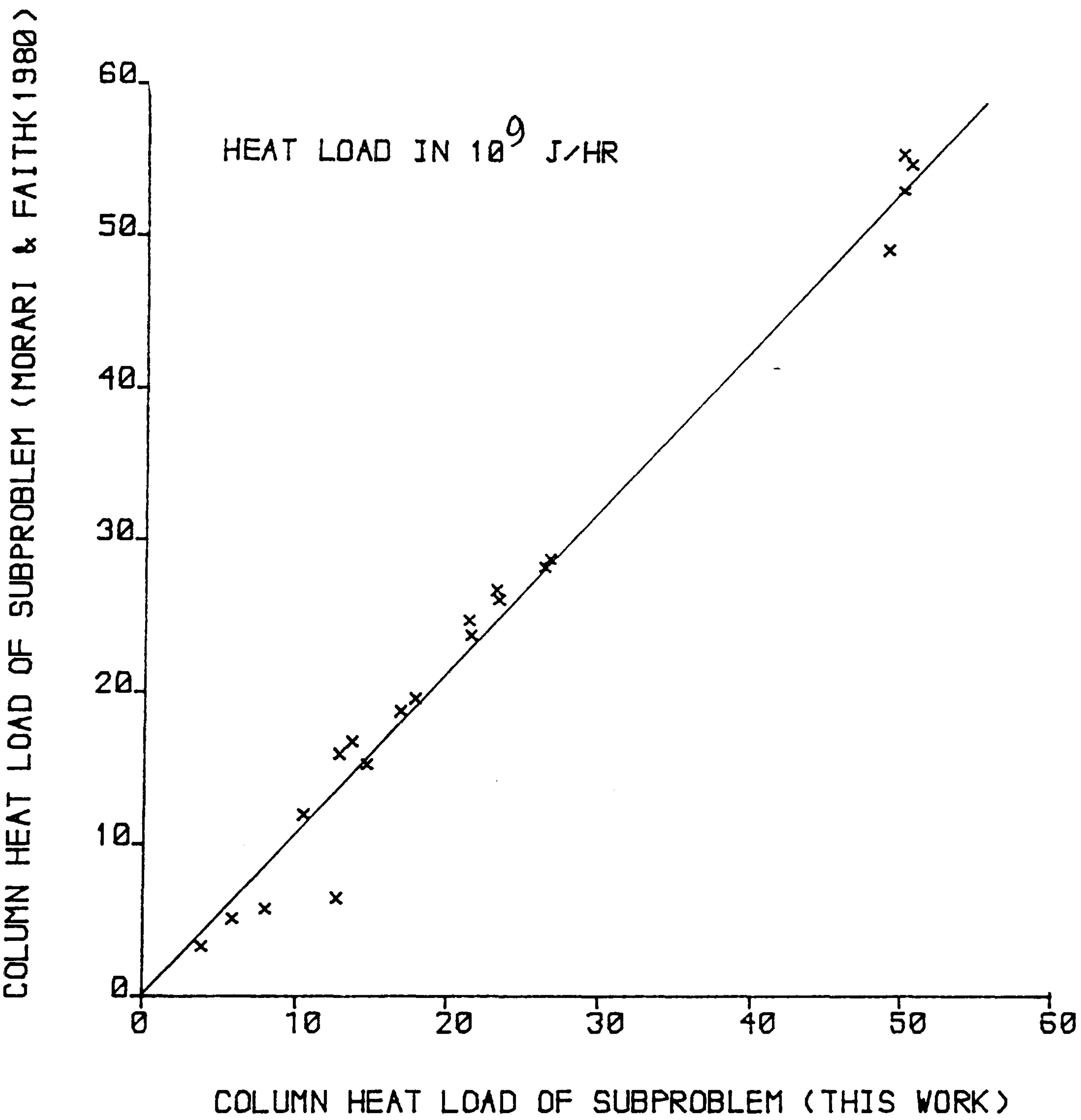


FIG. 4.2 COLUMN HEAT LOAD OF SEPARATION SUBPROBLEMS OF THIS WORK COMPARED WITH MORARI & FAITH(1980)

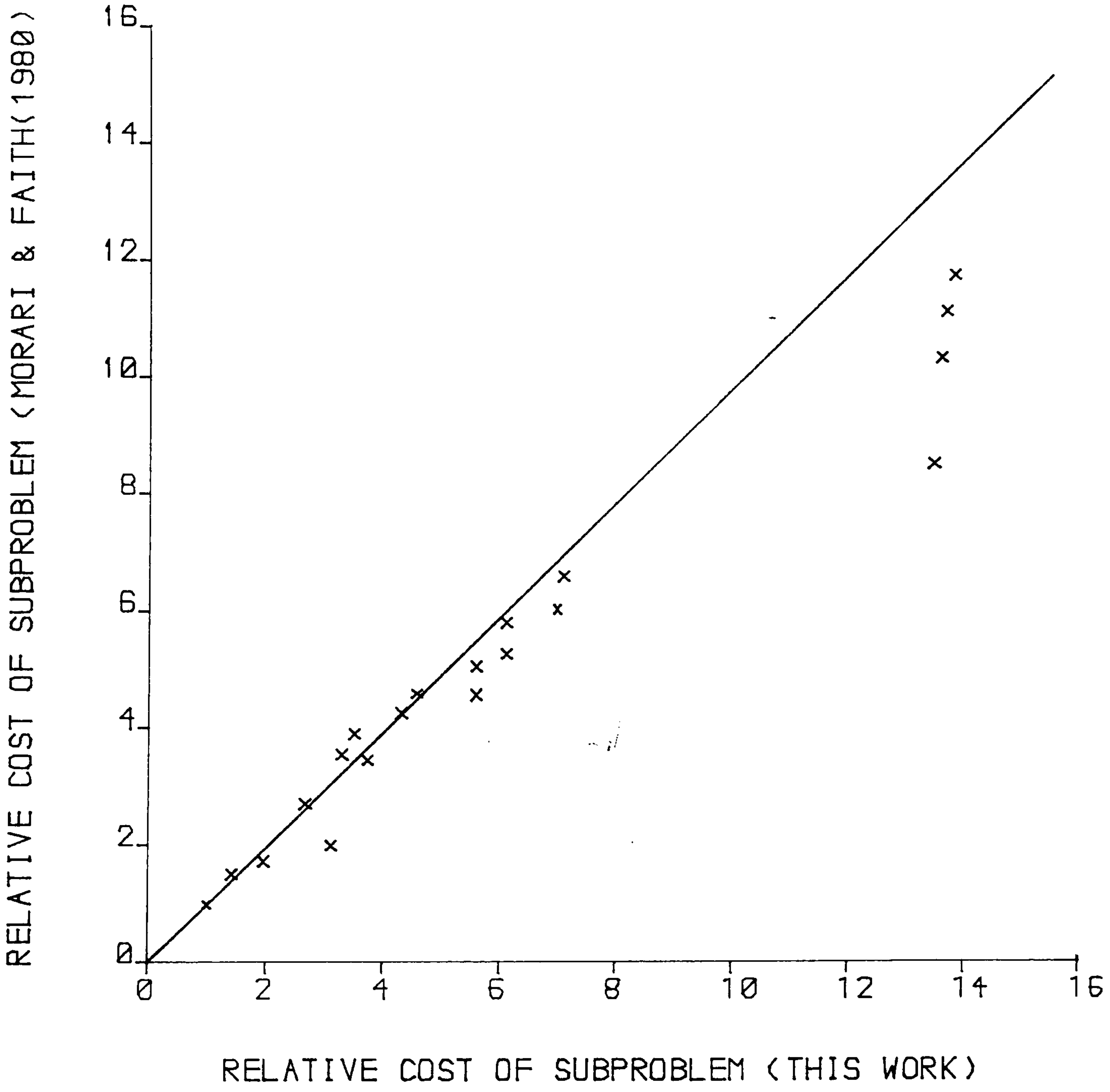


FIG. 4.3 REALTIVE COST OF SEPARATION SUBPROBLEMS OF THIS WORK COMPARED WITH MORARI & FAITH(1980)

4.4 Results and Discussions.

The results are shown in Tables A4.1 to A4.21 which are placed in the Appendix A page 28 to 56 , and Figure 4.4 to 4.24 [placed at the end of the chapter]. Only a sample result is shown in the text as Table 4.6 below. Tables A4.1 - A4.2 and Figures 4.4 - 4.5 show the variation of cost of 5-component feedstocks with various feed composition types (simply Feed Type). Similarly, Tables A4.3 - A4.7 and Figures 4.6 - 4.10 show the variation in cost of sequences of 4-component feedstocks for various feed types. And Tables A4.8 - A4.13 and Figures 4.11 - 4.16 are for the 3-component feedstocks. In all the tables, the first column shows the feed composition type, the third showing the annual capital cost, the fourth the annual energy cost and the fifth, the total annual cost of the sequences. The sixth column shows the fraction of the energy cost to the total annual cost; and the seventh column shows the order of the sequences in terms of the total annual cost with order number 1 being the sequence with the lowest cost. [For example see Table 4.6.].

The other tables show the effects of reflux ratio to minimum (Tables A4.14 - A4.16); recovery fractions (Tables A4.17 - A4.19) and thermal feed vaporisation (Tables A4.20 - A4.21) on the total annual cost of some four component feedstocks and feed composition type number 1. For example see Figures 4.17, 4.20 and 4.23.

TABLE 4.6: Total Annual Cost (TAC) of Sequences of a Four-component feedstock No. 1

A:	I-Butane	3.3104**
B:	I-Pentane	3.8201
C:	N-Hexane	2.8736
D:	N-Heptane	

Feed Type	Sequence Number	Capital Cost	Energy Cost	Total Cost	$\frac{\text{Energy}}{\text{Total}}$	Order*
1	1	42600	376651	419251	0.900	2
	2	43636	360599	404236	0.890	1
	3	48738	372087	420825	0.880	3
	4	50623	376345	426968	0.880	5
	5	46910	378612	425523	0.890	4
2	1	31561	208813	240375	0.870	1
	2	42171	262894	305065	0.862	4
	3	43023	248472	291495	0.852	3
	4	53938	301313	355251	0.848	5
	5	33938	209598	242883	0.863	2
3	1	44403	339344	383748	0.884	2
	2	44475	324321	368796	0.879	1
	3	64000	407387	471387	0.864	4
	4	64529	405303	469833	0.863	3
	5	63068	415661	478729	0.852	5
4	1	57714	497626	555340	0.896	4
	2	54210	437683	491894	0.890	1
	3	61056	487609	548665	0.889	3
	4	57923	438346	496269	0.885	2
	5	59745	499106	558851	0.893	5
5	1	36099	474031	510130	0.929	5
	2	34500	404929	439430	0.922	4
	3	29188	309879	339067	0.914	1
	4	29941	311583	341524	0.912	2
	5	32509	397931	430441	0.924	3

* Order in terms of the total annual cost.

** Relative volatility

Before going into a detailed discussion, the results, in general, show that the total annual cost and /or order of sequences varies with the various parameters considered. Their degree of sensitivity however varies from one variable to another.

All references to feedstocks, number of components and feedtypes are based on Tables 4.1 to 4.4 pages 153 to 156. The process topology of sequences is given in Appendix E from page 114. The reader would have to refer to these pages in addition to the pages containing the tables of results as the discussion of the results progresses. For example, a statement like "the third feedstock of a three component mixture, feed type 2" will refer to the component mixtures of i-Butane, n-Butane and n-Pentane (Table 4.1), and the feed composition of 0.80, 0.10 and 0.10 (Table 4.4). Also, a statement like "sequence 4 " when considering, say, a four-component mixture will refer to a sequence number 4 in Figure E1-2 of Appendix E.

4.4.1 Effects of feed composition, x_F

Feed composition is an important parameter in the sequencing of distillation columns. For the sharp separations (saturated liquid feed in particular) the feed concentration relates directly to the vapour flow in the column which in turn relates to the operating costs of the column. From the results, it is observed that in most of the cases;

(i) for the same amount of each component in the feed, the variations of total annual cost of one sequence to another is smaller than all other cases where the amount of component in the feed differs. For example, in Table 4.6 (Figure 4.6) the variation of the total annual cost (TAC) expressed as the ratio of the highest to the lowest TAC for feed type 1 (i.e feed type having the same amount of each component in the feed) is 1.056; and for feed types 2, 3, 4 and 5 is respectively 1.48, 1.30, 1.14 and 1.51.

(ii) the optimum or near optimum sequences are those that favour the balanced column in which there is about 50/50 splits in the columns.

For an example, in the second feedstock of the five-component mixture [Table A4.2 and Figure 4.5], feed type 1 has sequence number 2 as the optimum; feed type 2 has sequence number 11 as the best sequence; and feed type 6 having sequences numbers 7 and 6 as the optimum or near optimum sequences. This pattern is particularly true for cases where the relative volatility of each of the adjacent pair of components are nearly the same. In each of these optimum or near optimum sequences, there is about 50/50 split in the columns comprising the sequences.

(iii) Apart from 50/50 split there is no definite pattern in terms of cost observed to help in comparing one sequence against another in all the examples examined. However, feed type 2 (i.e.

the feed type with the first component being in excess) does appear to have the least total annual cost for the sequences of the five and most of the three and four component feedstocks examined. This is probably so because the removal of the component with largest feed composition leaves the remaining separations with lower feed rates requiring lower vapour flows. This may not be wholly valid for cases of very low relative volatilities between one or some pairs of adjacent components.

4.4.2 Effects of Relative Volatilities between the pair of adjacent component, α_{ij}

As has been pointed out, the variations in the relative volatilities are taken into account in this analysis by the type of component feedstocks selected for investigation. It can be observed from the results presented that in most cases:

(i) For a particular feed composition, the variations of cost of sequences are relatively smaller for feedstocks in which the relative volatilities vary widely than in the feedstocks in which the relative volatilities are nearly the same. For example, in Table A4.6 and in Figure 4.9 (four-component feedstock 4 in which the relative volatilities vary widely) the variations of total annual cost of sequences expressed as the ratio of the highest to the lowest TAC for feed types 1, 2, 3, 4 and 5 are respectively 1.040, 1.06, 1.04, 1.09 and 1.17. Similarly, for a three-component feedstock 5 shown in Table A4.12 and in Figure 4.15, the variations of total annual cost are respectively 1.02, 1.00, 1.00, 1.15 and 1.31 for feed types 1, 2, 3, 4 and 5. On the other hand, the variations of total annual cost of sequences for a four-component feedstock 1 (feedstock in which the relative volatilities are nearly the same) shown in Table A4.3 and in Figure 4.6 are respectively 1.06, 1.48, 1.30, 1.14 and 1.51 for feed types 1, 2, 3, 4 and 5. Similarly, for a three-component feedstock 4 shown in Table A4.11 and in Figure 4.14, the variations of TAC are 1.04, 1.42, 1.01, 1.28 and 1.45 respectively for feed types 1, 2, 3, 4 and 5.

(ii)Sequences in which the components are removed one by one in the column overhead (the direct sequence) are particularly more favoured or suitable for component-feedstocks in which neither relative volatility nor the feed composition in the feed vary very widely. A similar observation has been made by Henley and Seader(1981).

4.4.3 Effects of Recovery Fraction, x_R

By definition, the recovery fraction of a component in the products is the fraction of the amount of that component in the feed that goes into the product. The recovery fractions considered in this work are 0.90, 0.95, 0.99. This is carried out for the first three feedstocks of the four-component mixtures. Equal feed composition is maintained.

The results show that

(i) the higher the degree of recovery, the higher the total annual cost of the sequence in all the cases. This is due to the increase in the total number of plates and the minimum reflux ratio as the recovery fraction increases [See Figures 4.20 - 4.22 and in Tables A4.17 - A4.19].

(ii) the influence of the recovery fraction on the order of the sequences is not very pronounced. The best two sequences, at least, remain the same in all the cases of recovery fractions and feedstocks investigated.

This observation implies that the choice of the optimum sequences of distillation columns is unlikely to be influenced by the assumption of sharp separations (i.e. 100% recovery) that is usually made in the sequences of distillation columns.

4.4.4 Effects of the ratio of optimum reflux to minimum, R/R_m

By definition, the optimum ratio is the ratio that balances the equipment cost against the operating (energy) cost of a distillation column. The values of the reflux ratio to minimum used here are 1.10, 1.20, 1.30. The range covers the high energy cost of today to zero energy costs (see Chapter Three). The feed compostions of the feedstocks used are maintained equal.

The results show that although the total annual cost of sequences increases as the R/R_m increases [Figures 4.17 - 4.19], the optimum and the near optimum sequences obtained do not change with R/R_m. This is an important result of key significance. The cost of energy may continue to rise more than the capital costs. This thus affects the operating reflux ratio of a distillation column. Stating otherwise, the observation implies that the optimum sequence(s) obtained at any year or season may not be influenced by changes in the operating costs and indeed in the reflux ratio used.

4.4.5 Effects of Feed Vaporisation, q

A measure of the feed vaporisation is the quantity q which is typically defined as the heat required to convert one mole of feed from its condition to a saturated vapour divided by the molar latent heat of the feed. [Treybal(1980)].

$q < 0$: corresponds to a supersaturated vapour
$q = 0$: saturated vapour.
$0 < q < 1.0$: mixture of liquid and vapour.
$q = 1.0$: saturated liquid.
$q > 1.0$: liquid below bubble point.

In this investigation, q is chosen to cover the ranges given above. The specific values used are q = -0.5, 0.0, 0.5, 1.0, 1.20

and 1.50. This is done for feed type number 1 (i.e. same amount of components in the feed).

It is observed from the results that

(i) As q increases from its negative value to the positive value, the cost of the sequences decreases. This may be expected as more vapour flows through the column for lower values (i.e negative values) of q than at higher values for a constant reboiler heating [Figures 4.24 and 4.25].

(ii) Although there are discrepancies in the order of sequences, a pattern appears to emerge. For $q < 1.0$, the optimum or near optimum sequences are almost the same. Different optimum or near optimum sequences are obtained for $q > 1.0$. In other words the results are in two zones - the zone of pure liquid feed; and that of pure vapour and/or vapour plus liquid feed.

The direct sequence is the most expensive for the case of $q < 1.0$. The reverse is the case of $q > 1.0$. The fact that a feed is fully or partially vapourised thus generating more vapour at the top of the column for a constant reboiler heating makes a direct sequence a larger consumer of energy than other sequences in the case of $q > 1.0$.

4.5 Implications of the results on the use of Heuristic Rules.

Having examined the effects of the above parameters on the cost of sequences for different feedstocks of components, the question next considered is: What are the implications of these results on the use of heuristic rules as a technique for finding the optimum sequence(s) of distillation columns? Although some of the implications have been referred to in section 4.4, we in this section bring them into better focus by examining some of the "powerful heuristics" mentioned by Stephanopoulos et al(1982). These are

(1) Favour the easiest separation or Do the difficult separation last.

(2) Favour equimolar splits.

(3) Remove the most plentiful components first.

(4) Remove the lightest component (direct sequence).

In examining the heuristics in relation to the results obtained, the four component feedstocks are appropriate for doing this. Note that the result on the four-component feedstocks are shown in Tables A4.3 - A4.7 pages 34 to 38 ,and in Figures 4.6 - 4.10. For the feed type 1-3, the direct sequence is either the best or next best especially for the first three feedstocks. This tends to suggest heuristic 4. For these feed types, the worst sequence in most of the cases is sequence number 4 (the indirect sequence). This sequence is a direct opposite of the direct sequence. Instead of minimising the vapour flow rates along the column, the indirect sequence tends to maximise the vapour flow rates thus increasing the energy cost of the sequence. However, as observed below, this can be suppressed for very low feed composition values of components A, B and C compared with D.

But for the feed type 5, the direct sequence becomes the worst (i.e most expensive) or nearing the worst sequence. Heuristic 4 is now overidden by heuristics 3 and 2. The repeated processing of the plentiful component D tends to maximise the overall flow rates for the entire sequence which results in higher energy costs. For this same feed type 5, sequences 3 and 4 are the near optimum sequences. These sequences give a more equimolar division of the feed between the distillate and the bottom products. This confirms heuristic 2. This heuristic causes the reflux ratios in the sections above and below the feed to be better balanced. This is what Harbert(1957) called "the advantage of 50/50 split" and justified it on the basis of minimum heat requirement.

A conflict of heuristics can also be noticed on considering the third feedstock of the four component mixture [Table A4.5 page 36]. Split B and C is a difficult separation. But sequence 2 performing the B and C separation first is found to be the optimum in some of the feed composition types. Heuristics 2 and 3 overide the heuristic 1 in this case. Similarly, heuristic 3 overides heuristic 1 in the feed type 2 of the fourth of the four-component feedstock [Table A4.6 page 37]. The feed compostion of A which is participating in the difficult split is in excess. Sequence 1 which performs the difficult separation first is found to be the optimum sequence.

For the third feedstock of the four-component mixture [Table A4.5 page 36] however, after sequence 1, sequence 5 is found to be the next best for feed type 2. This suggests heuristic 1. In this sequence 5, the easy separation A/B is done first, and followed by the next easy separation C/D, leaving the difficult separation B/C until last in the sequence. Keeping the difficult separation last tends to keep the non-key flows "out of harms way". In the separation of close-boiling keys "reflux ratio in the column per unit mass flow is high resulting in large vapour flows. If non-key components are present in addition to the keys, the vapour flows would be significantly increased again." [Stephanopoulos et al(1982,1984)]. For some isolated cases of the 3-component feedstocks, this seems not always satisfied. For example, in the sixth feedstock of the 3-component mixtures and for the feed type 1 [Table A4.13 page 41], the indirect sequence is optimum instead of the direct sequence which is expected to be the optimum following the heuristic "Do the difficult separation last." Similar observations have been noted by Gomez-Munoz and Seader(1985).

In general, sequences number 1 and 2 are favoured for feed types 1 - 3 of the four-component feedstocks; and sequences 3 and 4 for feed types 4 and 5 [Tables A4.3 - A4.7]. Each of the four heuristics played a part in the choice of one optimum sequence or another. However, the heuristic "favour the 50/50 split" seems to be the most powerful of the four heuristic rules examined.

4.6 Relations between the Capital cost, Energy cost and the Total Annual Cost (TAC)

An important observation is that the ordering of the sequences in terms of the total annual cost in most cases follows the same pattern as the ordering in term of the energy cost. This is a very interesting and important observation. It means that, usually, optimum sequence(s) of distillation columns can be obtained by considering only the energy aspects of the costs of the sequences. A similar conclusion has been made by previous authors [Doukas and Luyben(1978), Chiang and Luyben(1983), Freshwater and Henry(1975), Cheng and Luyben(1985)]. A closer inspection of the results shows that this rule breaks down when one or more of the relative volatilities of the mixture is(are) close to 1.0. These observations may be explained as follows.

In general, the energy cost dominates the total cost of sequences in the case considered. Except for the fourth and fifth of the four-component feedstocks [Tables A4.6 - A4.7] where the difficult separations have very low relative volatilities of about 1.08, the energy costs constitute more than 80% of the total annual cost of the sequences. In some cases, it is as high as 93%.

These imply that the capital costs constitute only a small percentage of the total annual cost of a sequence. However, in all situations where one of the relative volatility is less than 1.1, the capital cost account for about 30% of the total annual cost. It would be higher as the relative volatility continue to get closer to 1.0. In other words, the energy cost cannot be said to completely dominate the total annual cost of the sequence in such cases. This observation has already been noted in Chapter Three. In practice, of course it may not be economically viable to use ordinary distillation column for the separation of components with such low relative volatilities. Alternative separation methods like the extractive distillation could be used. These points are taken up later in the thesis.

It may also be observed from the results that when ranking sequences by energy cost breaks down [e.g in Table A4.6 feed type number 3] for mixtures of difficult separations, then the total annual cost differences between different sequences are relatively small.

4.7 Summary and Conclusions.

The summary and conclusions for this chapter are given in this section. These are:

(i) Although heuristic rules are useful in the preliminary sequencing of separation processes, they are not infallible. Sometimes they contradict one and another and may therefore produce many sequences which are considered optimal by the application of the heuristics. The four heuristics examined already are indeed powerful in the sequencing of distillation columns. For the four-component feedstocks, heuristic Nos. 1 and 4 [as listed in page 173] tend to dominate for feed types 1 - 3 . Heuristic Nos. 3 and 2 dominate for feed types 4 and 5 (i.e. feed types in which the high volatility components have the dominant feed composition). The heuristic "favour the 50/50 split" appears to be most important of the four.

(ii) In general, energy cost is found to dominate the total cost of the sequences contributing over 80% in some cases to the total annual cost (TAC) of each sequence. But for a relative volatility close to 1.0, this is not so. The capital cost contributes as much as 30% to the TAC. Energy cost cannot be said to completely dominate the TAC in such cases. In most of the cases, the ordering of the sequences in terms of TAC follows the same pattern as that by the energy cost. It mean that finding the optimum sequence may be done by considering only the energy aspect of the TAC.

(iii) The direct sequence is not found to be optimum in all cases. However, the frequency of it being or nearing the optimum is higher than for any other sequence. It is particularly expensive for the feed types in which the dominant feed composition is towards the ends of the components when arranged in the descending order of volatility. This is in agreement with most of the analysis done by Feshwater and Henry(1975). Nevertheless, they reported that the direct sequence is the optimum in all of the cases they considered. They however noted that this might have been a consequence of the relative volatility or the degree of difficulty of the separation between the difficult pair for the feed mixtures they considered.

(iv) Of the parameters considered, the optimum reflux ratio to minimum and the recovery fraction have negligible influence on the order of sequences. At least, the best two sequences remain the same irrespective of the value of R/R_m or the recovery fraction used. This is important because it implies that the optimum sequence may be found on the basis of "sharp separations" and an arbitrary value of R/R_m. The total annual cost of the sequences on the other hand increases as the R/R_m or the recovery fraction increases.

The feed composition and the relative volatility between the adjacent pair of the components influence the order and cost of sequencing much more than any of the variables considered. It is thus not surprising that most of the heuristic rules are based on the feed composition of the components on one hand, and the relative volatilities between the pair of adjacent components on the other hand. In other words, many of the heuristics proposed utilise each of these two important variables in isolation of one and another. For example, "do the difficult separation last" depends only on the volatility whereas the heuristic "favour the plentiful component" depends only on the feed composition.

The optimum or near optimum sequences should be a function of both the relative volatility and feed composition. It is essential therefore to have a quantitative expression or analytical expression that takes into account these two variables. This is the subject of the next chapter. Such quantitative expressions would help to determine the numerical ranges of accuracy and bounds on the applicability of the heuristics and may overcome the problem that applying one heuristics may be contradicted by the application of another.

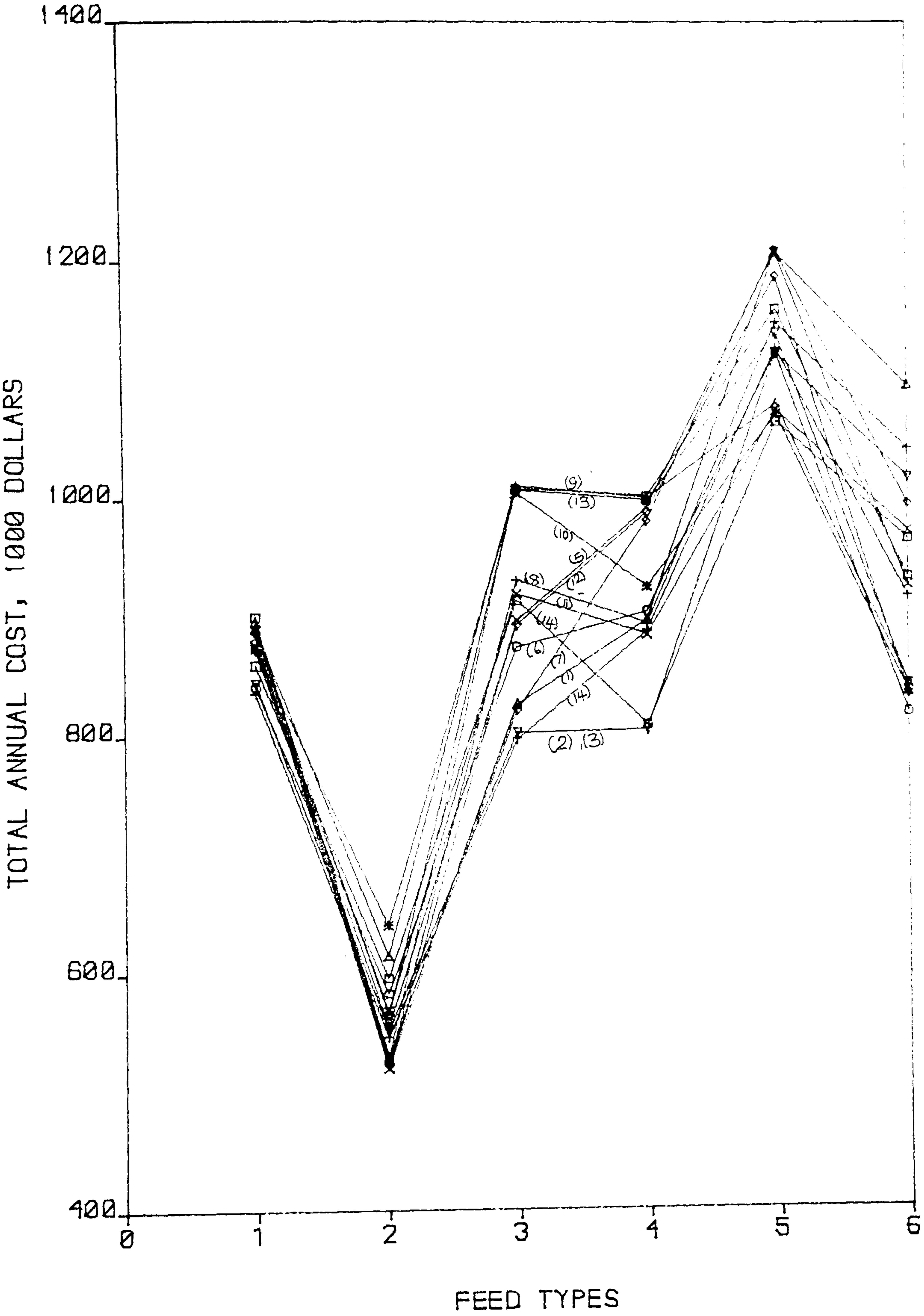


FIG. 4.4 TOTAL ANNUAL COST FOR POSSIBLE SEQUENCES OF A FIVE-COMPONENT FEEDSTOCK NO. 1

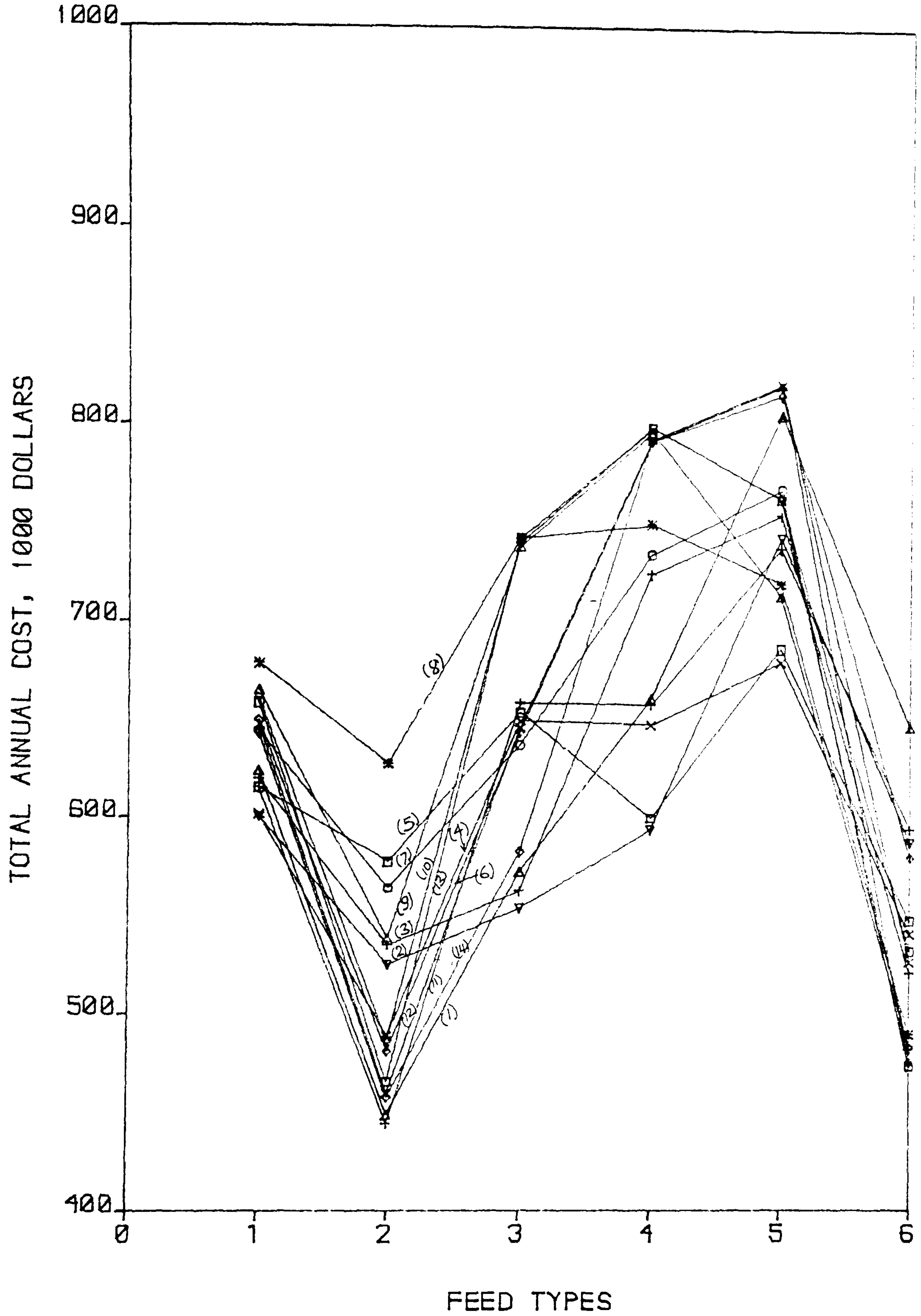


FIG. 4.5 TOTAL ANNUAL COST FOR POSSIBLE SEQUENCES OF A FIVE-COMPONENT FEEDSTOCK NO. 2

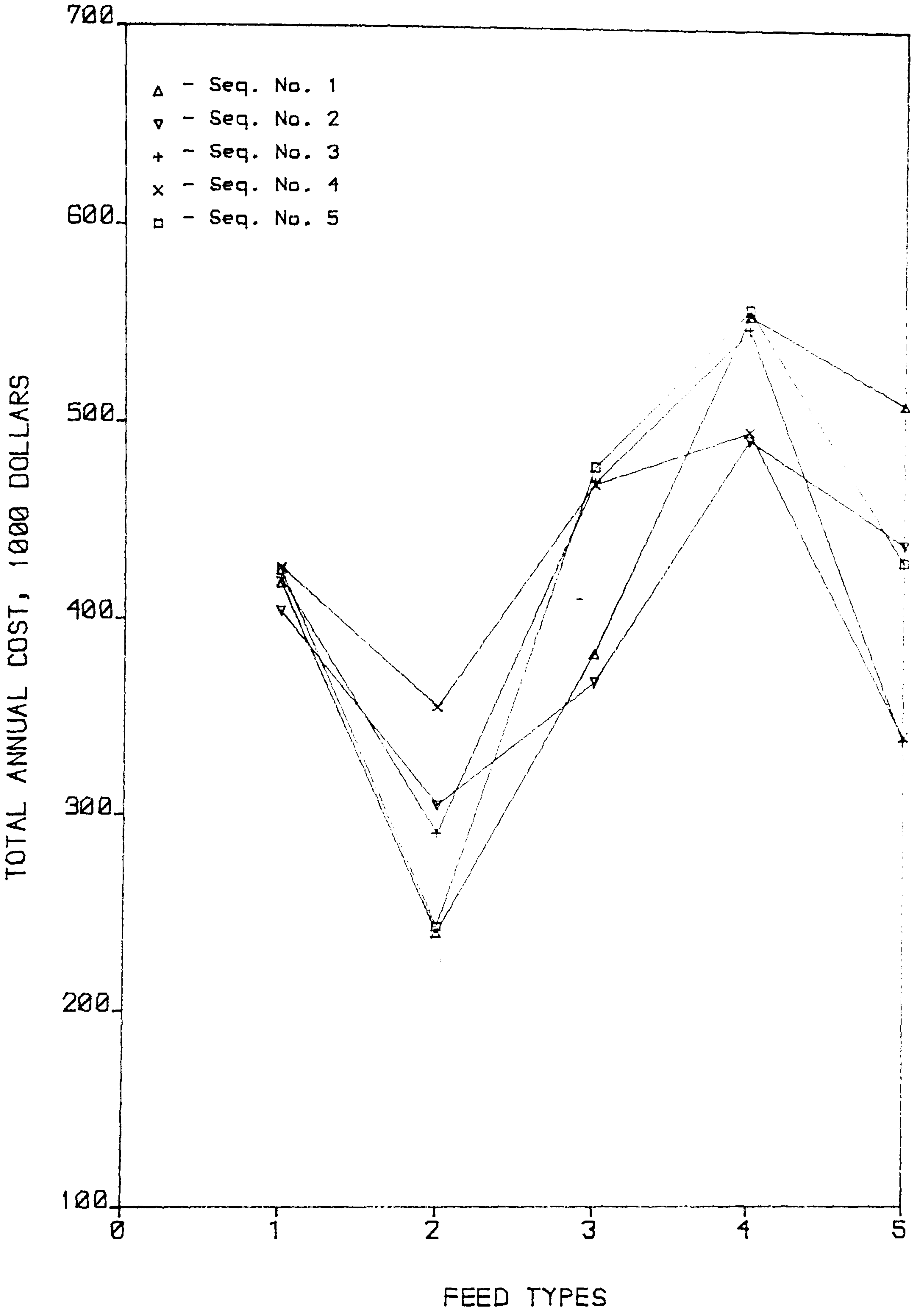


FIG. 4.6 TOTAL ANNUAL COST FOR POSSIBLE SEQUENCES OF A FOUR-COMPONENT FEEDSTOCK NO. 1

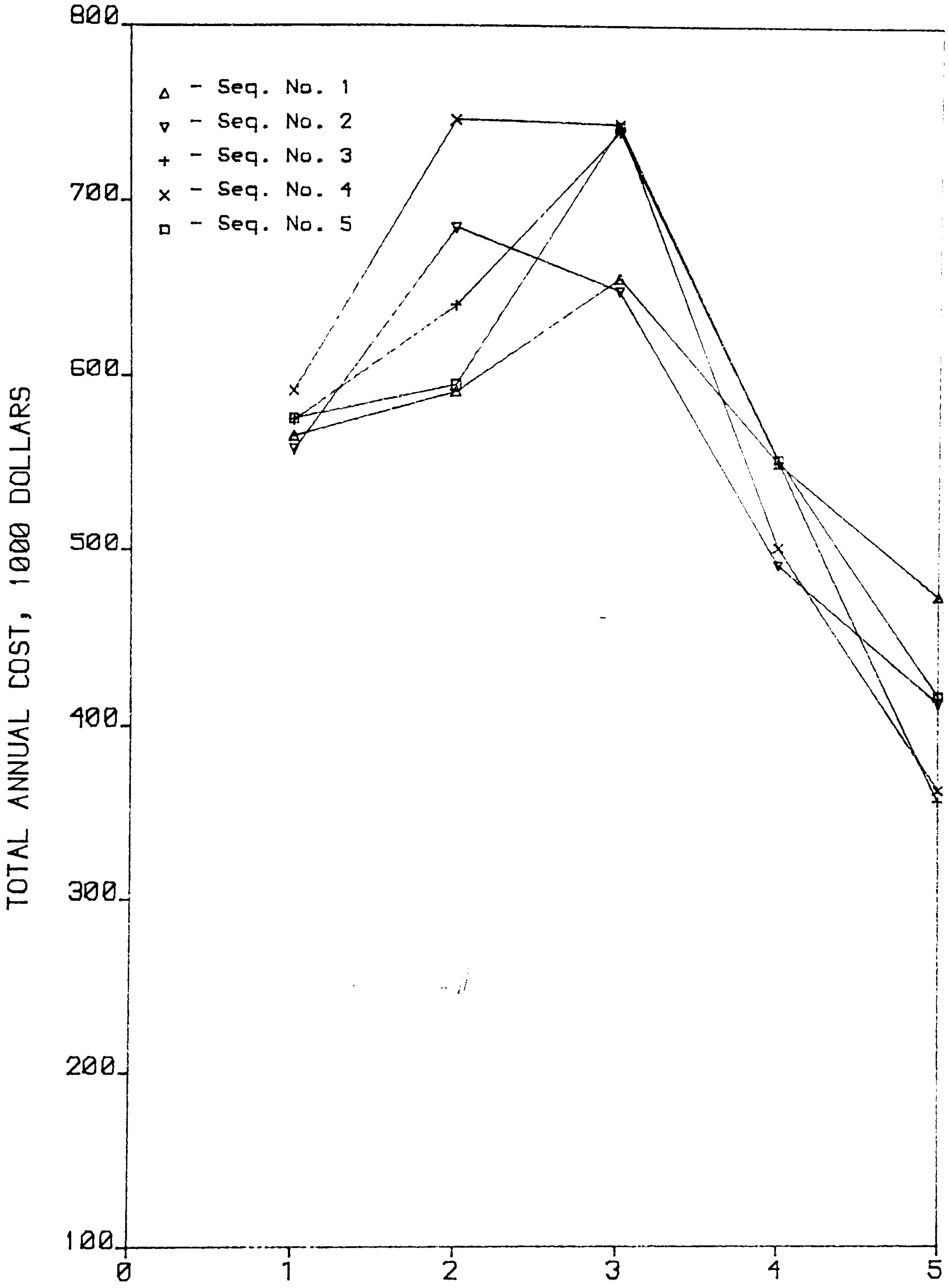


FIG. 4.7 TOTAL ANNUAL COST FOR POSSIBLE SEQUENCES OF A FOUR-COMPONENT FEEDSTOCK NO. 2

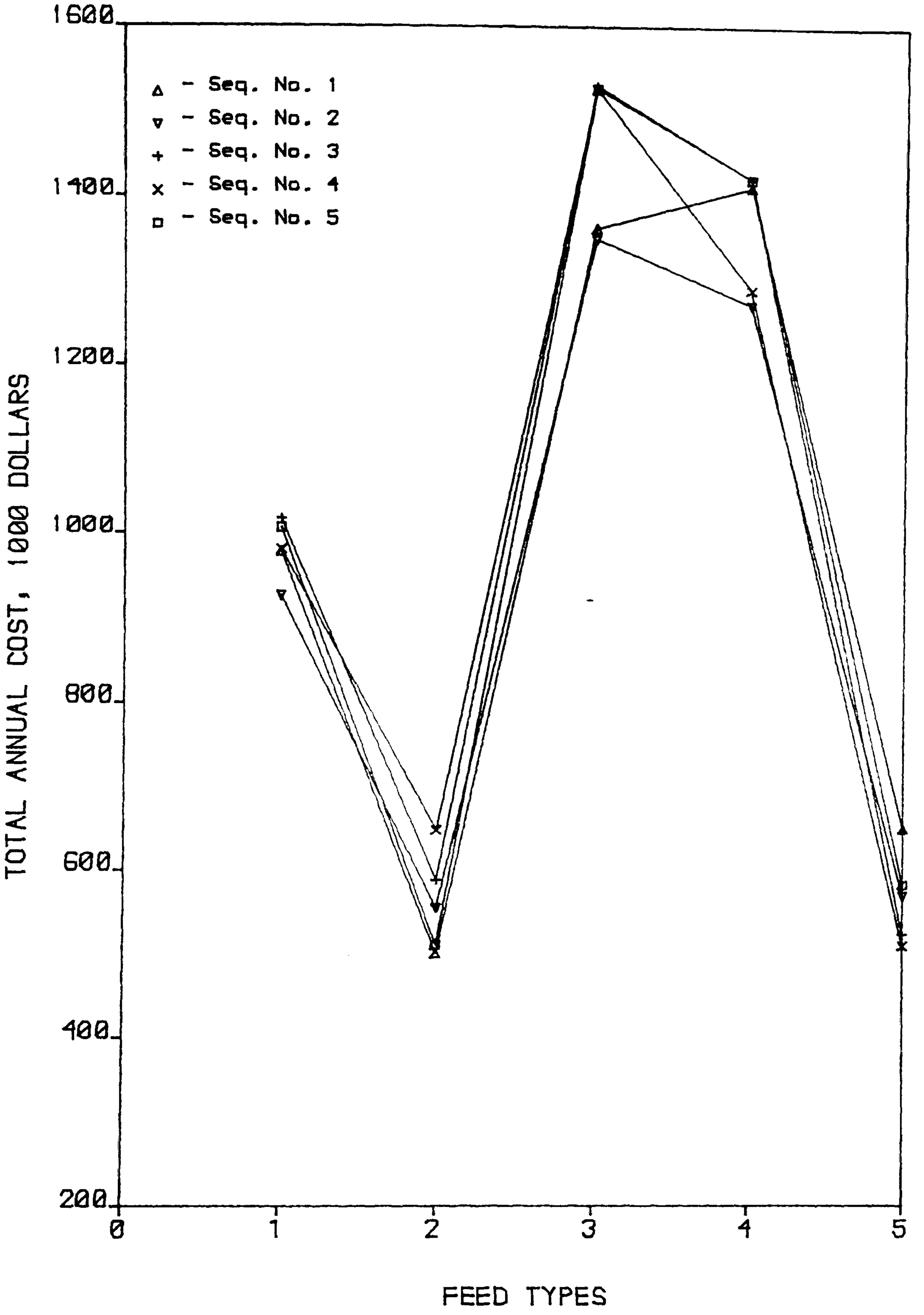


FIG. 4.8 TOTAL ANNUAL COST FOR POSSIBLE SEQUENCES OF A FOUR-COMPONENT FEEDSTOCK NO. 3

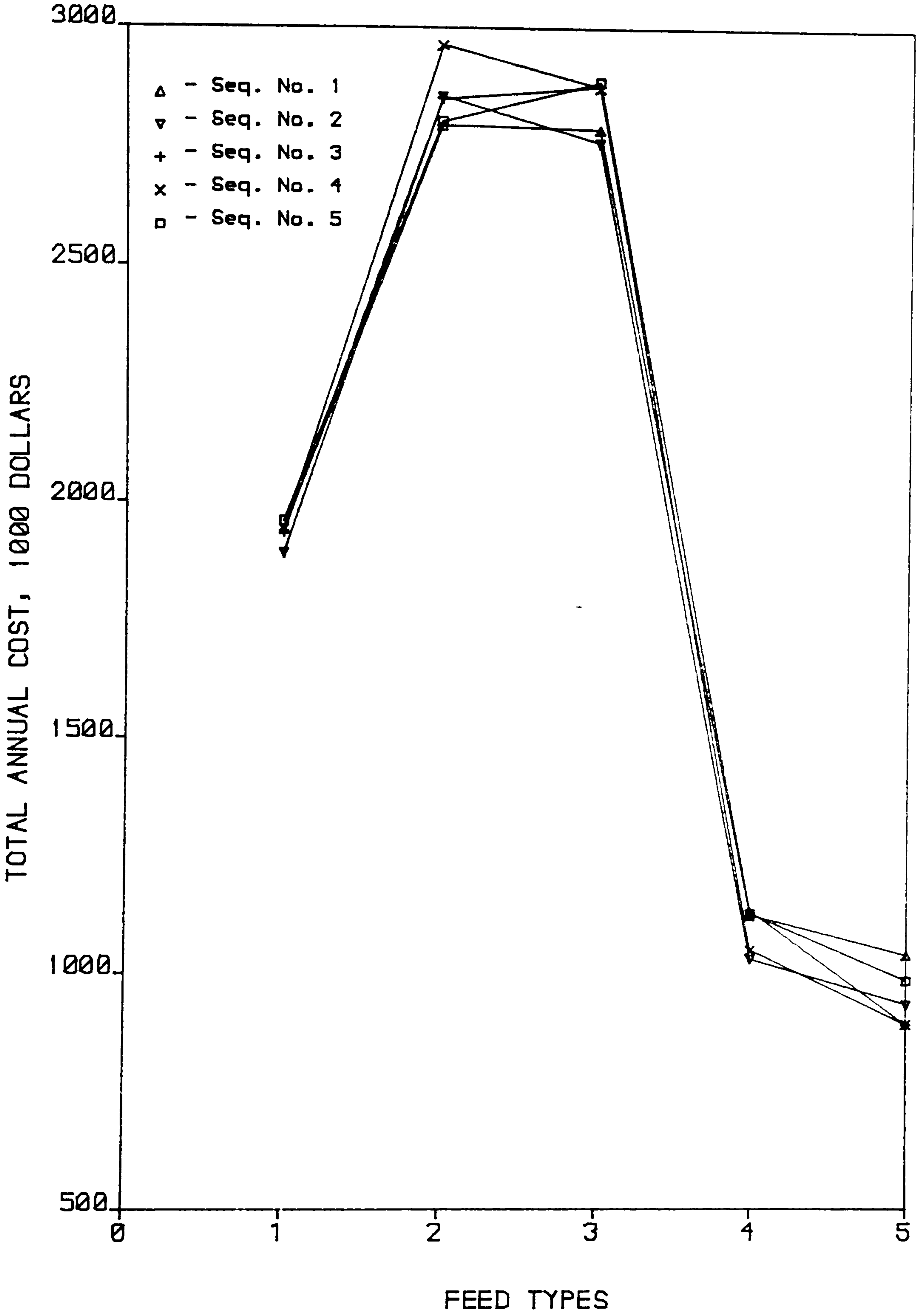


FIG. 4.9 TOTAL ANNUAL COST FOR POSSIBLE SEQUENCES OF A FOUR-COMPONENT FEEDSTOCK NO. 4

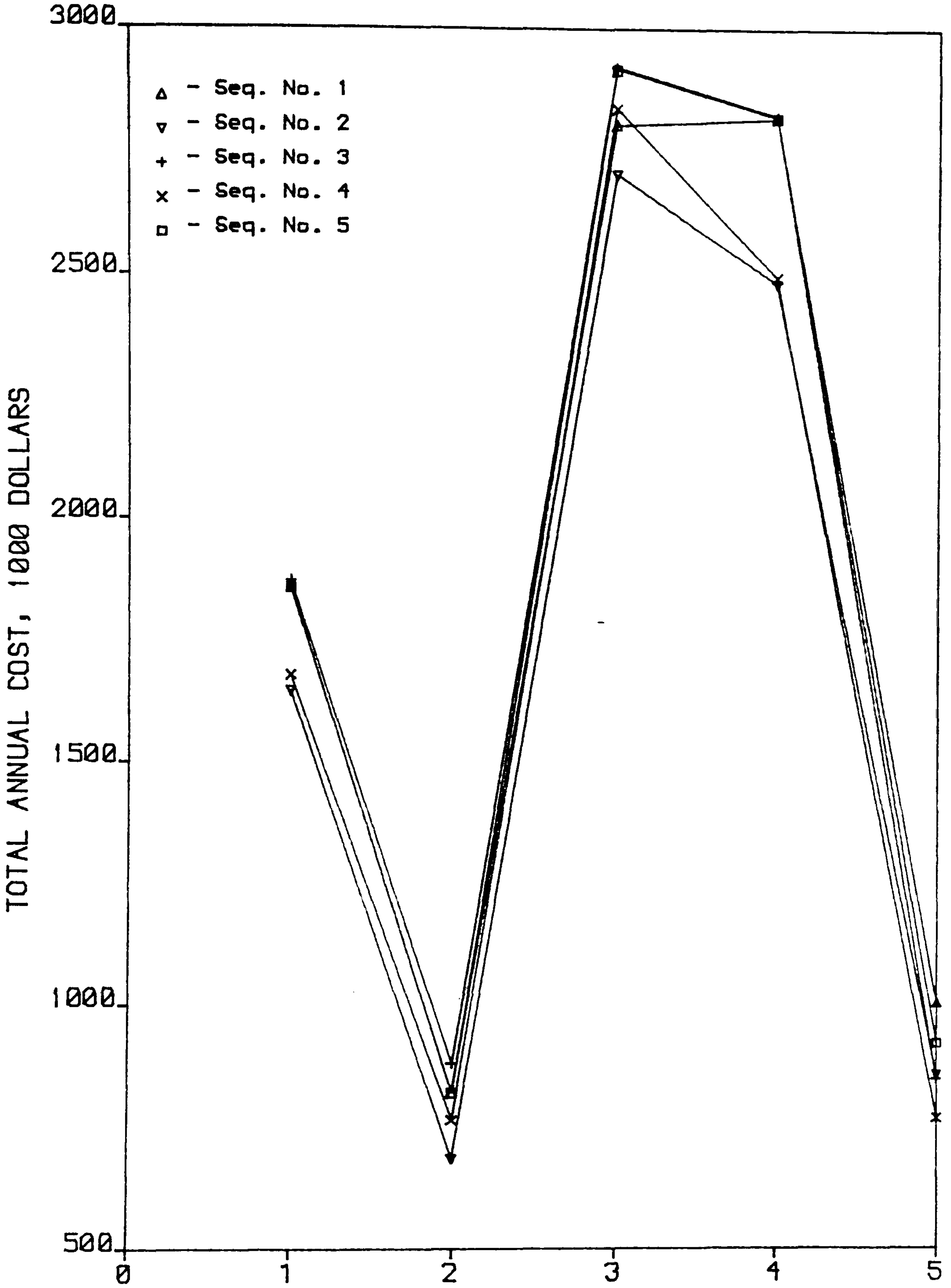


FIG. 4.10 TOTAL ANNUAL COST FOR POSSIBLE SEQUENCES OF A FOUR-COMPONENT FEEDSTOCK NO. 5

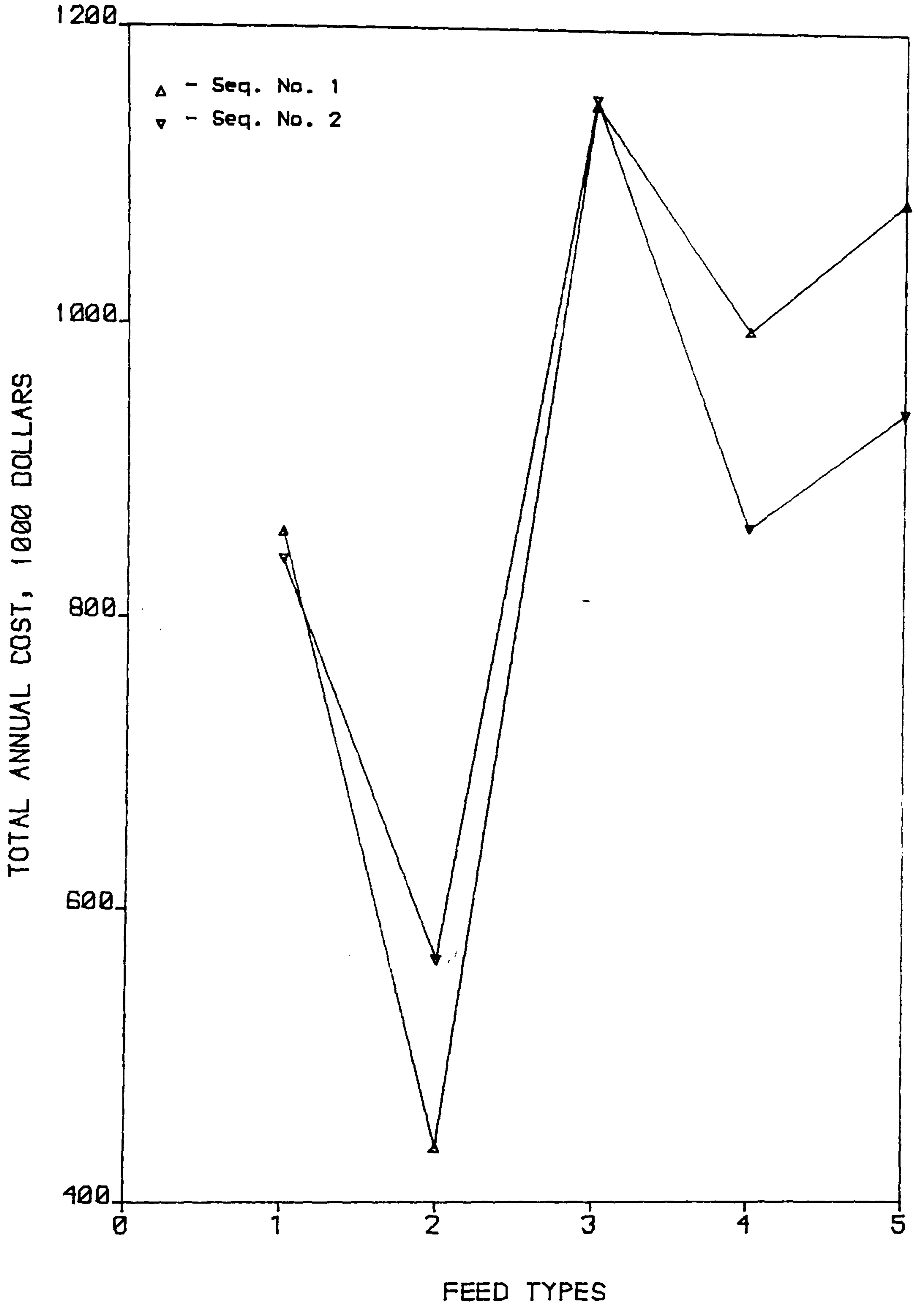


FIG. 4.11 TOTAL ANNUAL COST FOR POSSIBLE SEQUENCES OF A THREE-COMPONENT FEEDSTOCK NO. 1

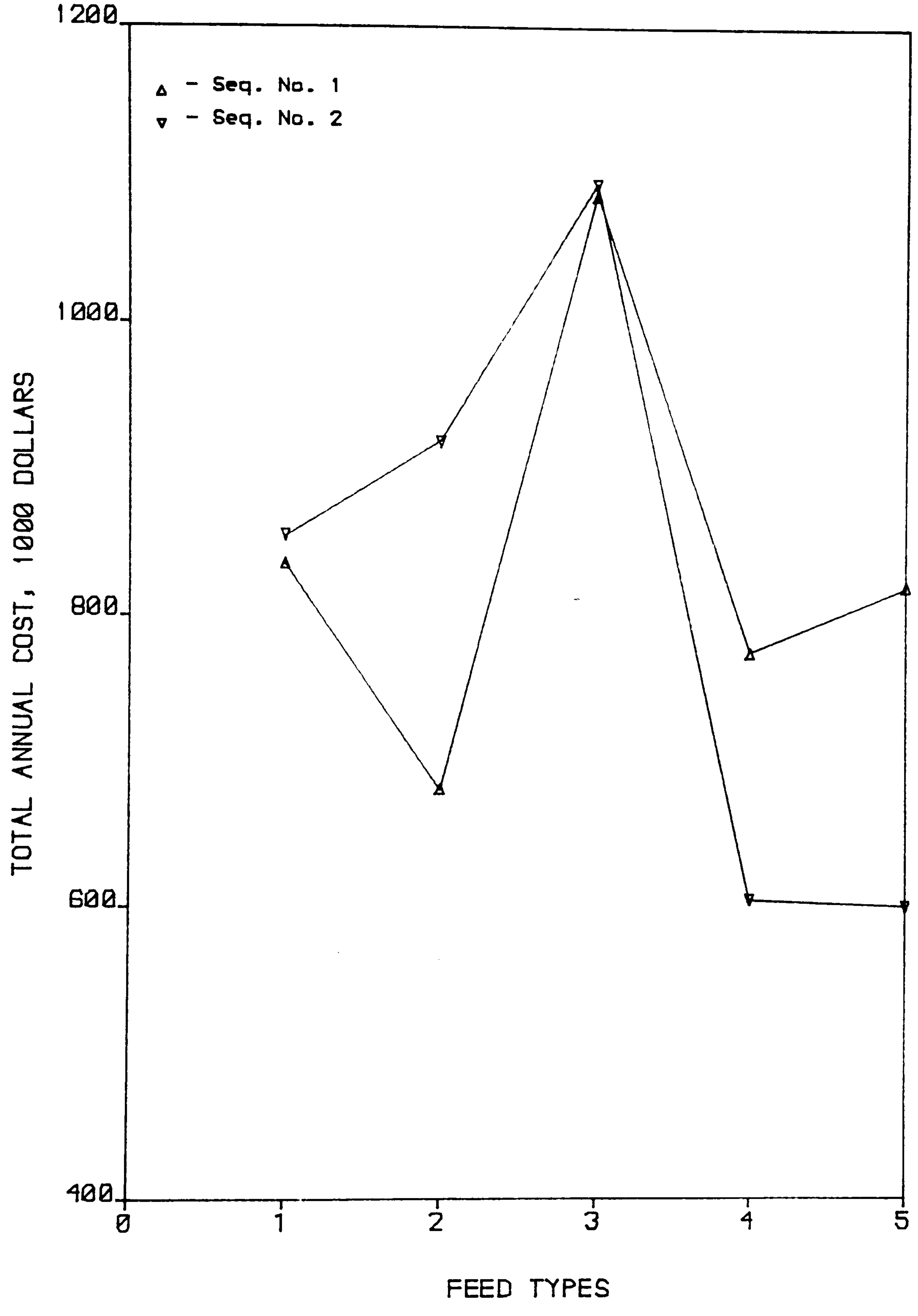


FIG. 4.12 TOTAL ANNUAL COST FOR POSSIBLE SEQUENCES OF A THREE-COMPONENT FEEDSTOCK NO. 2

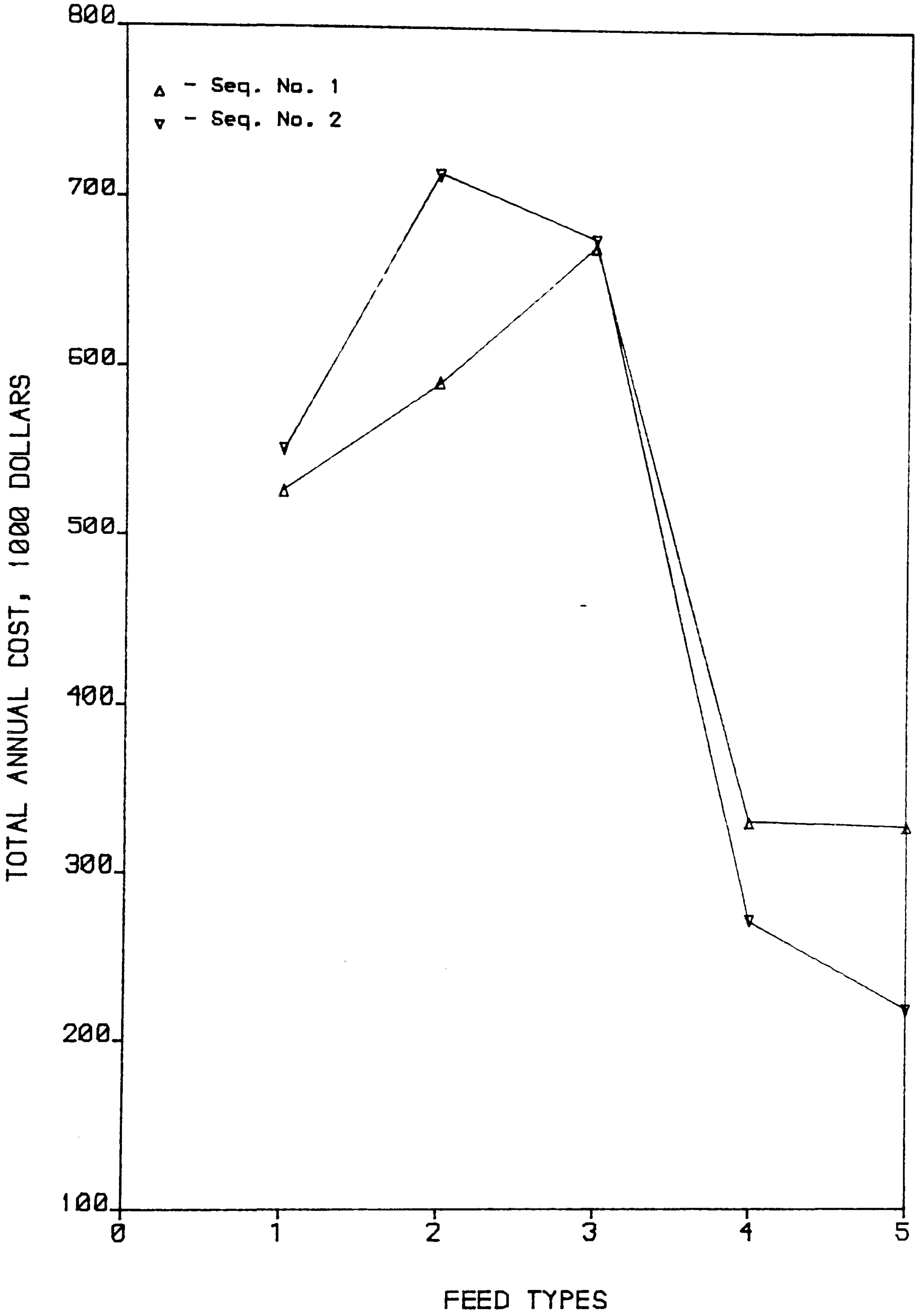


FIG. 4.13 TOTAL ANNUAL COST FOR POSSIBLE SEQUENCES OF A THREE-COMPONENT FEEDSTOCK NO. 3

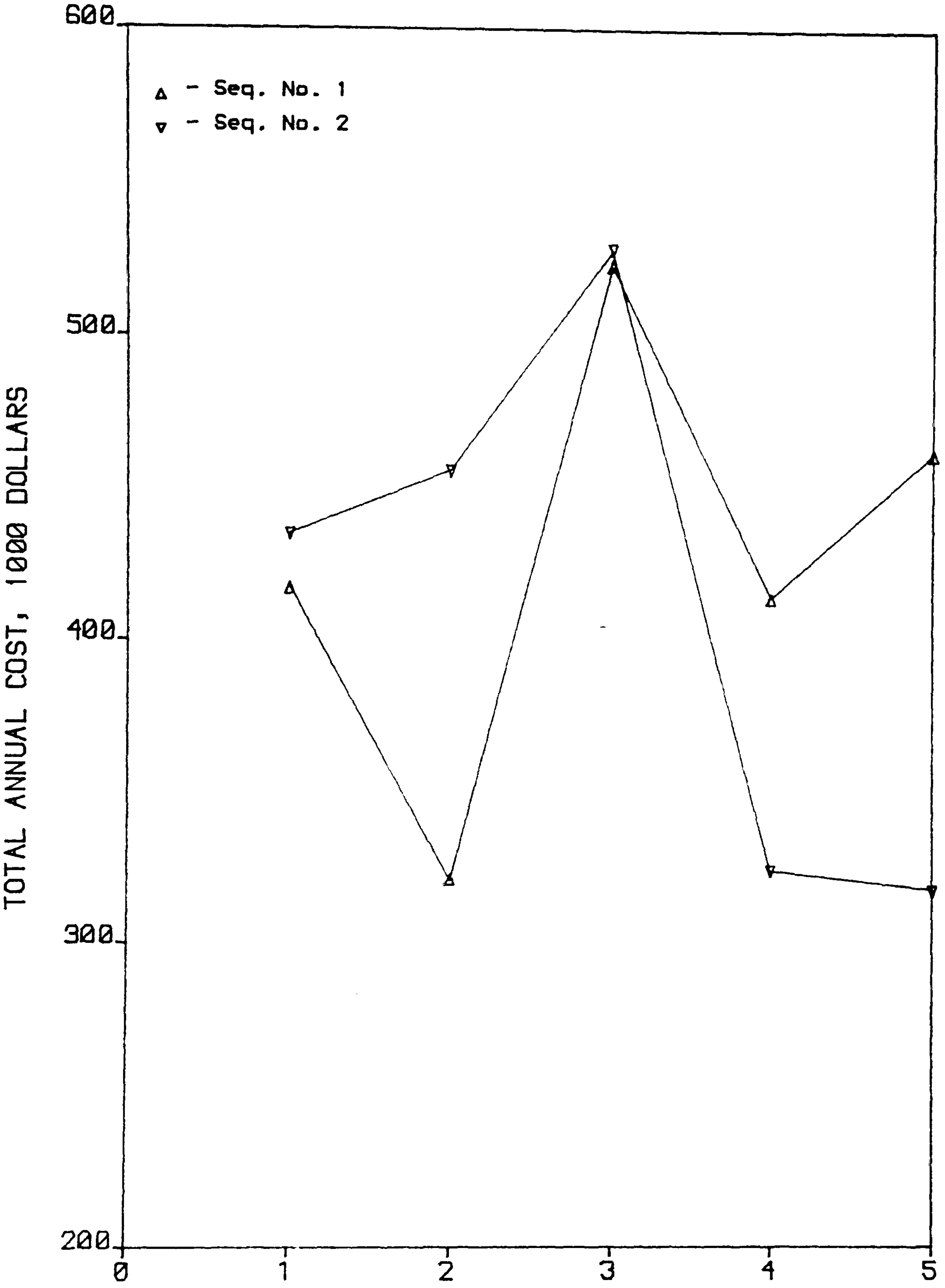


FIG. 4.14 TOTAL ANNUAL COST FOR POSSIBLE SEQUENCES OF A THREE-COMPONENT FEEDSTOCK NO. 4

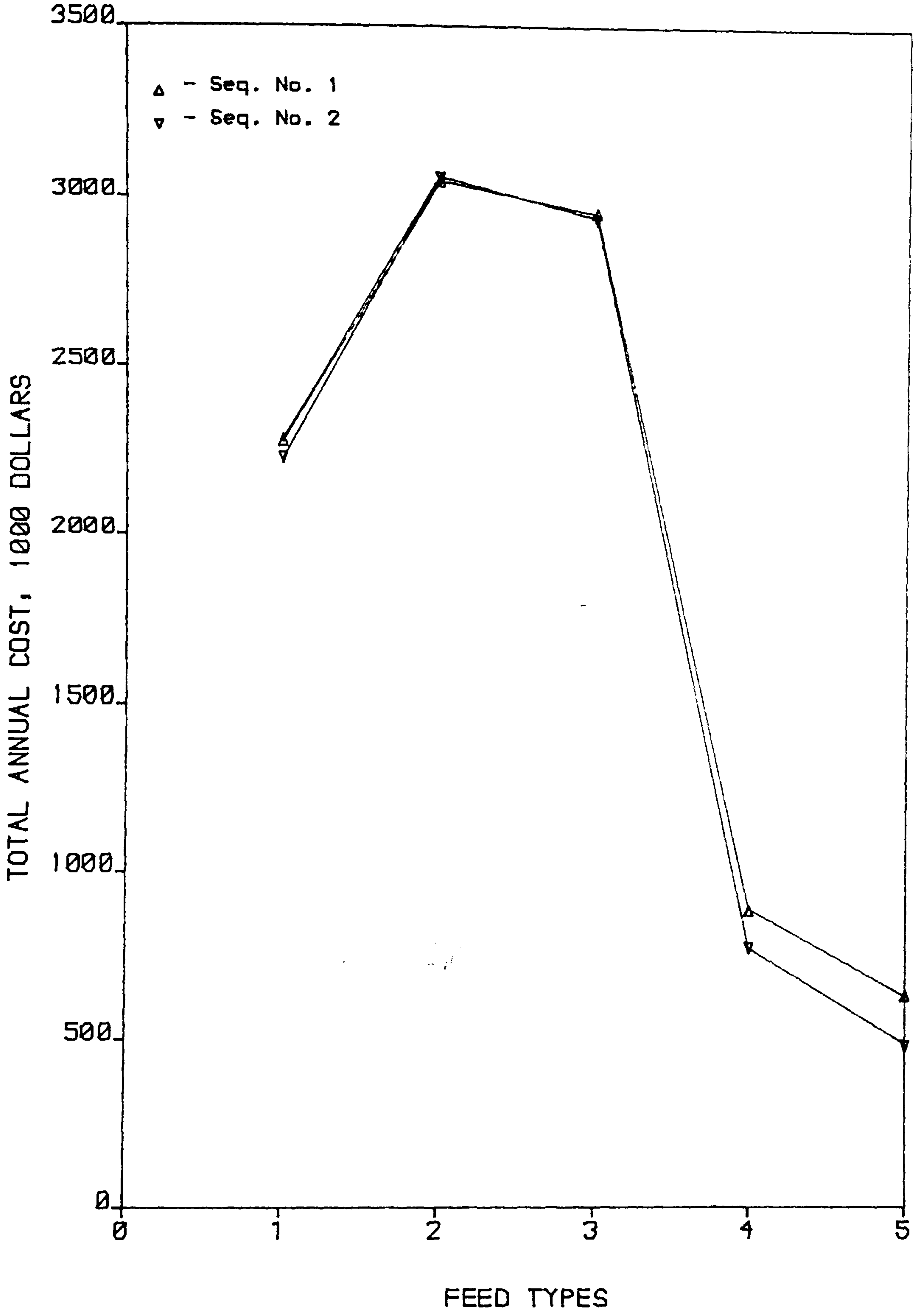


FIG. 4.15 TOTAL ANNUAL COST FOR POSSIBLE SEQUENCES OF A THREE-COMPONENT FEEDSTOCK NO. 5

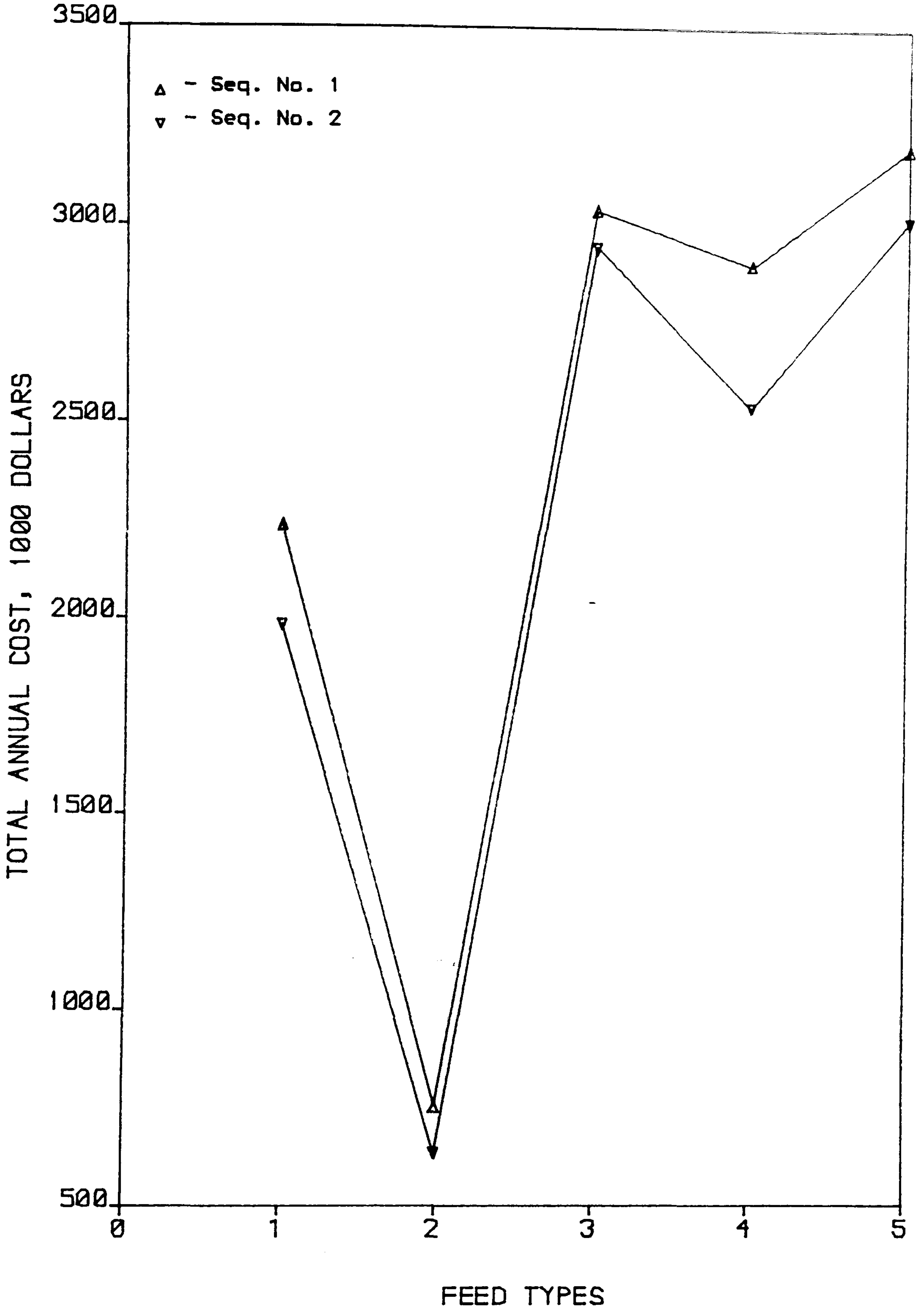


FIG. 4.16 TOTAL ANNUAL COST FOR POSSIBLE SEQUENCES OF A THREE-COMPONENT FEEDSTOCK NO. 6

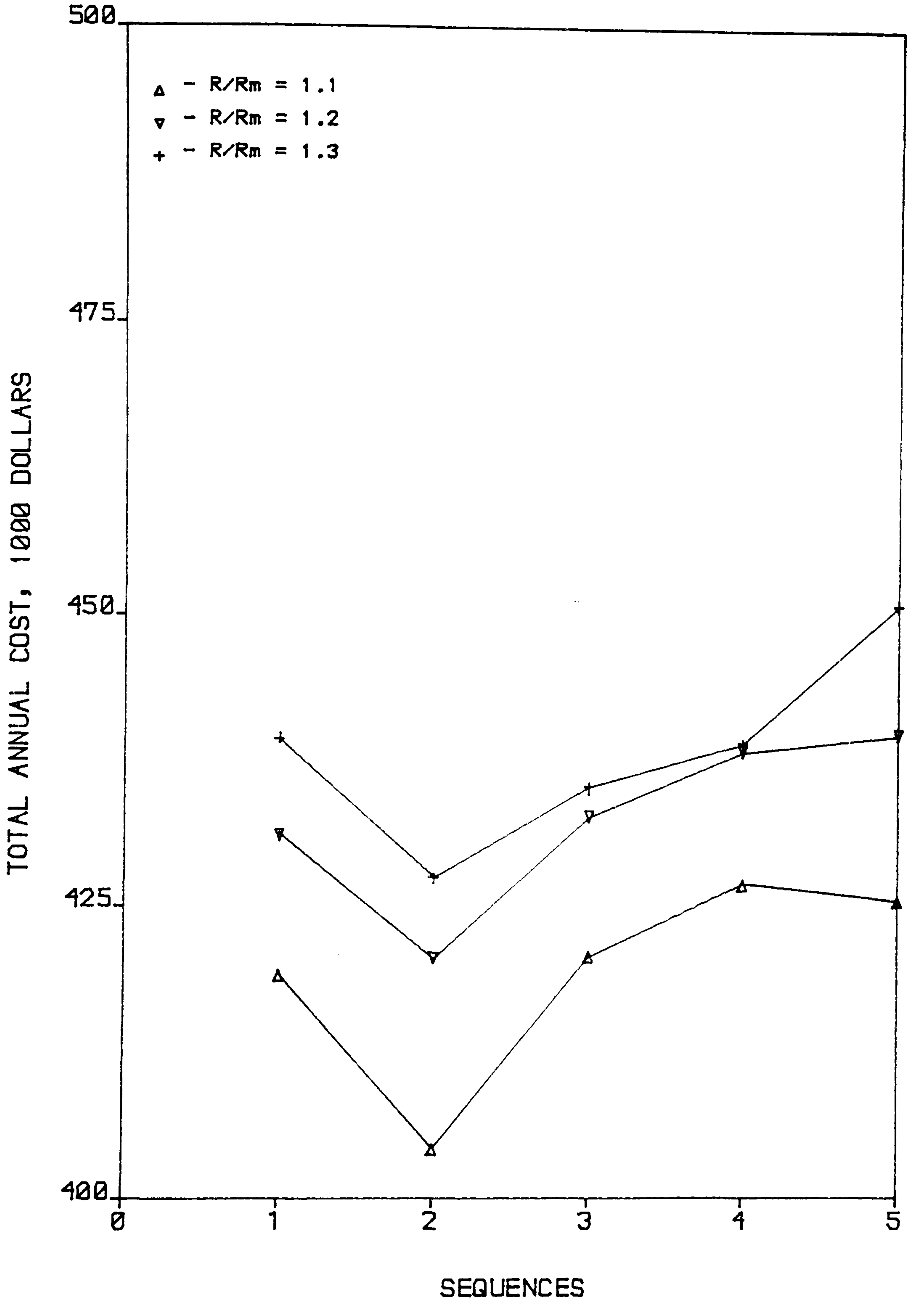


FIG. 4.17 THE EFFECT OF THE R/Rm ON THE TOTAL ANNUAL COST OF A FOUR-COMPONENT FFEDSTOCK NO. 1

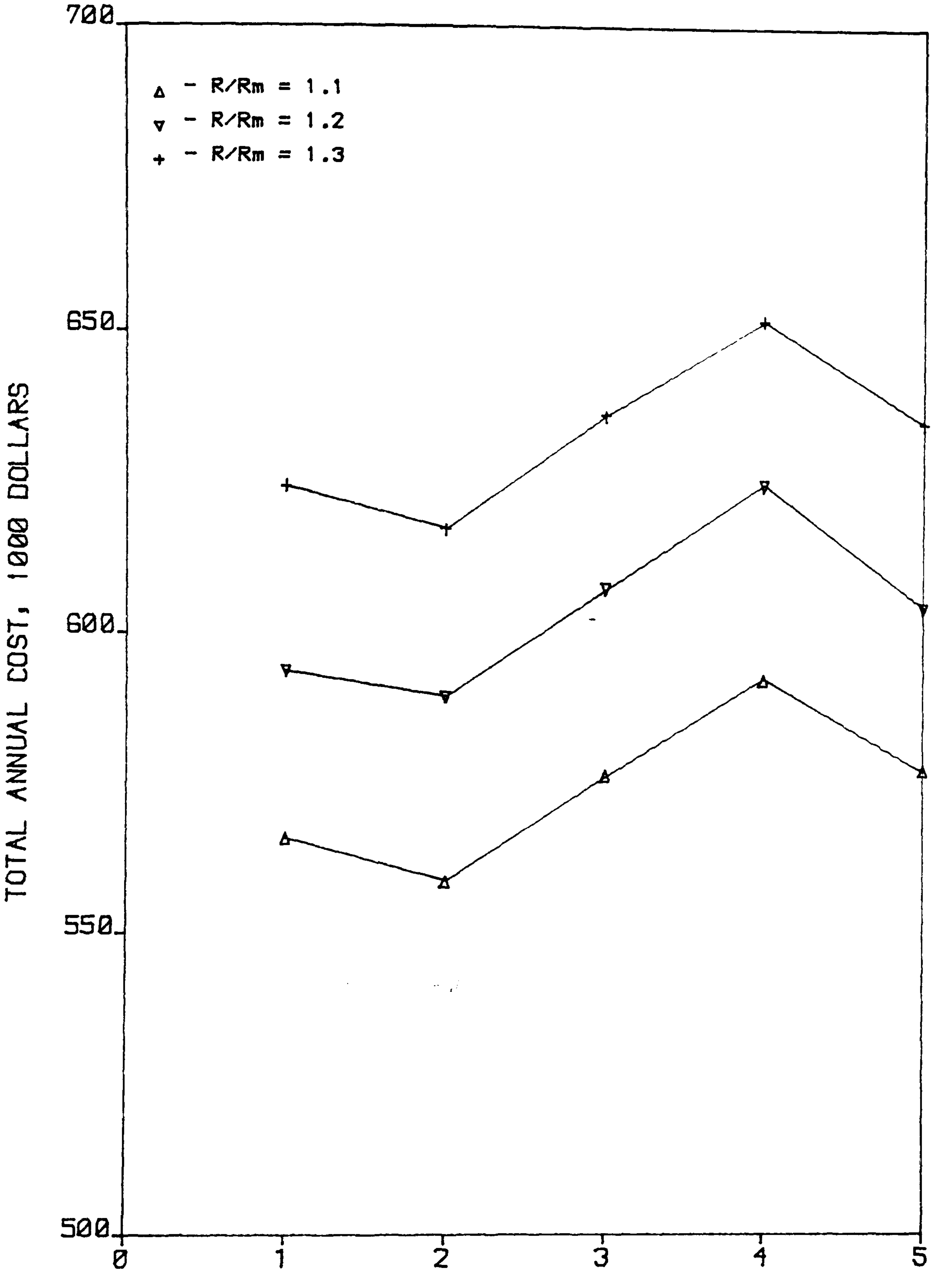


FIG. 4.18 THE EFFECT OF THE R/Rm ON THE TOTAL ANNUAL COST OF A FOUR-COMPONENT FFEDSTOCK NO. 2

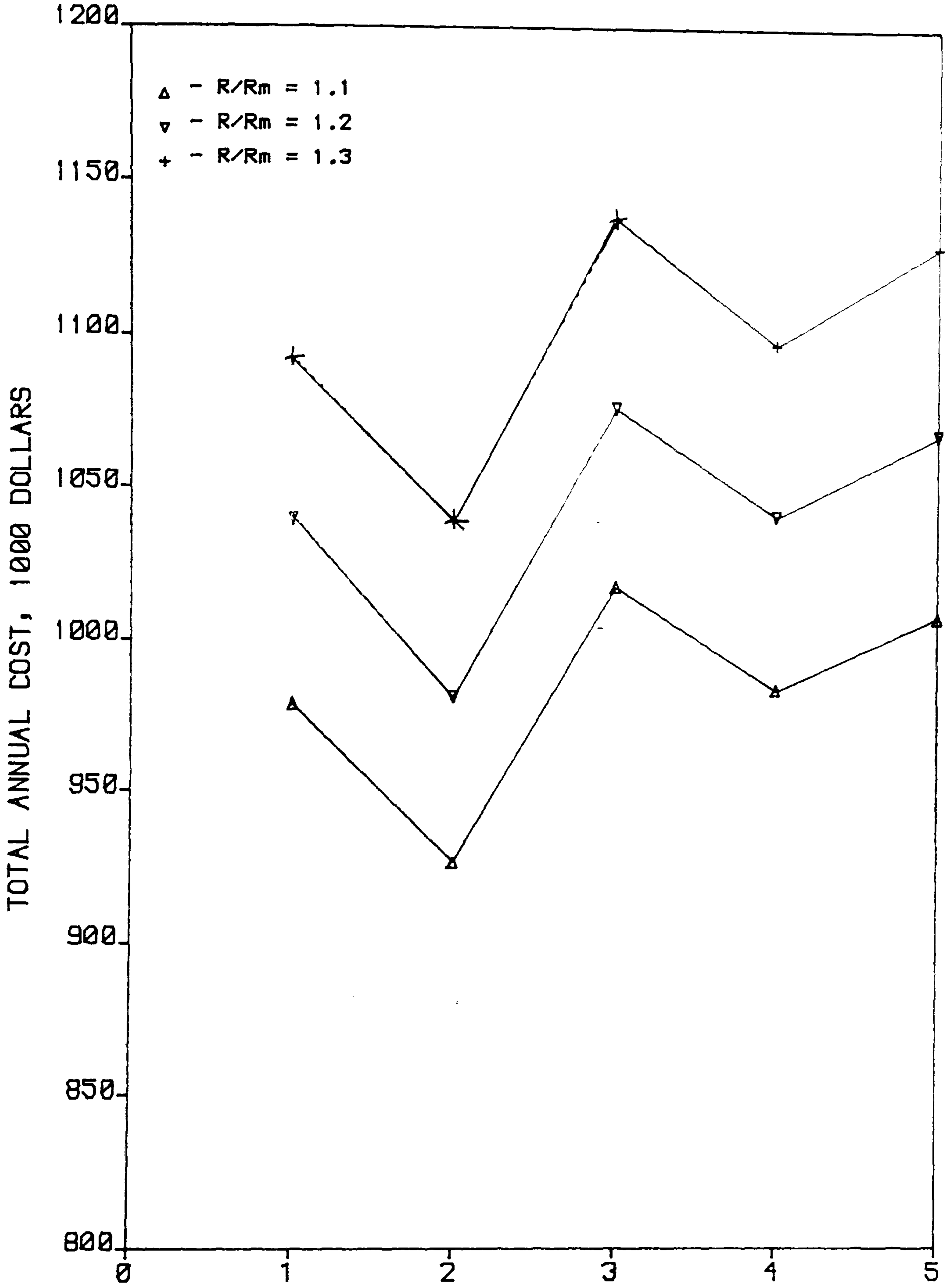


FIG. 4.19 THE EFFECT OF THE R/Rm ON THE TOTAL ANNUAL COST OF A FOUR-COMPONENT FFEDSTOCK NO. 3

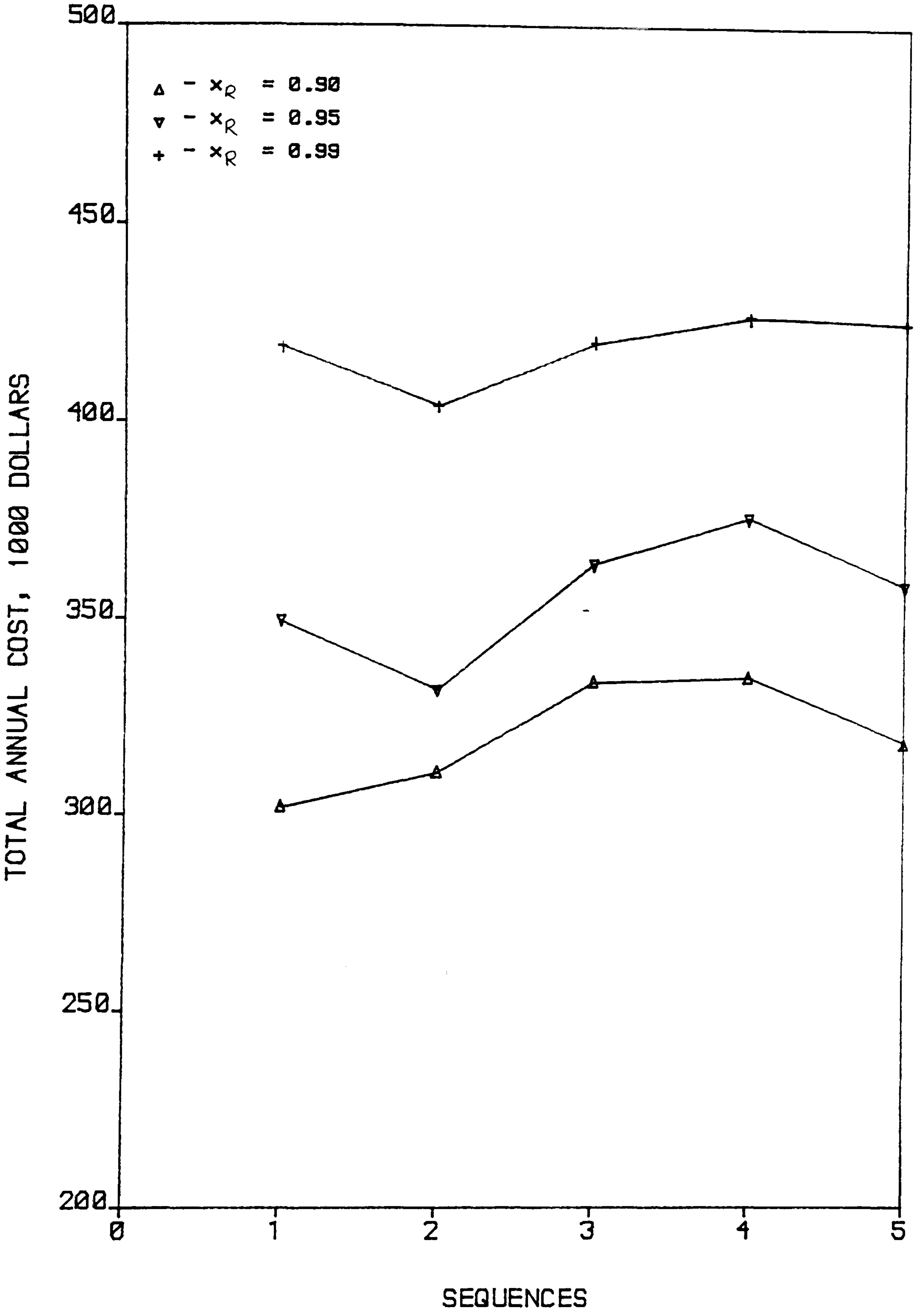


FIG. 4.20 THE EFFECT OF THE RECOVERY FRACTION ON THE TOTAL ANNUAL COST OF A FOUR-COMPONENT FEEDSTOCK NO. 1

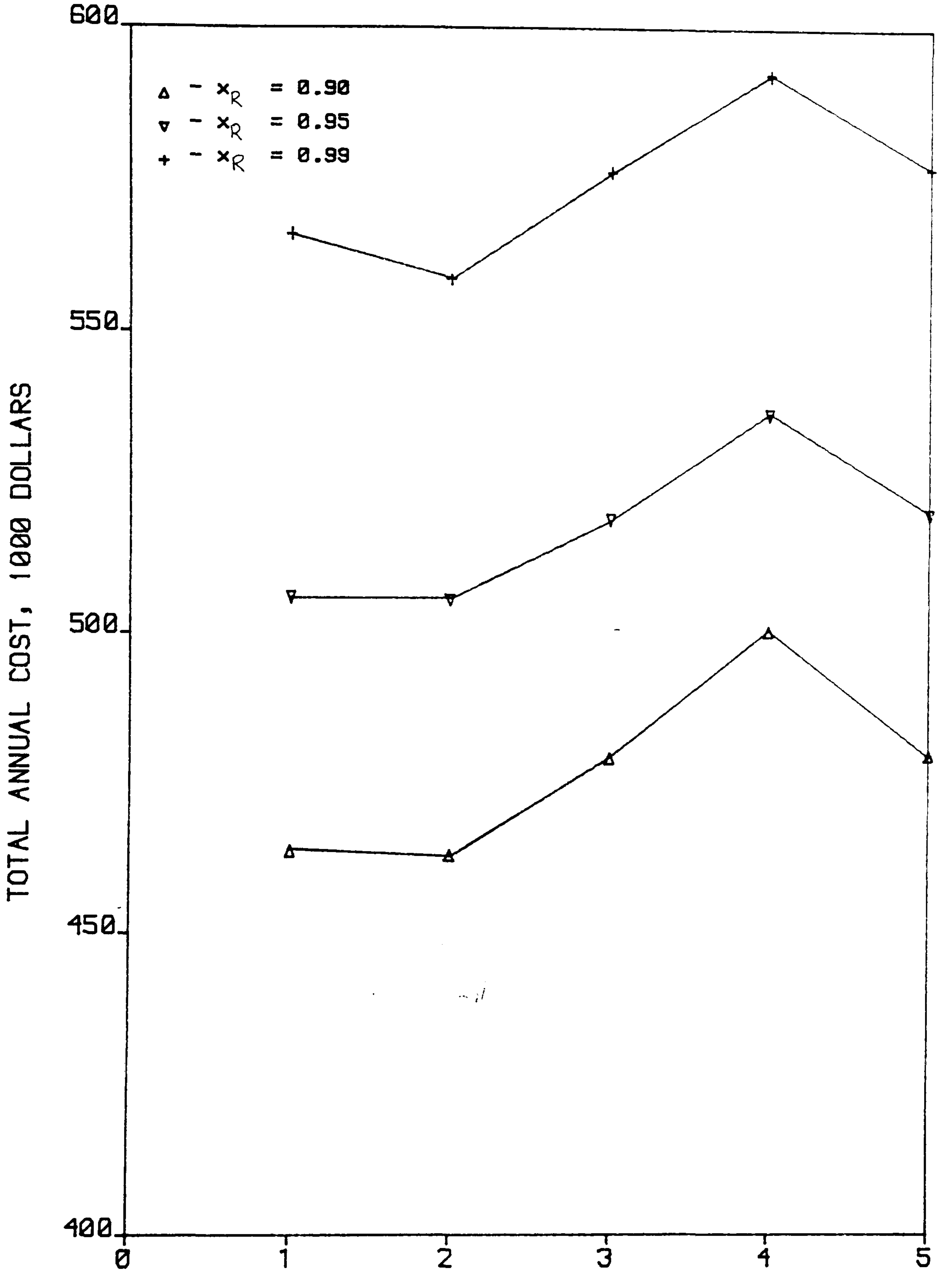


FIG. 4.21 THE EFFECT OF THE RECOVERY FRACTION ON THE TOTAL ANNUAL COST OF A FOUR-COMPONENT FEEDSTOCK NO. 2

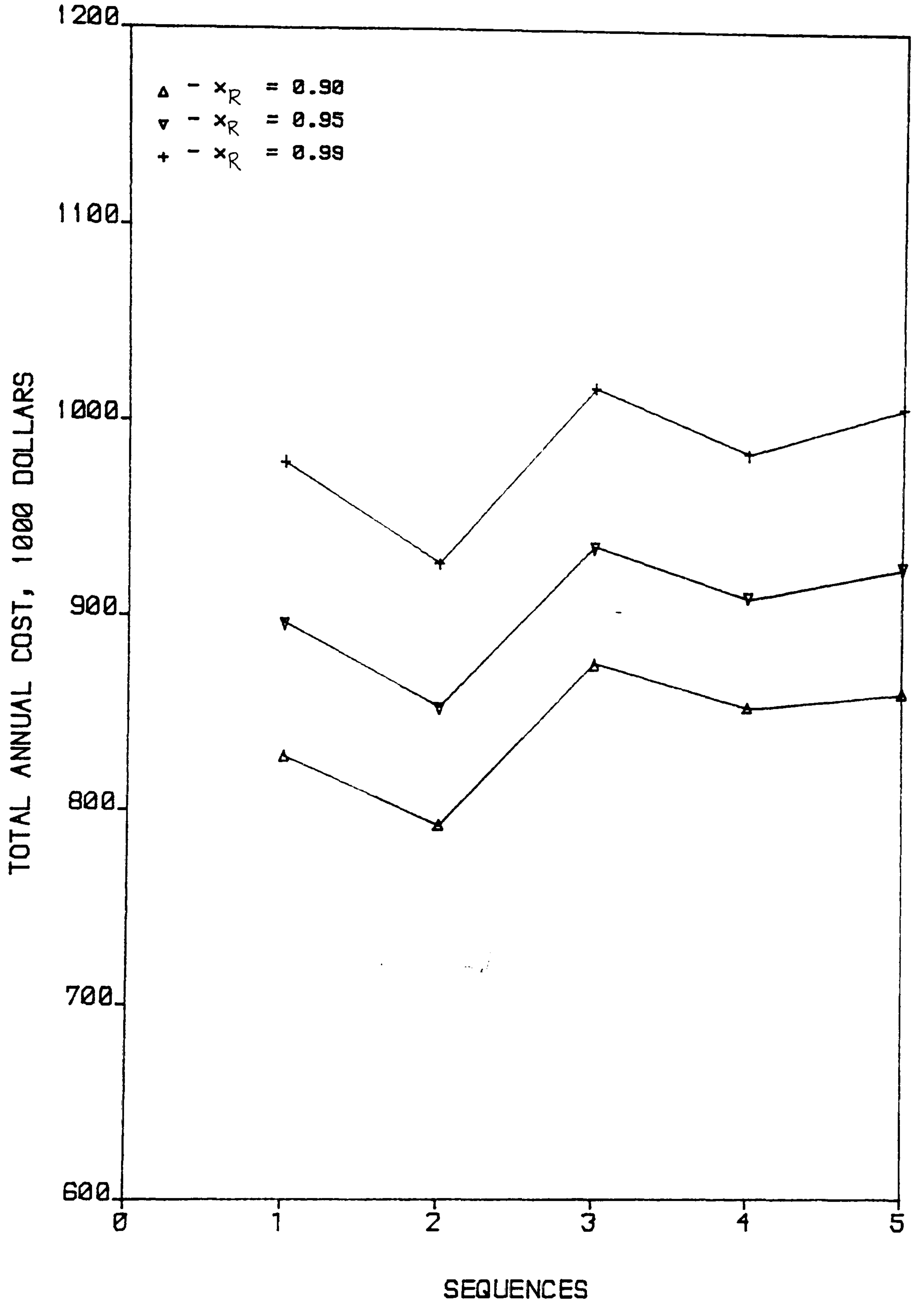


FIG. 4.22 THE EFFECT OF THE RECOVERY FRACTION ON THE TOTAL ANNUAL COST OF A FOUR-COMPONENT FEEDSTOCK NO. 3

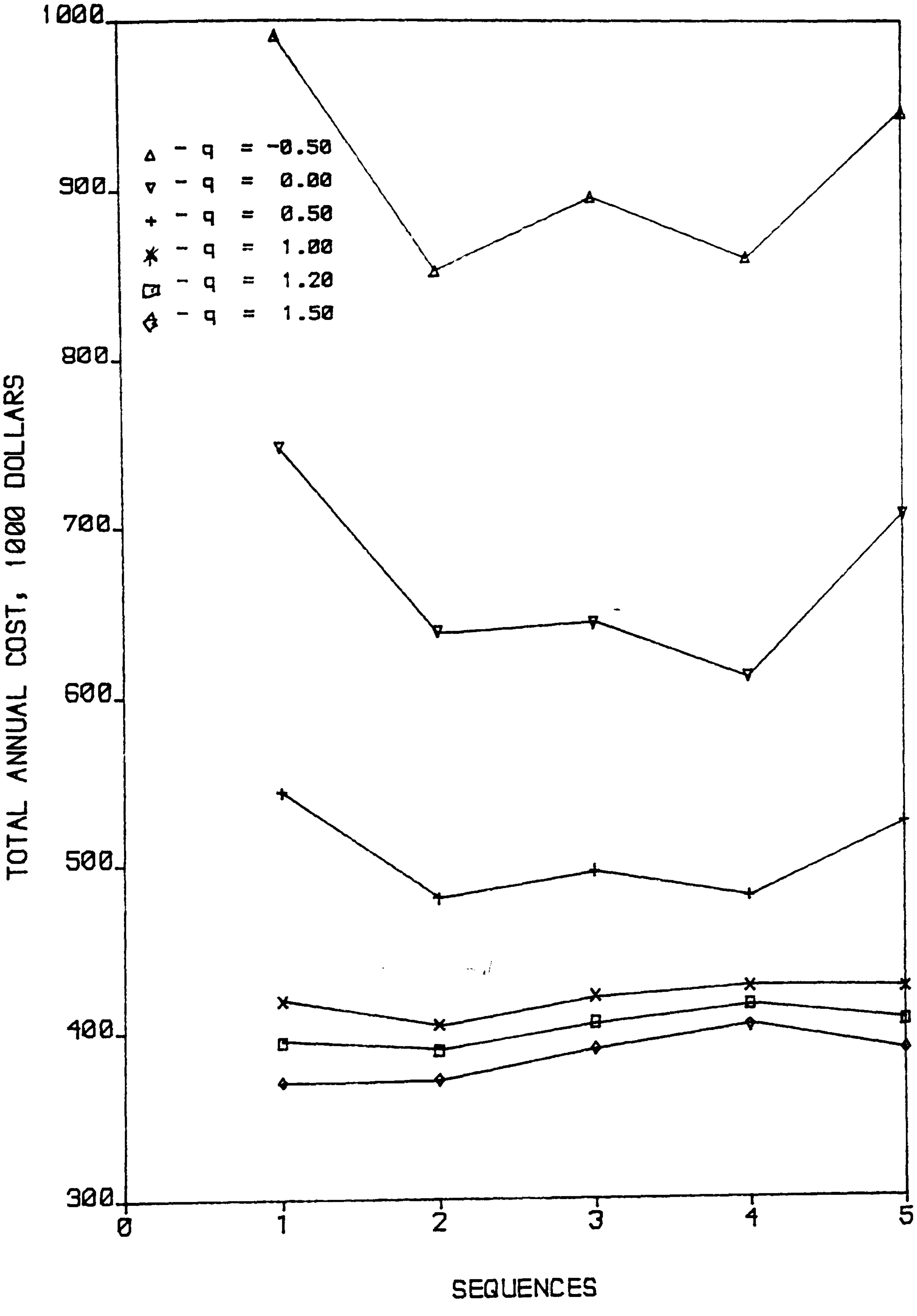


FIG. 4.23 THE EFFECT OF THE FEED VAPORISATION ON THE TOTAL ANNUAL COST OF A FOUR-COMPONENT FEEDSTOCK NO. 1

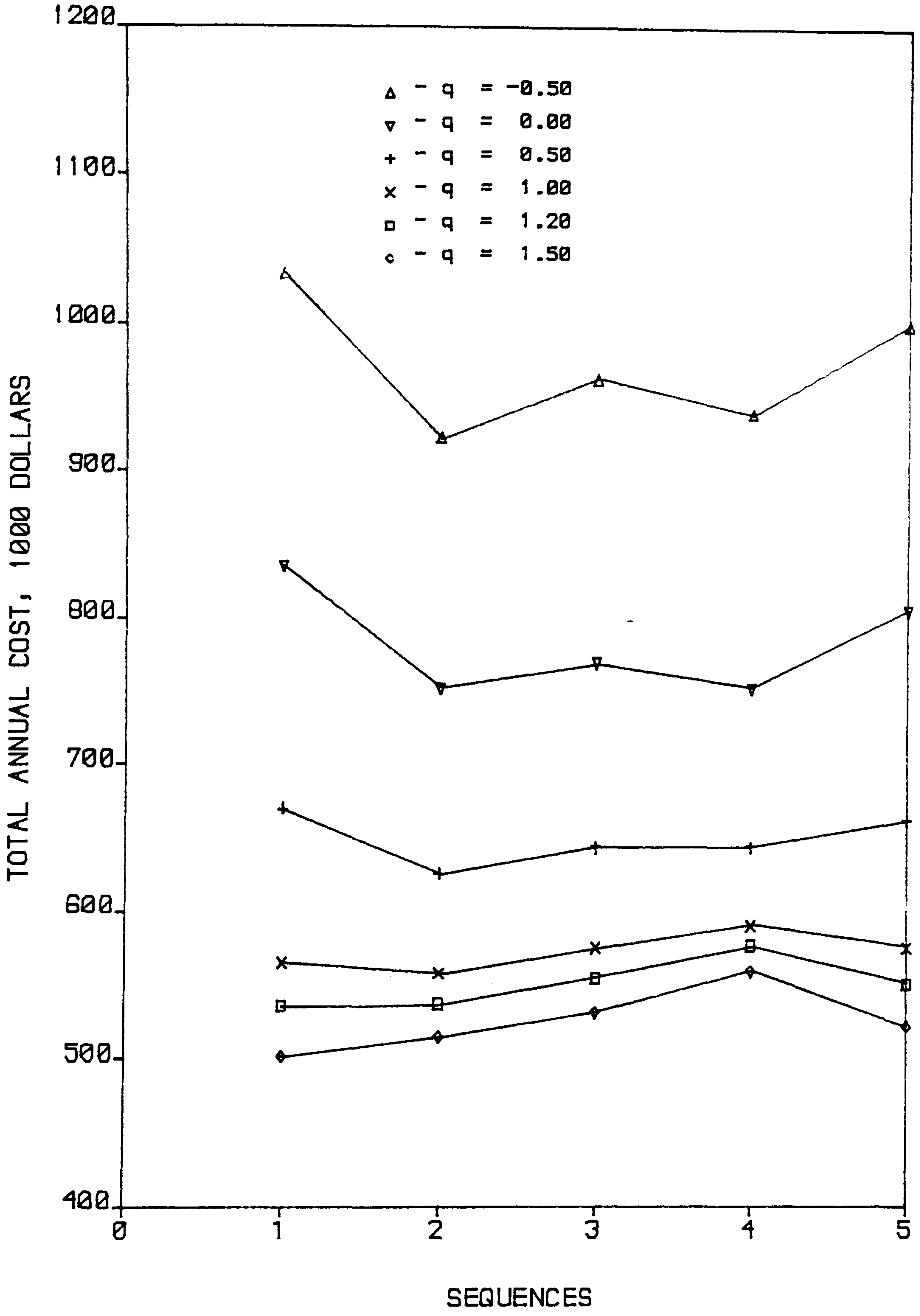


FIG. 4.24 THE EFFECT OF THE FEED VAPORISATION ON THE TOTAL ANNUAL COST OF A FOUR-COMPONENT FEEDSTOCK NO. 2

CHAPTER FIVE

AN EQUATION TO REPLACE THE "RULES OF THUMB"

5.1 Introduction

As already mentioned in chapter Four, a multicomponent mixture may be separated by alternative sequences of distillation columns. Thus for a ternary mixture ABC (where components A, B and C are listed in order of their volatilities) there are two possible sequences: either first separate A from BC and then separate B and C; or first separate C form AB and then separate A and B. And the number of possible sequences increases with increase in the number of components in the feed.[Table E1-1 in Appendix E].

Of the three techniques that are used for determining the optimal sequences of separation processes, the heuristic approach is the simplest. The other two (the algorithmic and evolutionary techniques) are complex, time consumming and require great mathematical background and computational skills from the users. In order to reduce this considerable amount of computation required by these methods, it is recommended [Seader and Westerberg(1977)] to start the optimisation calculation by first finding one or two sequences which are likely to be at or near the optimum. This is where the application of heuristics comes into play. In other words, most of the algorithmic and evolutionary techniques rely on the heuristics both to reduce the size of the search space and to provide a good initial solution for the evolutionary procedure.

More than 20 basic heuristics (rules of thumb) have been gathered in the literature. These have been identified in Chapter Two of the thesis. And as shown in chapter Four, the heuristics sometimes contradict each other. For example, if for a given separation the split that gives the lowest relative volatility between the key components has one of the components in excess, the two heuristics ["Remove the most plentiful component first" and "Do the difficult separation last"] point towards different decision. This sort of conflict, notwithstanding, the complexity and computational involvement of the other two techniques means that the heuristic technique will continue to play a significant role in the sequencing of separation processes. Therefore, it is worth deriving a quantitative expression to replace or supplement the heuristic rules. This is the core of this chapter.

The application of the new derived quantitative equation to all of examples published in the literature is examined. The simple equation makes an estimate of the cost of one sequence relative to that of another, and identified the optimum or near optimum sequences for all of the examples to which it was applied.

In fact, it provides a quantitative representation of the most powerful heuristics mentioned in the last chapter.

5.2 The Binary Distillation Total Vapour Load (BDTVL) Equation.

In the last chapter and from the published works, it was shown that the feed composition and the volatilities of the components involved in the feed to the sequence influence the order and cost of sequencing much more than any other variable. These variables (feed composition and relative volatility) are the ones usually used in the heuristics. Therefore, the equation which is derived below uses only this information used in the heuristics. The equation calculates an approximate value of the total vapour flow per mole of feed rate required for each sequences. The optimum sequence is that which requires the smallest value of the total vapour flow rate per mole of feed calculated by the equation.

The equation is based on the simplification of the problem listed below. It should be noted that because our objective is only to put all the possible sequences in order of their relative cost, a greater degree of simplification is permissible than if our objective was to approximate to the actual cost or actual vapour load of each sequences.

5.2.1 Simplifications and Assumptions.

The simplifications and assumptions to be used in the derivation of the equation are:

(1) Ignore the capital cost implications and base the analysis on energy cost only. This assumes either that a distillation is dominated by the energy cost or that there is a constant ratio between the energy cost contribution to the total cost and that of the capital cost. That a distillation sequence is dominated by energy cost have been shown to be true in the last two chapters. Many other workers [Doukas and Luyben(1987), Cheng and Luyben(1985), etc] have shown too that energy cost contributes as much as 80% to the total cost of a distillation column sequences, and in the last chapter, it was shown that listing sequences in order of energy cost in general produced the same order as in order of total annual cost.

(2)Assume that the total energy costs are proportional to the total overhead vapour load. Thus, the most economical sequence will be that with the minimum total vapour flow. This assumption has been used in previous works by Rod and Marek(1959) and Malone et al(1985).

(3) Assume sharp separations throughout the sequences. That is, the distillate contains only the light key and lighter components and the bottom contains only the heavy key and heavier components. This is the state of the art in synthesis of

distillation columns at the moment. All the previous workers utilised this simplification. Also it has been shown in previous chapter that degree of recovery has no effect on the choice of optimum sequence.

(4) Assume that the minimum reflux ratio, R_m, for the column may be calculated by the simple method for a binary mixture applied to the key components. That is, for key components, LK (Light Key) and HK (Heavy Key),

$$R_m = \frac{1}{(\alpha_{LH} - 1)}\left[\frac{x_{D,LK}}{x_{F,LK}} - \alpha_{LH} \cdot \frac{x_{D,HK}}{x_{F,HK}}\right] \qquad .....(5.1)$$

where subscript D and F refer to distillate and feed. [This simplification is the most difficult to justify and is discussed further towards the end of the chapter. The simplification implies that pinching occurs at the feed plate which may not be true for multicomponent distillation mixtures.] The actual reflux ratio, R, is then calculated by multiplying the minimum reflux ratio by a constant factor, R_f, of 1.1 or by a factor which varies to take into account materials of construction, cost of energy, etc. This is the sort of analysis carried out in Chapter Three. However, for the examples tested a factor of 1.1 is used.

It was shown in the previous chapter that R_f (i.e. R/R_m) has no effect on the choice of optimum sequences.

(5) The relative volatilities between the pair of adjacent components are constant throughout the sequence. The values are either taken from the literature where available or calculated at the feed conditions to the first column in the sequence.

5.2.2 Derivation

The equation derived is subsequently referred to as the Binary Distillation Total Vapour Load equation (BDTVL).

In the derivation of the BDTVL equation, it is to be noted that the assumption of the sharp separations implies that on the basis of one mole of feed, then mole fractions in the feed are equivalent to the molar flows of those components entering or leaving a column in the sequence.

Consider the separation of A + B +, ...LK from one mole of mixture of A + B +, ...LK + HK +...L + M. Assume that there are no HK+ ......L + M at the top. That is, x_{HK} and other heavier components are zero at the top of the column. Then from equation (5.1)

$$R_m = (x_{D,LK} / x_{F,LK}) \frac{1}{(\alpha_{LH} - 1)} \qquad \text{........(5.2)}$$

where α_{LH} is the relative volatility between the Light (L) and Heavy (H) key components.

But the vapour flow, V, for individual column is

$$V = (1 + R)\, D \qquad \ldots\ldots\ldots\ldots(5.3)$$

where D is the moles of distillate.

For $R = R_f R_m$ Equation (5.3) becomes

$$V = (1 + R_f\, R_m)\, D \qquad \ldots\ldots\ldots(5.4)$$

$$= \left[\frac{(\alpha_{LH} - 1) + R_f(x_{D,LK} / x_{F,LK})}{(\alpha_{LH} - 1)}\right] D \qquad \ldots\ldots(5.5)$$

$$V = \left[\frac{\Delta_{LH} + R_f\, x_{D,LK} / x_{F,LK}}{\Delta_{LH}}\right] D \qquad \ldots\ldots(5.6)$$

[Note: $\Delta_{LH} = \alpha_{LH} - 1$]

$$\text{Now } D = x_A + x_B + x_C + \ldots\ldots x_{LK} \qquad \ldots\ldots(5.7)$$

and $$x_{F,LK} = x_{LK} / (x_A + x_B + x_C \ldots + x_{LK} + x_{HK} + \ldots\ldots x_M) \qquad \ldots(5.8)$$

$$x_{D,LK} = x_{LK} / (x_A + x_B + x_C \ldots + x_{LK}) \qquad \ldots\ldots\ldots(5.9)$$

Substituting Equations (5.7) to (5.9) in Equation (5.6) gives

$$V = (x_A + x_B + \ldots . x_{LK}) + \frac{R_f}{\Delta_{LH}} (x_A + x_B + \ldots x_{LK} + x_{HK} + \ldots\, \ldots x_M) \qquad \ldots\ldots\ldots\ldots(5.10)$$

This is the equation which links relative volatilites and concentrations.

For the sequence as a whole, the total vapour load per mole of feed is the sum of the vapour loads for each of the individual column which is thus

$$V_B = \sum_{j}^{nc} V_j \qquad \text{.........(5.11)}$$

(nc is the number of columns in the sequence)

By inspection and intuitive analysis, Equation (5.11) results in a general equation of the form

$$V_B = \sum_{i=1}^{n} k_i x_i + R_f \left[\frac{1}{\Delta_{LH,1}} + \sum_{j=2}^{nc} \sum_{i=1}^{n} \frac{r_i x_{i,j}}{\Delta_{LH,j}} \right] \qquad \text{....................(5.12)}$$

where

V_B = total vapour load per mole of feed for the sequence as a whole.

k_i = number of times component i appear in top product either alone or with other components throughout the sequence.

$\Delta_{LH,1}$ $\Delta_{LH,j}$ = $(\alpha_{LH} - 1)$ of the first and j column respectively in any sequence. α_{LH} is the relative volatility between the light (L) and Heavy (H) key components.

x_i = mole fraction of component i in the original feed.

$x_{i,j}$ = mole fraction of component i in the original feed for a stream entering column j

r_i = 1: if component i exists in the stream entering column j.

= 0: if component i does not exist in the stream entering column j.

n, nc = number of components and columns respectively.

5.2.3 Using the equation for calculating vapour loads.

Equation (5.12) is simple to use in calculating the total vapour flow rate per mole of feed throughout a particular sequence. We shall just illustrate this with three sequences of say a five-component mixture. Consider sequences 1, 8 and 3 of Figure E1-3 (in Appendix E). These are reproduced below in Figure 5.1 for easy illustration.

The steps of calculation are set out in Table 5.1 below which is self-explanatory.

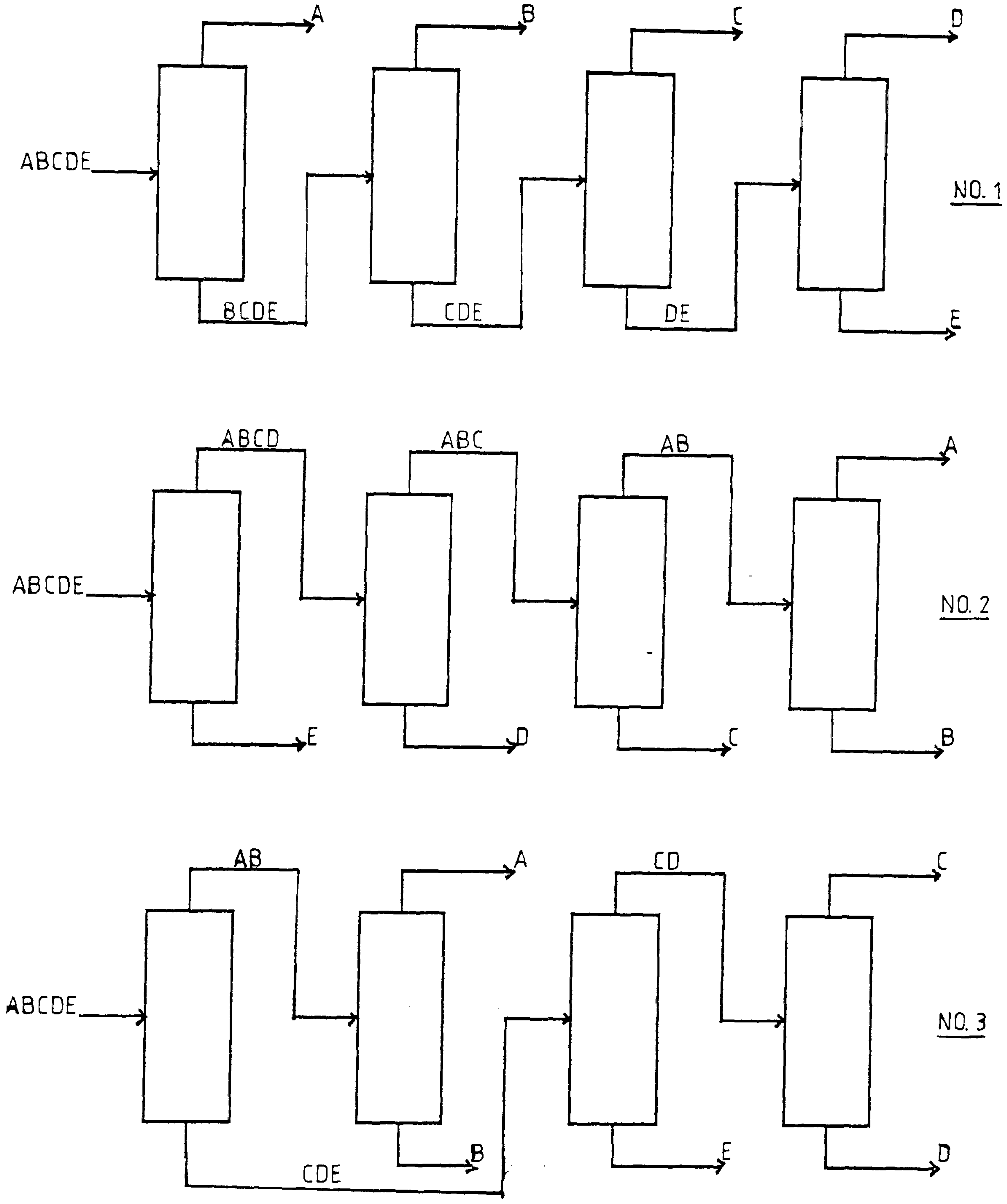


FIG. 5.1 SAMPLE OF THREE POSSIBLE SEQUENCES OF A FIVE-COMPONENT MIXTURE.

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TABLE 5.1: Calculating the binary vapour flow rate by the BDTVL equation.

Variables	Sequence No. 1	Sequence No. 2	Sequence No. 3
No. of times component a appears as top product, i.e k			
k_A	1	4	3
k_B	1	3	1
k_C	1	2	2
k_D	1	1	1
k_E	0	0	0
For col. 2 (i.e. j=2)	LK=B;HL=C	LK=C;HK=D	LK=A;HK=B
r_A	0	1	1
r_B	1	1	1
r_C	1	1	0
r_D	1	1	0
r_E	1	0	0
For col. 3 (i.e. j=3)	LK=C;HL=D	LK=B;HK=C	LK=D;HK=E
r_A	0	1	0
r_B	0	1	0
r_C	1	1	1
r_D	1	0	1
r_E	1	0	1
For col. 4 (i.e. j=4)	LK=D;HL=E	LK=A;HK=B	LK=C;HK=D
r_A	0	1	0
r_B	0	1	0
r_C	0	0	1
r_D	1	0	1
r_E	1	0	0

For the sequence No.1 in the Figure 5.1,

$$V_B = x_A + x_B + x_C + x_D + R_f\left[\frac{1}{\Delta_{AB}} + \frac{(x_B + x_C + x_D + x_E)}{\Delta_{BC}} + \frac{(x_C + x_D + x_E)}{\Delta_{CD}} + \frac{(x_D + x_E)}{\Delta_{DE}}\right. \qquad \ldots\ldots\ldots(5.13)$$

For sequence No. 2,

$$V_B = 4x_A + 3x_B + 2x_C + x_D + R_f\left[\frac{1}{\Delta_{DE}} + \frac{(x_A + x_B + x_C + x_D)}{\Delta_{CD}} + \frac{(x_A + x_B + x_C)}{\Delta_{BC}} + \frac{(x_A + x_B)}{\Delta_{AB}}\right. \qquad \ldots\ldots\ldots(5.14)$$

For sequence No. 3,

$$V_B = 2x_A + x_B + 2x_C + x_D + R_f\left[\frac{1}{\Delta_{BC}} + \frac{(x_A + x_B)}{\Delta_{AB}} + \frac{(x_C + x_D + x_E)}{\Delta_{DE}} + \frac{(x_C + x_D)}{\Delta_{CD}}\right. \qquad \ldots\ldots\ldots(5.15)$$

The Equation (5.12) as illustrated from the examples above is straightforward and easy to use. It does not require any mathematical technique or skill form the user. Any number of component mixtures can be evaluated easily on a hand calculator.

5.3 Further Applications to Examples of Real mixtures.

To test the applicability of the equation derived above, the equation is applied to all the examples published in the literature which we have found so far for an ordinary distillation column sequences. The various authors are cited on the tables of results given.

Many other examples of real mixtures (e.g those of previous chapter) some of which have been invented by us are also tested.

All the results are listed in Tables 5.2 to 5.5 and Tables A5.1 to A5.10 in Appendix A.

Note that the Underwood total vapour load is calculated as define by Equation (5.3) with R_m obtained from the two equations (B2-1) and (B2-2) defined in the Appendix B as also given below:

$$1 - q = \Sigma \frac{\alpha_i x_{F,i}}{\alpha_i - \theta} \quad \text{........(B2-1)}$$

$$\text{and } R_m + 1 = \Sigma \frac{\alpha_i x_{D,i}}{\alpha_i - \theta} \quad \text{.......(B2-2)}$$

where q is the q-line which is usually defined as the heat required to convert one mole of feed from its condition to a saturated vapour, divided by the molar latent heat.[Treybal(1980)] x is the mole fraction of feed (F) or distillate (D); and θ is the root of the equation.

The Underwood equation is a well established shortcut method for determining the minimum reflux ratio for multicomponent mixtures in a distillation column.

TABLE 5.2: List of BDTVL vapour load, Underwood vapour load and the Total Annual Cost (TAC) in dollars.

Six-component mixture [Stephanopoulos et al(1982,1984)] of

	Mole fraction	Relative Volatility.
A: i-Butane	0.05	1.3714
B: n-Butane	0.05	1.3929
C: neo-Pentane	0.10	2.2308
D: n-Pentane	0.15	2.9678
E: n-Hexane	0.25	2.8736
F: n-Heptane	0.40	

Feed: Saturated liquid in all colums (453.6 Kmol/hr)

Sequence in the order of TAC*	V_B	V_U	TAC in Dollars
1	3.0595	2.3894	2746441
2	3.0901	2.4090	2821804
3	3.1659	2.4196	2830617
4	3.3031	2.4298	2831493
5	3.3287	2.4474	2856575
6	3.3431	2.4718	2905981
7	3.3914	2.4731	2915669
8	3.4092	2.4917	2920143
9	3.4349	2.4927	2940751
10	3.4493	2.5135	2953942
11	3.4976	2.5219	2995507
12	3.5153	2.5255	3012023
13	3.6220	2.5290	3029305

* the order of cost as taken from the reference.

V_B = vapour flow per mole of feed by the BDTVL Equation.

V_U = vapour flow per mole of feed by the Underwood Equation.

TAC = total annual cost in dollars as calculated by the design and costing equations described in Chapter Nine.

TABLE 5.3: List of BDTVL vapour load, Underwood vapour load and the Total Annual Cost (TAC) in dollars.

Five-component mixture [Nadgir and Liu(1981); Stephanopoulos et al(1982,1984)] of

	Mole fraction	Relative Volatility.
A: Propane	0.05	2.00
B: i-Butane	0.15	1.33
C: n-Butane	0.25	2.40
D: i-Pentane	0.20	1.25
E: n-Pentane	0.35	

Feed: Saturated liquid in all colums (907.2 Kmol/hr)

Sequence in the order of TAC*	V_B	V_U	TAC in Dollars
1	5.8257	5.3320	8342116
2	5.8840	5.3473	8490177
3	6.3998	5.3947	9075389

* the order of cost as given by the authors.

TABLE 5.4: List of BDTVL vapour load, Underwood vapour load and the Total Annual Cost (TAC) in dollars.

Five-component mixture [Stephanopoulos et al(1982,1984)] of

	Mole fraction	Relative Volatility.
A: i-Butane	0.200	1.9102
B: neo-Pentane	0.175	2.2308
C: n-Pentane	0.200	2.2166
D: 2-Methyl Pentane	0.250	1.9992
E: Cyclohexane	0.175	

Feed: Saturated liquid in all colums (907.2 Kmol/hr)

Sequence in the order of TAC*	V_B	V_U	TAC in Dollars
1	3.4049	2.6547	5602310
2	3.6021	2.7547	5700857
3	3.6668	2.7879	5933722

* the order of cost as given by the authors.

TABLE 5.5: List of BDTVL vapour load, Underwood vapour load and the Total Annual Cost (TAC) in dollars.

Three-component mixture [Nishimura and Hiraizumi(1971); Doukas and Luyben(1978)]

	Relative Volatility.
A: Benzene	2.8664
B: Toluene	2.6200
C: O-xylene	

(Feed rate) Feed Composition	Seq. in order* of cost	V_B	V_U	TAC in Dollars
(270) 0.37,0.37,0.26	1	1.7571	1.6308	1659263
	2	2.2251	1.9849	1815548
(300) 0.33,0.33,0.34	1	1.7043	1.5398	1854914
	2	2.0580	1.8245	1923381
(900) 0.11,0.11,0.78	1	1.1387	0.9968	4242720
	2	1.4137	1.0574	5544617
(1200) 0.083,0.083,0.834	1	1.0258	0.9094	5526720
	2	1.3780	1.0028	7472997

* the order of cost as given by the authors.

5.4 Discussion of the Results.

Equation (5.10) provides a quantitative expression for the most powerful heuristics. Thus heuristic "To favour the direct sequence" produces a minimum value of the sum of the first (distillate) terms, while the heuristics "Do the easiest separation first" and "Do the most difficult separation last" comply with a minimum value for the sum of the second (feed) terms. The heuristic "Remove the dominant component first" will correspond to reducing the values for both the sum of the first and second terms in the subsequent columns.

Furthermore, the heuristic "Favour 50/50 split" also complies with the minimum value for the sum of the second terms.

In Table 5.2 we list the binary distillation total vapour flows per mole of feed calculated by BDTVL equation (5.12) for 13 sequences considered by Stephanopoulos et al(1982,1984) to be the near optimum sequences out of the 42 possible sequences for the six-component mixture used as an example by the authors. The results given in Table 5.2 are listed in the order of cost calculated by them. The table shows that the BDTVL values appear in the same order. Also shown is the total vapour flow based upon Underwood(1948) equation and the total annual cost (TAC) calculated by our own cost estimating computer program which is based on the design method of Hengstebeck-Geddes(1958) - Fenske(1932) - Underwood(1948) - Erbar-Maddox(1961) relations combined with a rigorous multicomponent distillation design procedure based on the model of Naphtali and Sandholm(1971). The order of sequence as given by our BDTVL equation agrees with that of Stephanopoulos et al(1982,1984) and with that calculated by the Underwood equation and our total annual cost.

Tables 5.3 to 5.5 list similar results for other published examples. In each case only the results for the three lowest cost sequences are shown. This is as put in the order calculated in the reference(s) shown. The BDTVL equation has identified the lowest cost sequence for each case shown.

Some other results for 10 of the feedstocks used in the previous chapter are discussed later in the chapter. The results are given in Tables A5.1 to A5.10 in Appendix A.

This is a useful result but somewhat surprising in view of the simplifications used in the derivation of the equation (5.10) particularly the assumption that the minimum reflux ratio may be calculated as for a binary mixture in terms of the relative volatility of the key components only. It is known that the presence of other components and their volatilities influences the separation, and that more complicated methods are required to calculate the minimum reflux ratio, such as the method of Underwood(1948) or a numerical calculation for each column.

It is of interest to consider why the method based on the Equations (5.10 and 5.12) succeeds in the way it does as shown in the tables of results. Figure 5.2 shows sequences presented in their order of relative cost by Stephanopoulos et al(1982,1984), the relative total vapour loads calculated by the Underwood minimum reflux equation and the BDTVL equation. The comparison of Underwood with Stephanopoulos et al's relative costs provides an illustration of the validity of the assumption that the total vapour of a sequence is in reasonable agreement with its total cost. The comparison of the relative BDTVL vapour load with the other two lines shows that the BDTVL method is a more sensitive way of distinguishing between sequences; and this method of comparison becomes more accurate as the optimum or near optimum column sequences are approached. This is illustrated also in Figure 5.3 which compares the BDTVL vapour load with the vapour load estimated by the more accurate Underwood method for the 42 sequences of the six-component mixure of Stephanopoulos et al. [The lowest number on the graph is the best sequence followed by number two, then three, etc.].

The accuracy of the BDTVL vapour load method increases significantly as the optimum sequence is approached. This is because as the optimum sequence is approached, the difficult separations which require most of the energy and capital costs move towards the end of the sequence. [That is, they tend to become binary separations], whereas easy separations become the multicomponent separations at the beginning of the sequence. This is in agreement with the rules of thumb as discussed above.

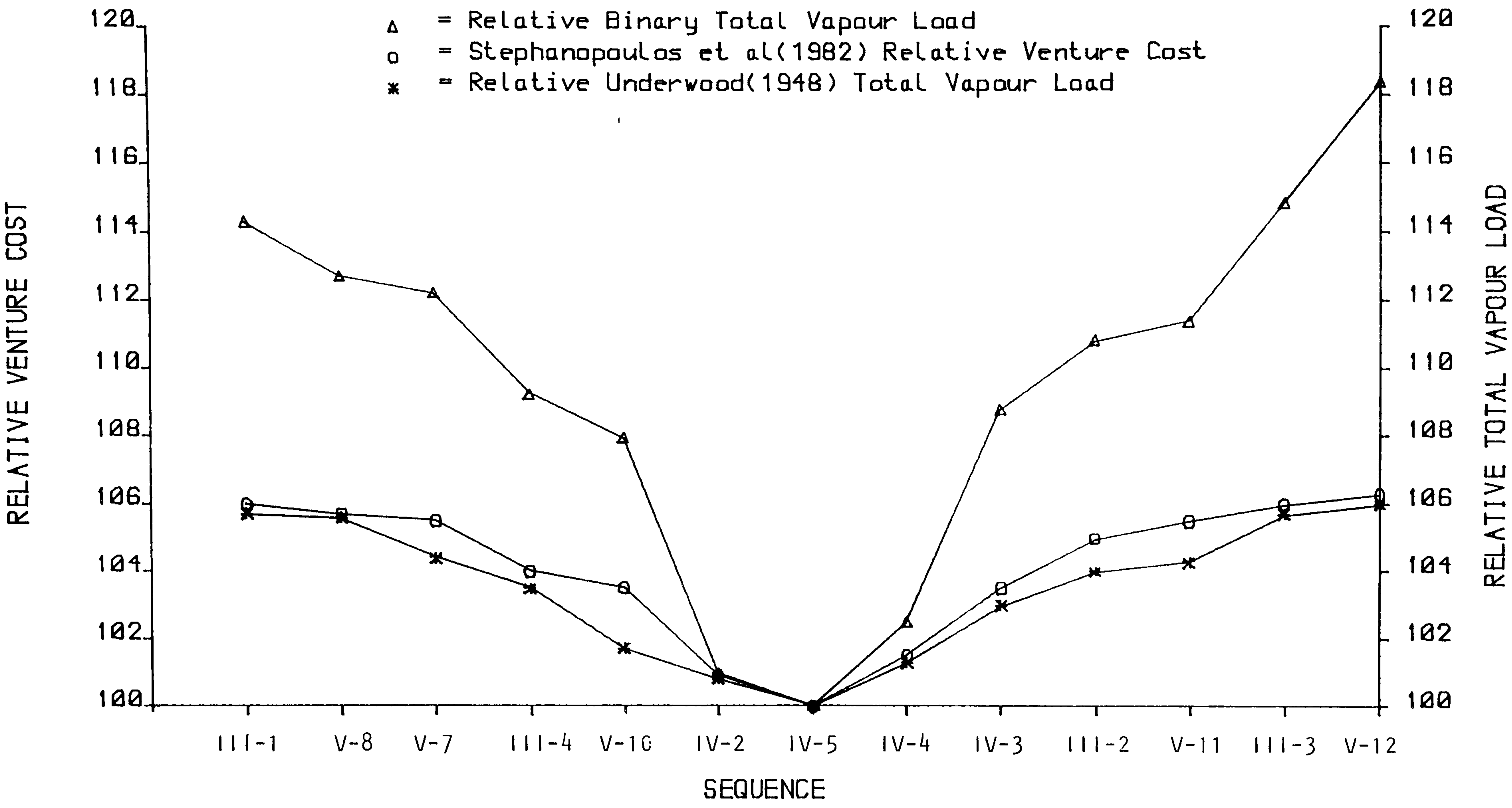

FIG. 5.2 RELATIVE VENTURE COST AND TOTAL VAPOUR LOAD COMPARED

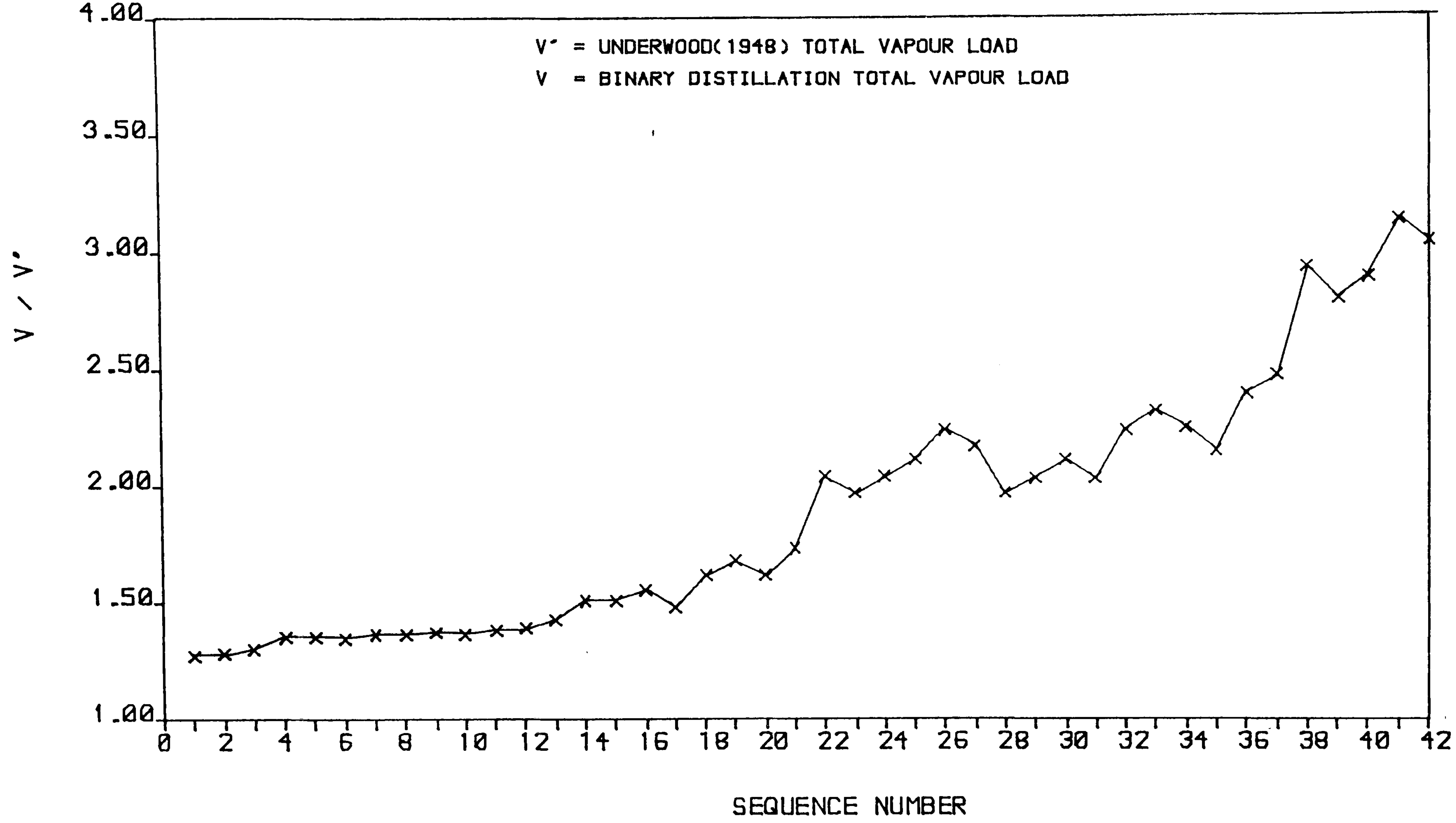

FIG. 5.3 ;UNDERWOOD AND THE BINARY DISTILLATION TOTAL VAPOUR LOADS COMPARED

For example, the best sequence of the six-component mixture of i-Butane(A), n-Butane(B), neo-Pentane(C), n-Pentane(D), n-Hexane(E) and n-Heptane(F) given by Stephanopoulos et al is the sequence with splits ABCD/EF, E/F, ABC/D, AB/C, and A/B. The easy separation ABCD/EF is performed first followed by the next easy separation E/F, then ABC/D, AB/C; and the most difficult separation A/B is performed last.

Those columns requiring the largest vapour flow and which are the biggest contributions to cost are usually difficult binary separations for which the calculation of vapour load by the BDTVL method is valid. The multicomponent separations for which the binary method may be less accurate are those with a smaller vapour load and a relatively small contribution to cost.

As mentioned earlier, the other results on the applicability of the BDTVL equation to real mixtures are given in Tables A5.1 to A5.10 (Appendix A) for various feed compositions of different four- and three-component feedstocks. Some of these real mixtures are those examined in Chapter Four and some of which are taken from the work of Freshwater and Henry(1975). Altogether, 10 feedstocks (many of which consisted of components where the relative volatility of at least one pair of adjacent components is close to 1.0) and 50 cases (i.e. sum of the number of feedstocks and the number of feed composition types) are examined. This gives 160 number of sequences and 420 number of columns. There is a good agreement between the order of results obtained by the BDTVL equation and those by the Underwood vapour flow and by the total annual cost of the sequences. There are few discrepancies (between BDTVL and Underwood methods and both with the total annual cost) especially for the feedstocks in which the relative volatilities between one of the pair of adjacent component is close to 1.0. The probable reasons for this observation are taken up in the next chapter. Of the 50 cases, the BDTVL method gives the correct best two sequences (i.e. first two sequences with minimum total annual cost) in 45 cases. It gives the best sequence in 35 cases. For all of the cases where the BDTVL method gives the optimum sequence or near optimum sequences that is(are) different from that picked by the total annual cost (TAC), it is observed that the differences in TAC between the optimum sequence given by the BDTVL method and that by the TAC are small. For example, in Table A5.3 (Appendix A) feed type 2 the difference in cost between the optimum sequence given by the BDTVL method and that by the TAC is 1.8%. In just one extreme case of all the cases studied, a difference of about 17% [Table A5.4, feed type 2] is observed.

5.5 Concluding Remarks.

Thus we conclude that the problem of choosing the optimum sequence of distillation columns may be made by the simple expedient of estimating the total vapour required by the BDTVL equations. The sequence with the lowest vapour flow is the optimum or the near optimum sequence.

The methods of Rod and Marek(1959) and recently Malone et al(1985) are based on getting a good estimate of the total vapour flow rate without resource to the iteration method of Underwood(1948). However, the complexity of even the simplified approaches is such that these method may only be used for three-component mixtures. Now that computer calculations are normal design tool, the evaluation of accurate vapour flow may be based on the method of Underwood (which requires a trial and error calculation of θ, the root of the equation) instead of using any other approximate equation which would be as complex and yet less accurate.

The BDTVL method derived here is similar to but different in intention and applications to the methods mentioned above. We do not claim it provides a good estimate of the actual vapour load. Our equation, however, represents the powerful heuristic rules and has been shown to work for most of (or all) the prevously published cases of even a six-component mixture. It is a very sensitive way of distinguishing between sequences. It gives larger differences in the vapour load between the optimum or near-optimum and non-optimum sequences. It thus provides a more reliable method of identifying the optimum sequences than the techniques based on the use of heuristics.

We should note that the final design and choice of an optimum sequence of distillation columns may depend on many other factors. But it is essential, in distillation column sequencing, to first find one or two or three sequences which are likely to be at or near the optimum before embarking on the final optimisation calculations. This is what our proposed method intends to achieve; and this is in line with the various works in sequences of distillation columns at the moment.

CHAPTER SIX

LIMITATIONS OF THE BDTVL METHOD AND ITS POTENTIAL IN ENERGY INTEGRATION.

6.1 Introduction

In the last chapter, we derived a simple Binary Distillation Total Vapour Load (BDTVL) method for finding the optimum sequence of distillation column trains. The method which makes an estimate of the cost of one sequence relative to that of another, identified the near optimum sequences for the examples which we have found so far in the literature and which have been solved using other methods. It was also shown that the method provides a quantitative expression of the most powerful heuristics found in the literature.

However, the method may pick a wrong sequences in certain combinations of relative volatilities of feed components. Therefore, in this chapter, we set out to examine the limits or ranges of applicability of this simple method in sequencing the distillation column trains. This examination becomes more necessary since recently, Malone et al(1985) in examining hypothetical three-component mixtures noted that some of the most widely used heuristics are sometimes incorrect. For example, in contradiction to many of the previous studies, they observed that in some cases the most difficult separation should be done first rather than last.

Henry(1986) in a numerical analysis of a three-component mixture observed that the overhead vapour methods are generally feasible only for those feedstocks in which the difficult separation exists between the two most volatile components in a three-component feedstock (i.e when $\alpha_{AB} << \alpha_{BC}$). He did not examine the cases of equal or near equal volatilities. And he arrived at the above conclusion by a comparison of the difference between the direct and indirect sequences of a three-component feedstock using the reboiler heat load as the objective function on one hand, and the Underwood overhead vapour rate on the other. He, however, offered no explanation for this observation.

In examining the ranges of the applicability of the BDTVL method we, like the above authors, limit ourselves to mainly three-component mixtures.

6.2 Analysis

The analysis involves investigating the regions of optimality for direct and indirect sequences of a three-component mixture at some selected relative volatilities including those employed by Malone et al(1985) and Henry(1986). In other words, each run is characterised by a different ESI (ease of separation index) factor as defined by Tedder and Rudd(1978)

$$ESI = \frac{\alpha_{AB}}{\alpha_{BC}} \qquad \ldots\ldots(6.1)$$

ESI is a measure of the relative ease of performing the AB and BC splits. The ESI factor used in this study are shown in Table 6.1, and this is varied from 0.130 to 3.478

TABLE 6.1: Spectrum of Relative Volatilities used in the Triangular Diagrams.

α_{AB}	α_{BC}	$ESI = \frac{\alpha_{AB}}{\alpha_{BC}}$
2.100	2.100	1.000
1.500	1.316	1.140
3.000	2.500	1.200
2.667	1.500	1.778
3.530	1.080	3.269
4.000	1.150	3.478
2.667	3.727	0.715
1.143	3.500	0.327
1.150	4.000	0.288
1.080	8.330	0.130

For most cases, the test components are n-Butane(A), i-Pentane(B) and n-Pentane(C). The specification of the real components and associated physical properties is necessary to be able to calculate the actual total annual cost of the sequences. These components and properties are maintained for the various ESI factors used (i.e the relative volatility are assumed to change but the other physical properties are kept the same). This keeps constant or eliminates the influences or effects of other variables (which would have been introduced using different components each time) on the total annual cost other than the relative volatility and the feed composition changes which are the main variables under investigation.

The regions of optimality are displayed on the triangular, Δ , diagrams showing the regions as defined by Underwood method, Malone et al(1985), BDTVL and the total annual cost (TAC). A line on the diagram shows where the cost of separation by the direct sequence is the same as the cost of separation by the indirect sequence. Different lines are calculated for the different methods of finding the optimum sequence. These are a) the real total annual cost, b) Underwood vapour load, c) Malone et al vapour load, and d) BDTVL vapour load method. In other words, for each method a line is drawn which shows when the costs or vapour flow rates calculated for the direct and indirect sequences to be the same. Thus in the region above the line, direct sequence is optimum; below the line the indirect sequence is less expensive.

The minimum reflux ratio, R_m, is calculated using the equations B2-1 and B2-2 (in appendix B) from which the Underwood vapour rate is obtained. Equation 2.3 is used to calculate the Malone et al(1985)'s vapour rate and Equation 5.10 for the BDTVL vapour rate; all per mole of feed rate.

The engineering and process design and the costing of columns are as explained in section 4.3.1 and in chapter Nine. It is not necessary to repeat them here.

To illustrate the potential of the BDTVL method in energy integration, the T-Q diagrams (Q is the condenser heat load in KJ/hr and T is the temperature in Kelvin) were constructed for some component feedstocks.

In all the analysis, the feed rate of 100 Kmol/hr is used.

6.2.1 Plotting the Triangular diagrams.

The steps followed in the plotting of the triangular diagrams are given below:

(1) For a particular value of say, x_B, and for various values of x_C/x_A, the differences in the vapour rate, ΔV, between the direct and indirect sequences are obtained. These values of ΔV are plotted against x_C/x_A as shown in the sample Figure 6.1. This is carried out for the Underwood equation, Malone et al equation and the BDTVL equation.

(2) The point at which each curve crosses the zero ΔV line indicates a condition in which the vapour flow rate of the direct

sequence equals that of the indirect sequence. Thus gives the ratio of x_C/x_A at which the vapour rates are equal.

(3) Another value of x_B is chosen and steps (1) and (2) above are repeated. This is done for as many values of x_B that are sufficient enough to establish the various curves for the Underwood, Malone et al and the BDTVL methods.

(4) The boundary lines for the total annual cost are more tedious to locate.

(a) various points (x_A, x_B, x_C) are selected and the total annual cost for the two sequences are obtained.

(b) the fraction of indirect to direct total annual cost is the calculated.

(c) if this fraction is very far from 1.0, another point is selected and steps 4(a) and 4(b) are repeated. The choice of the next point or points to be tested depends on how close the fraction is to 1.0.

(5) The results from steps 1-4 are plotted on the triagular graphs shown.

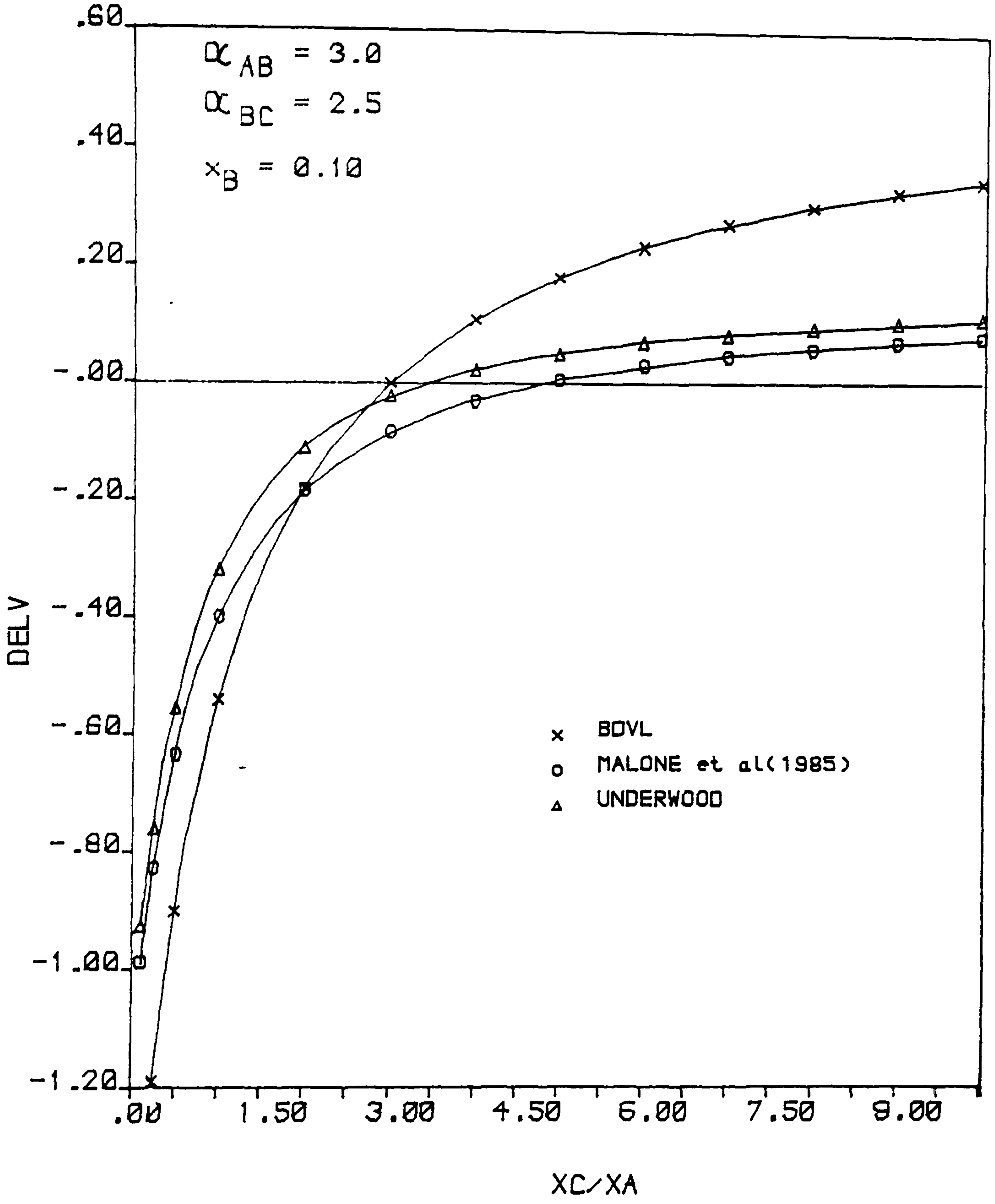

FIG. 6.1 SAMPLE RESULT OF COMPARISON OF THE ΔV VALUES

6.3 Results and Discussions

The results obtained are shown in the triangular Figures 6.2 to 6.11 and Tables A6.1 to A6.10 in Appendix A. In the figures, the numbers in the big circles represent the fraction of the total annual cost (TAC) of indirect sequence to that of direct sequence for the points on which they are located. This is done for the entire composition range of the triangular diagram. The triangular figures also incorporate the regions of optimality as defined using the Underwood, Malone et al(1985), the BDTVL equations and the total annual costs of the direct and indirect sequences.

It is observed that for the three-component feedstocks,

(1) The closer the α_{AB} to α_{BC}, the better the agreement of the BDTVL method with the total annual cost curve. The variations of the TAC between the direct and indirect sequences is high.

(2) For cases of $\alpha_{AB} = \alpha_{BC}$, the BDTVL method may approximate better to the total annual cost curve than either of Underwood or Malone vapour loads.

(3) For the cases in which one of the adjacent relative volatilities is very small (close to 1.0) compared with the other, the boundary between the direct and the indirect sequences given by the BDTVL method is very different from the boundary shown by the total annual cost (TAC).

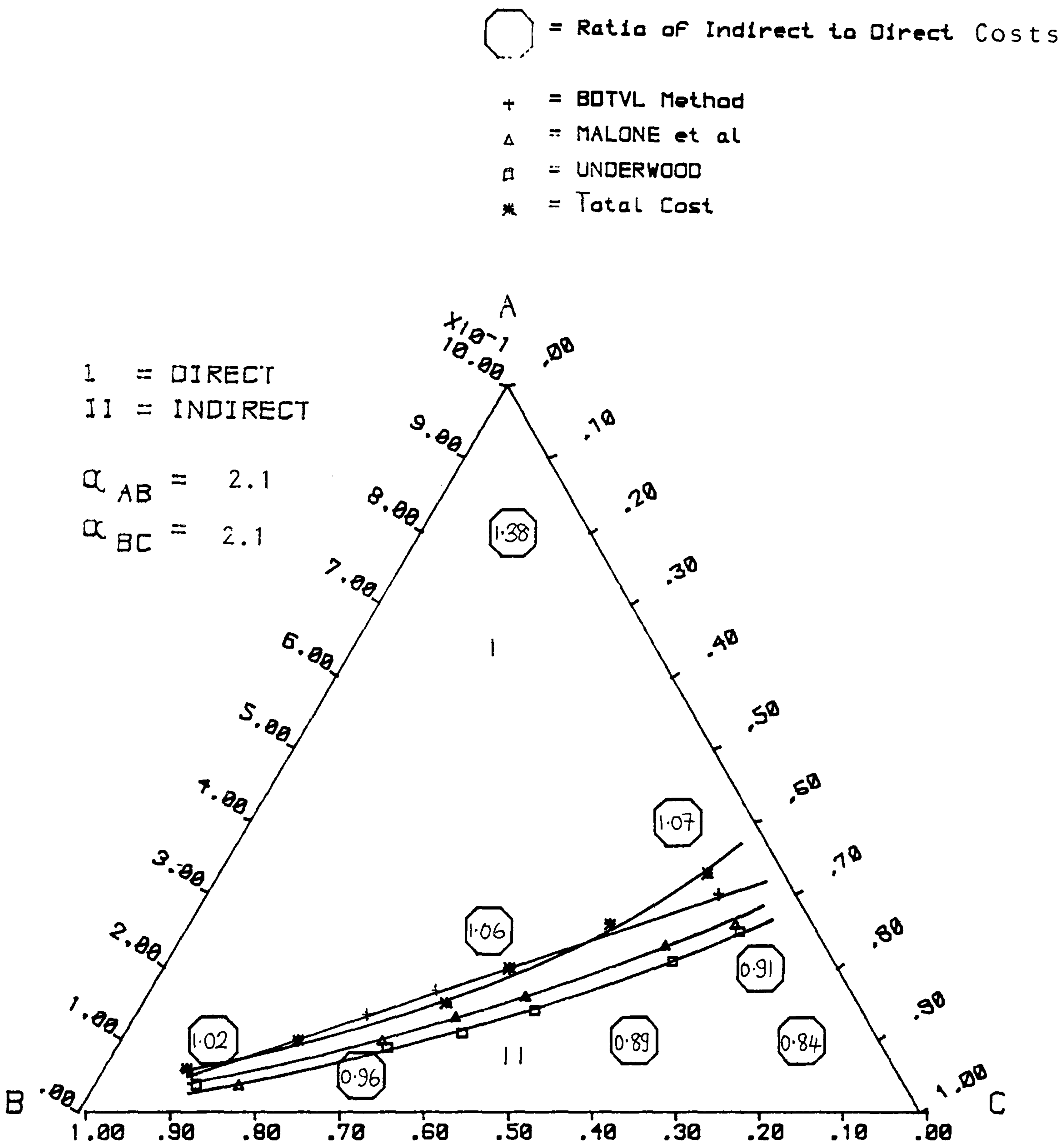

FIG: 6.2 REGIONS OF OPTIMALITY FOR DIRECT AND INDIRECT SEQUENCES

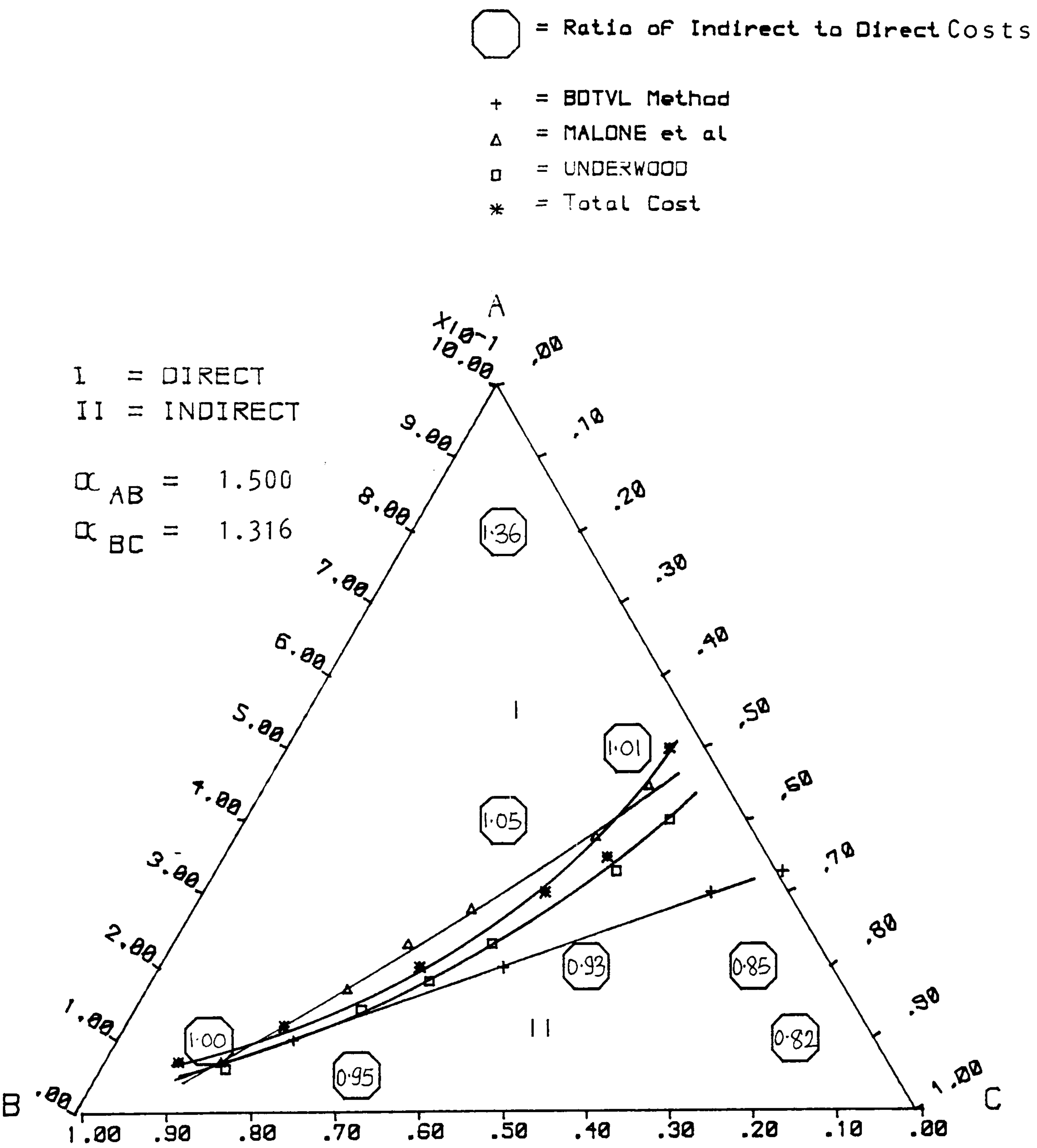

FIG: 6.3 REGIONS OF OPTIMALITY FOR DIRECT AND INDIRECT SEQUENCES

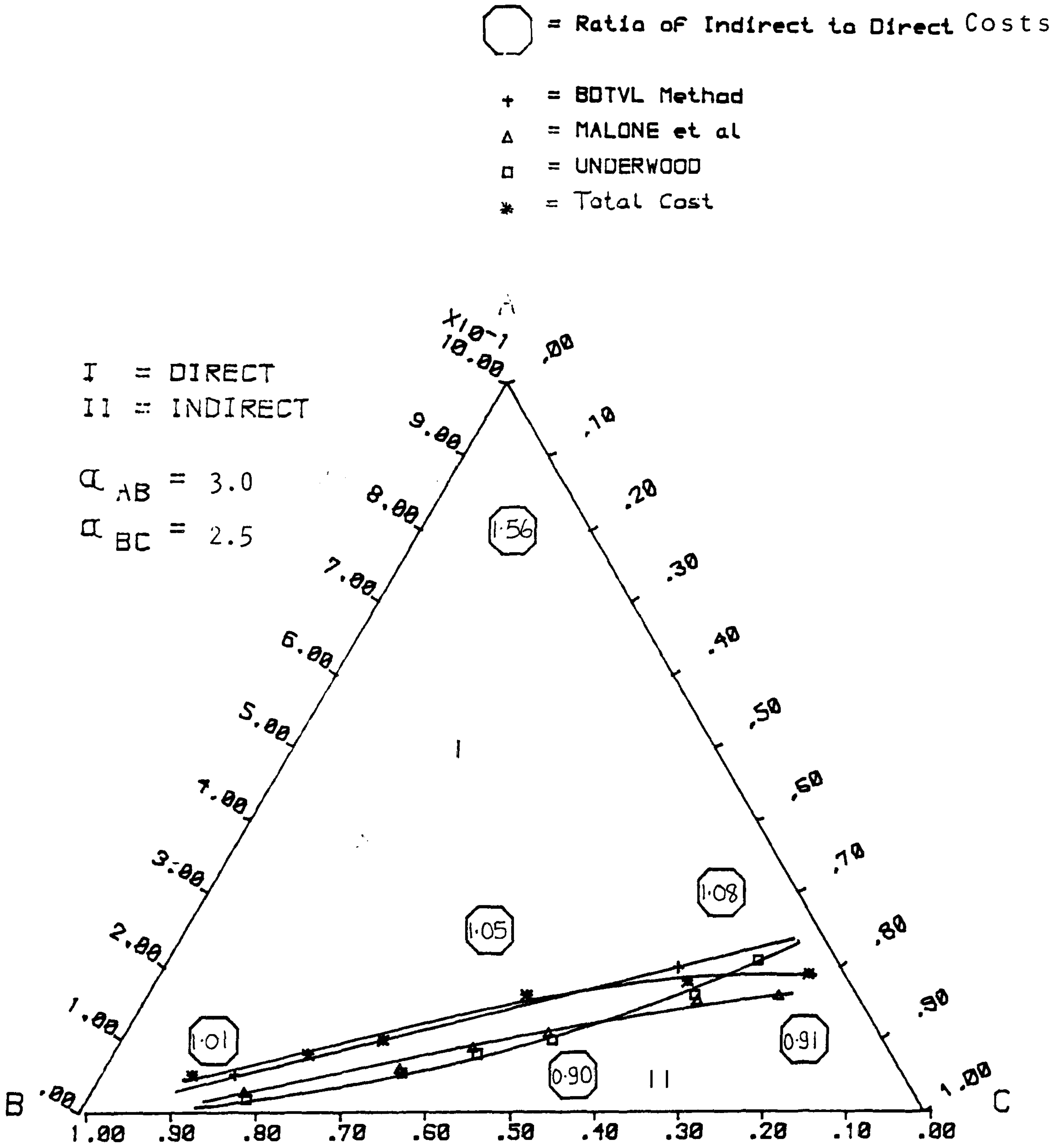

FIG: 6.4 REGIONS OF OPTIMALITY FOR DIRECT AND INDIRECT SEQUENCES

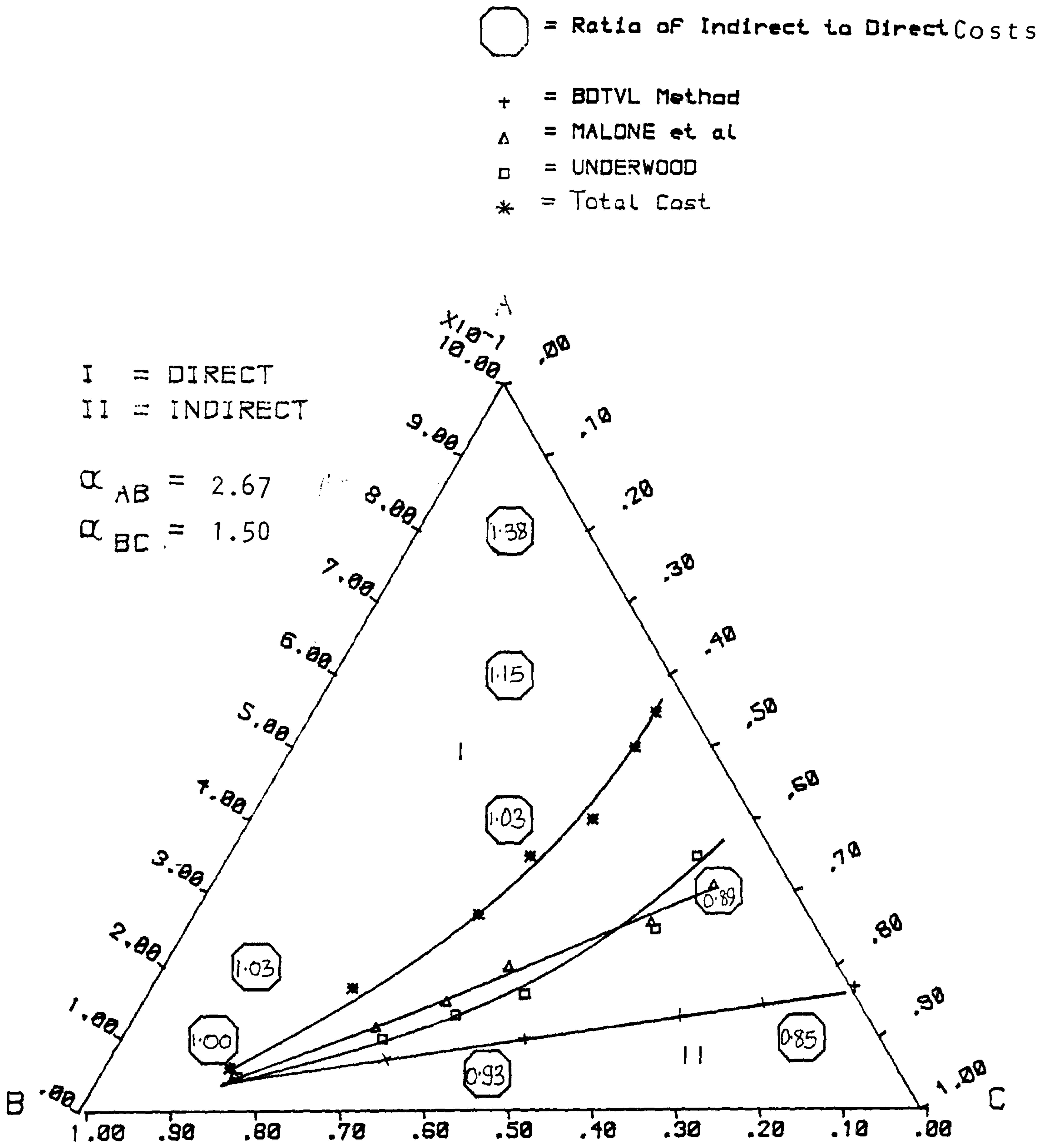

FIG: 6.5 REGIONS OF OPTIMALITY FOR DIRECT AND INDIRECT SEQUENCES

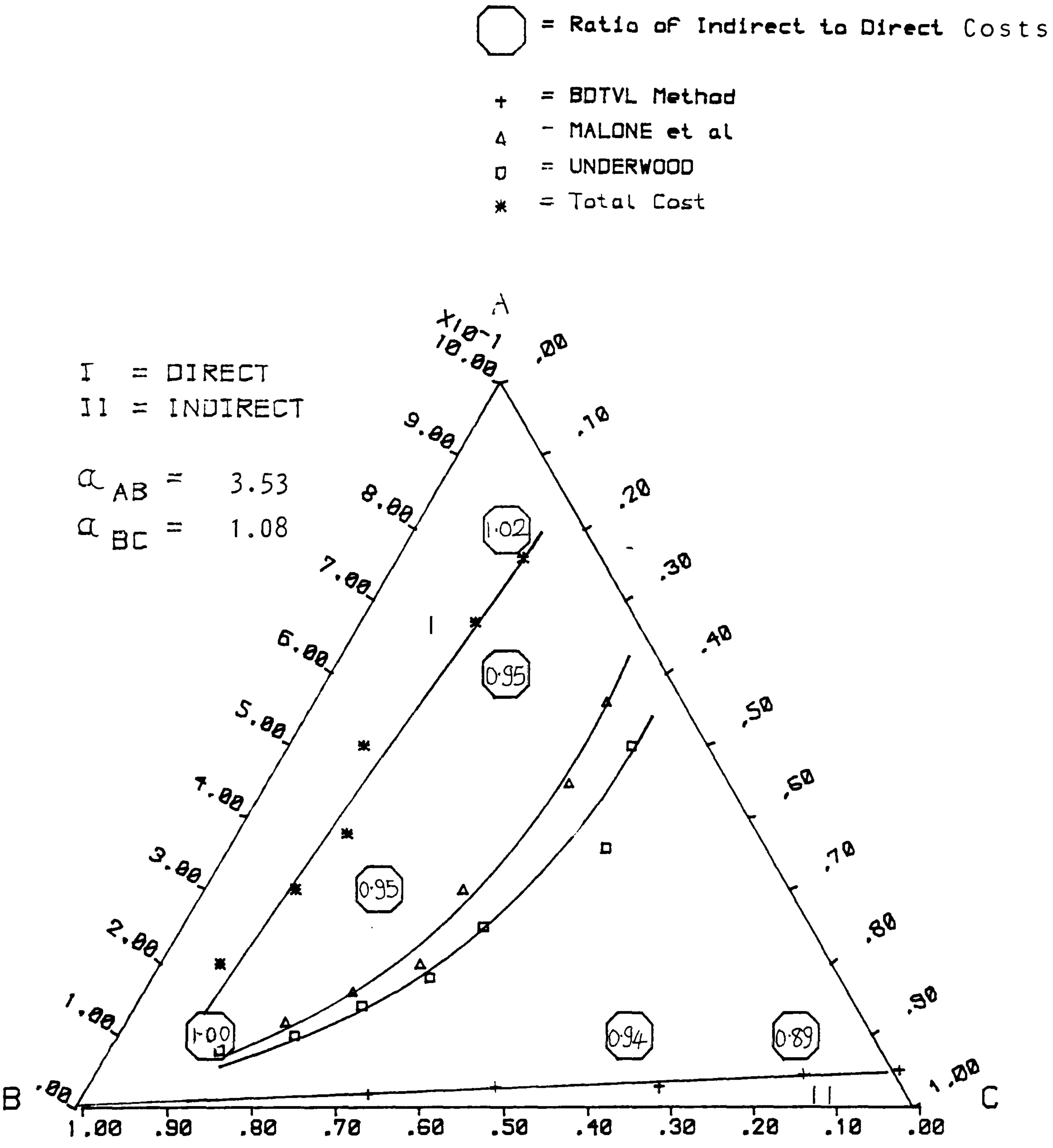

FIG: 6.6 REGIONS OF OPTIMALITY FOR DIRECT AND INDIRECT SEQUENCES

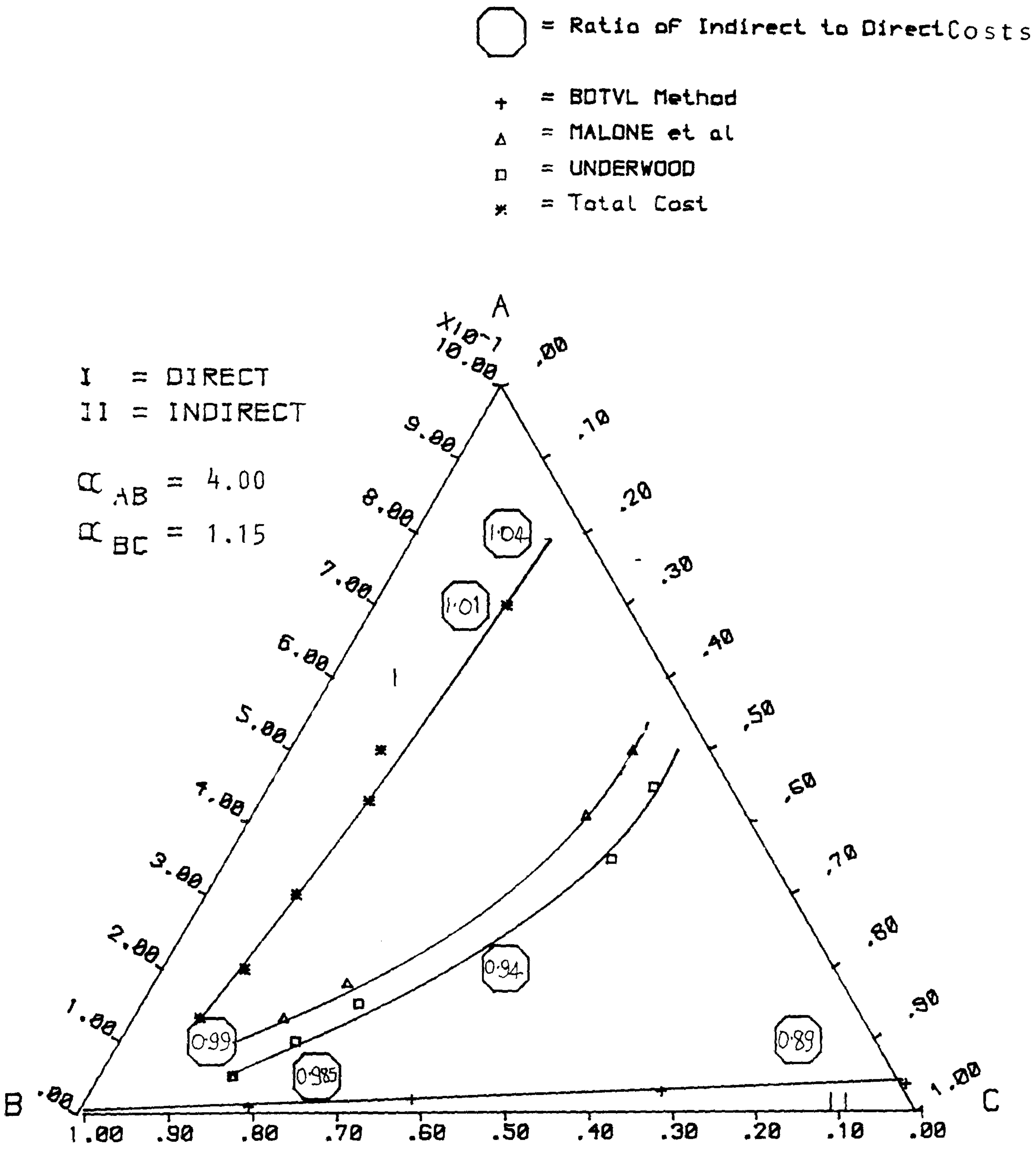

FIG: 6.7 REGIONS OF OPTIMALITY FOR DIRECT AND INDIRECT SEQUENCES

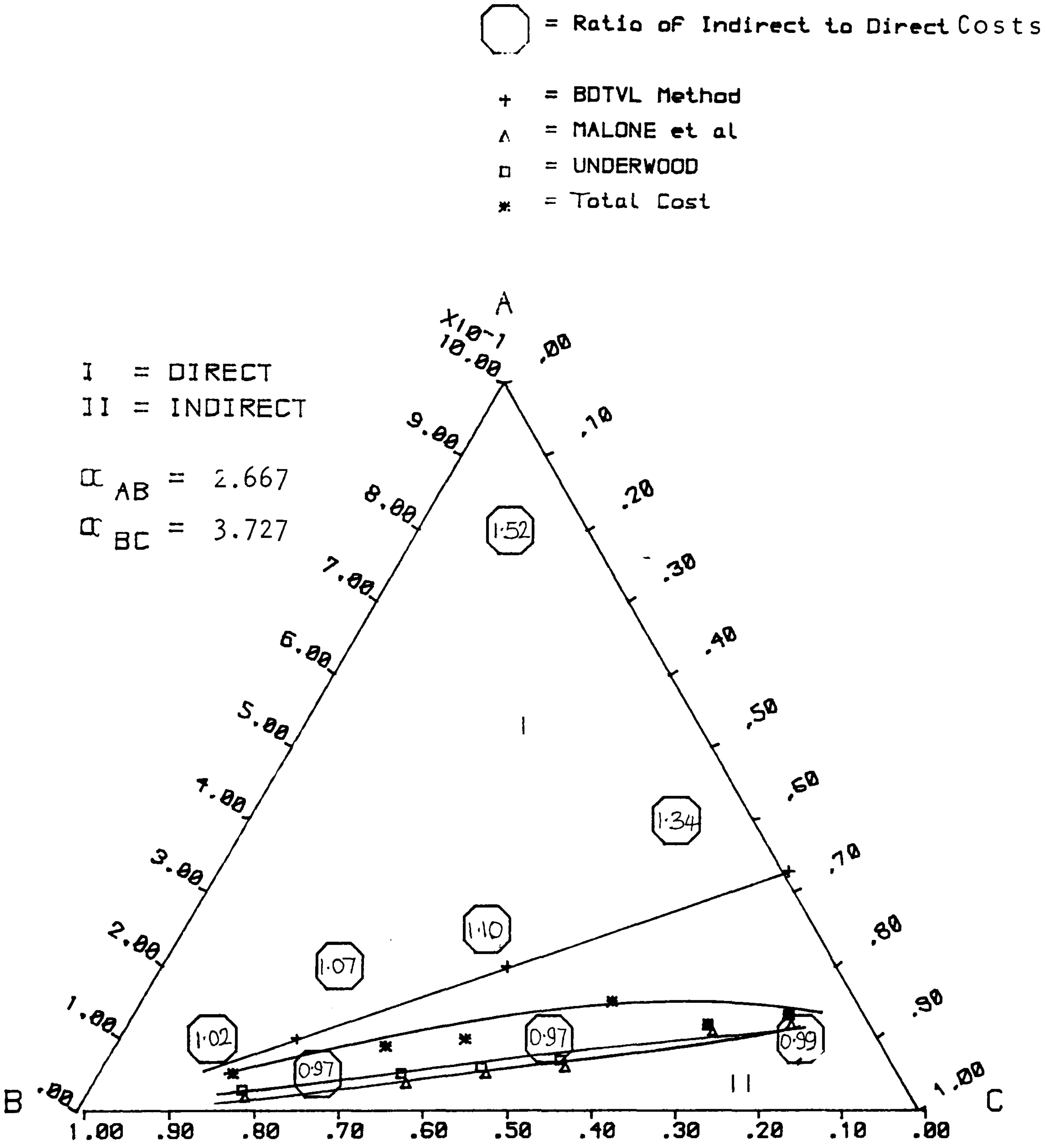

FIG: 6.8 REGIONS OF OPTIMALITY FOR DIRECT AND INDIRECT SEQUENCES

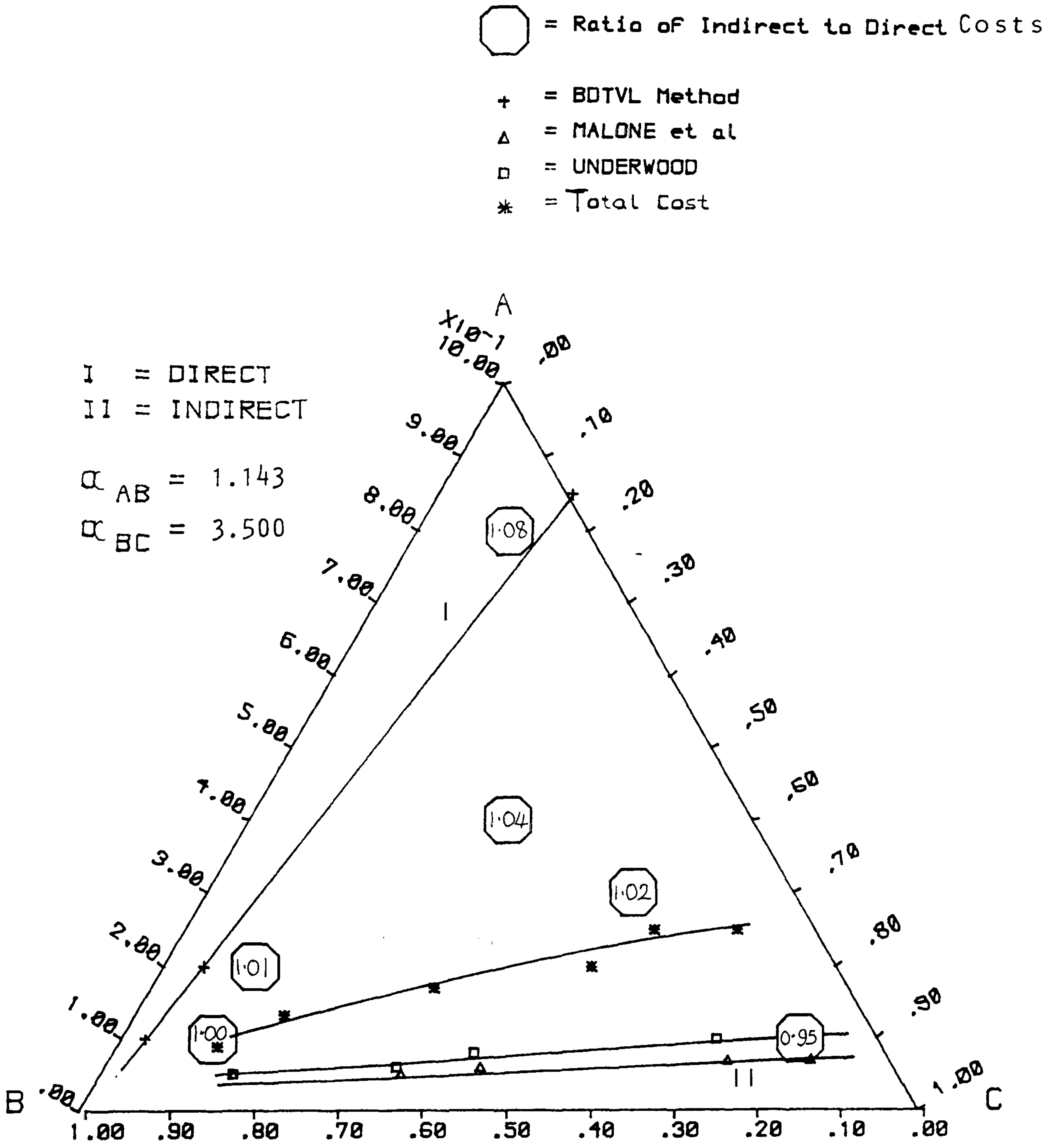

FIG: 6.9 REGIONS OF OPTIMALITY FOR DIRECT AND INDIRECT SEQUENCES

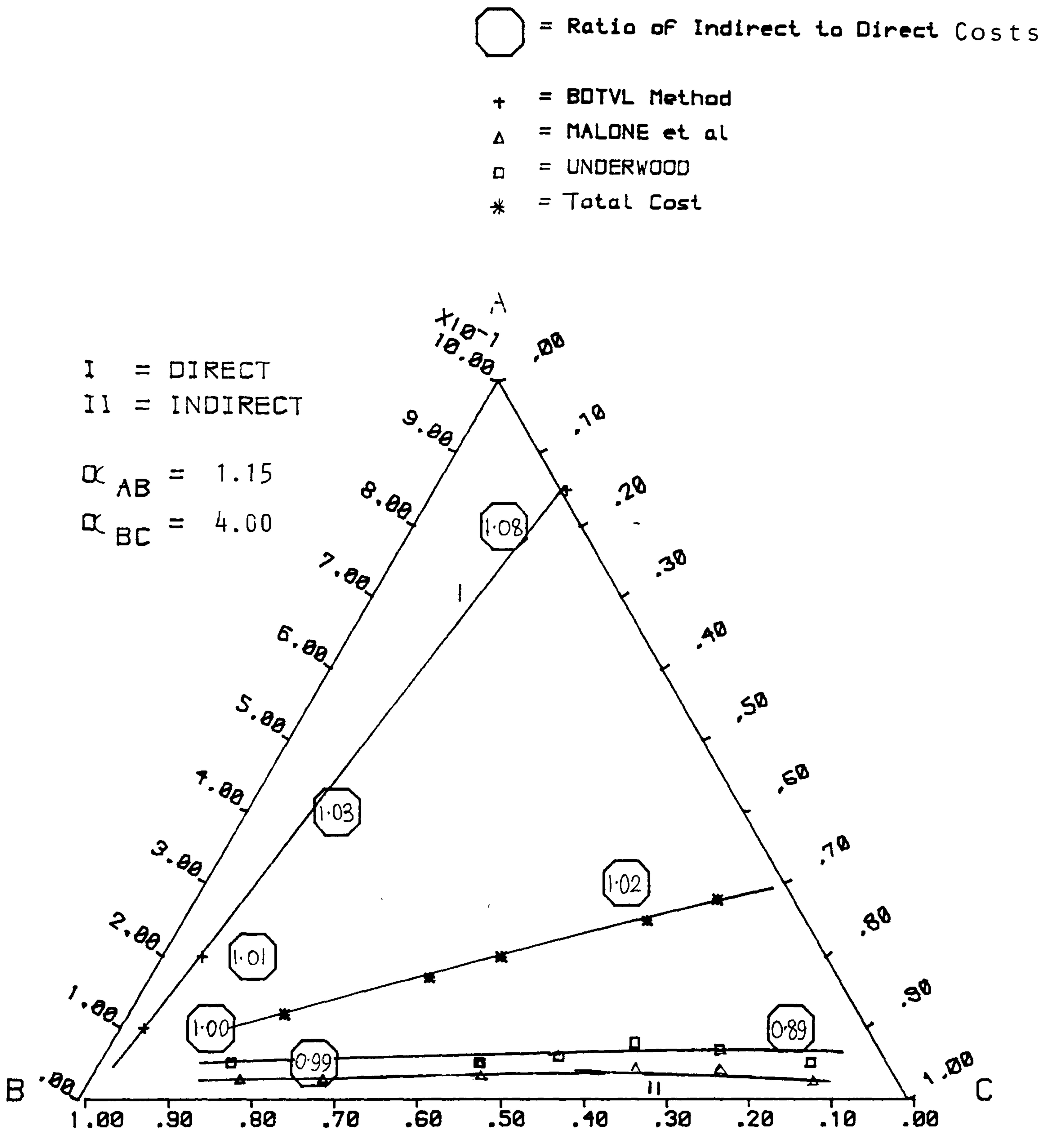

FIG: 6.10 REGIONS OF OPTIMALITY FOR DIRECT AND INDIRECT SEQUENCES

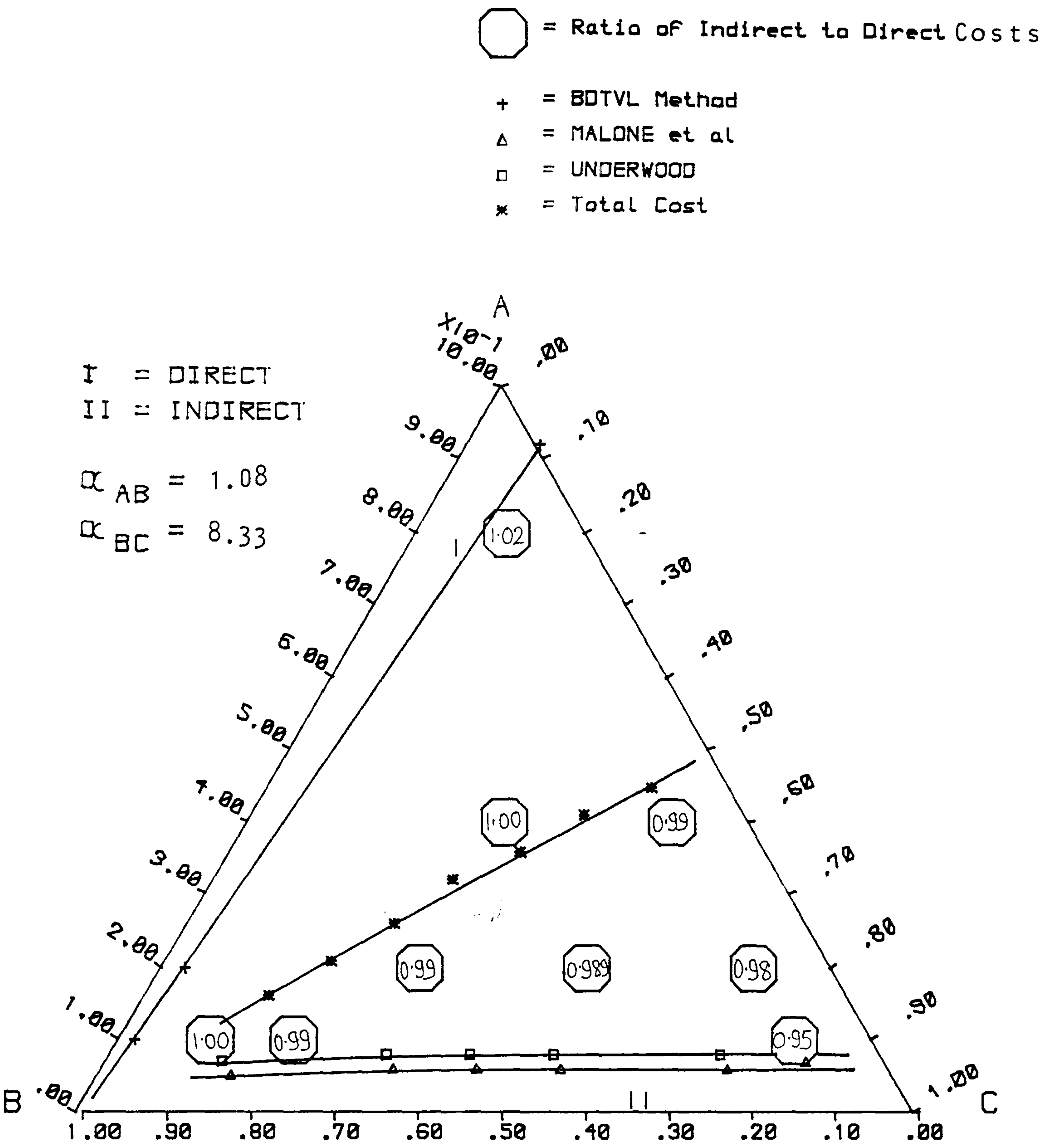

FIG: 6.11 REGIONS OF OPTIMALITY FOR DIRECT AND INDIRECT SEQUENCES

(4) For these cases in which the BDTVL method is way off the line for the total annual cost curve, the differences in the TAC between the direct and the indirect sequences are generally very small.

These points are developed further in the rest of the chapter.

The implication of the third point above is that the proposed BDTVL method may pick a wrong sequence to be optimum for cases where the relative volatility for a pair of adjacent component is very small compared with the next or previous pair of components (i.e when $\alpha_{AB} = 1.0 << \alpha_{BC}$, or vice-versa). This result challenges the heuristic "Do the difficult separation last". The heuristic fails and so does the BDTVL which represents the heuristics.

The reason for the failure of the proposed method (and indeed any method based only on the vapour flow rates for such low 's) may be explained by examining again the results shown in Figure 3.14 of Chapter Three and the tabulated results of Chapter four. As the relative volatility between the key components becomes close to 1.0, the capital cost becomes a substantial portion of the total annual cost. The energy cost cannot be said to completely dominate the total annual cost any more. Thus, any method based on the vapour flow, which is directly related to the energy cost may not be very reliable at such low values of relative volatility between a pair of adjacent components.

Furthermore, the sensible heats and the molar latent heats due to the differences in the vapour and liquid enthalpies are involved in a distillation process. These factors are the inherent nature of a distillation process since the separation of components by distillation involves temperature changes along the column; and these changes are measures of heat capacities along the column. King(1980) noted that these factors can be very important if there are large amounts of components in the feed which are very light or very heavy relative to the components being separated. He went further that the effects of these factors are complicated and no completely general rule can be formulated. Sometimes the factors compensate each other to large extents. Based on the above, we anticipate that these factors are very likely to influence the feasibility of the use of methods based only on vapour flows in sequencing distillation trains especially when one of the α's is very small and the others large. This provides basis and explanation for Henry(1986)'s observation.

In the fourth point above, it was pointed out that the differences in cost between the direct and the indirect sequences for the cases in which the proposed method stands way off the cost curve is generally very small compared with the other cases. This is an interesting observation. It means that the percentage error incurred in terms of cost in selecting the optimum sequence using the BDTVL proposed method instead of the total annual cost is low for the cases where a wrong optimum sequence may be picked by the method. The reverse is observed for the cases where the proposed method do not differ significantly from the TAC curve. The cost differences are high.

These low percentage variations are not surprising. As the relative volatility of any of the key components becomes nearer to 1.0, the order of sequencing becomes more or less immaterial. The cost of the difficult separation split dominates the total annual cost of any of the sequences whether the split is performed first or last. This is evident, for example, in Tables 6.2 and 6.3 (page 253) which are to be discussed later in the chapter. For the different feedstocks of the three-component mixtures shown in the tables, the percentage of the cost of the difficult separation split to the total annual cost of each of the sequences is about 94% and above. In other words, the easy separation split contributes less than 6% to the total annual cost of each of the sequences. For such separations with very low relative volatility between a pair or pairs of adjacent components, one may suggest that it would be advisable to try an extractive distillation instead of the ordinary distillation operation. This is the intention of the next two chapters.

6.4 BDTVL Potentials in Energy Integration

It is shown below that even when the BDTVL method predicts the wrong optimum for an unintegrated sequence, the method gives the sequence with a better or larger potential for energy integration. In other words, heat exchange between the condensers and reboilers is feasible or more feasible even for the case where the optimum sequence produced by the proposed method differ from that by the use of the total annual cost. The condenser profiles are always more closer (and sometimes overlap) for the optimum chosen by the BDTVL method than for that chosen by the total annual cost.

Thermodynamically, a column receives heat input Q_r into the reboiler at temperature T_r. The column extracts work by degrading this heat to a lower temperature T_c, where it is expelled in the condenser. The temperature-heat load (T-Q) diagrams as shown in the Figures 6.13 to 6.16 below constitute a simple way to represent the energetic conditions of the streams present in a distillation sequence. This representation portrays the heat acceptance (a higher profile) and heat rejection (lower profile) of each column in the sequence.

Andrecovich and Westerberg(1985a), Westerberg(1985) have shown that $Q \Delta T$, the product of the condenser or reboiler heat load and the temperature difference between the reboiler and condenser can be used as tool for designing heat-integrated distillation sequences. They argue that it is sensible to suggest that the sequence having the minimum sum of QΔT areas is the best for energy integration. This same observation was also implied in the work of Stephanopoulos et al(1982,1984) and Hindmarsh and Townsend(1984).

Basically, one way to heat integrate columns is to use the heat released in some condensers to heat the reboilers of some columns in the sequence. This implies that, within the sequence, there should be a condenser or some condensers whose temperatures are higher or can easily be made higher (by pressure changes) than a reboiler temperature of at least one column. The narrower the gap between the temperature profiles (i.e of condenser of one column and a reboiler of another) the better the potential for energy integration. As we have already discussed in Chapter Five, the BDTVL method pushes the difficult separation to the end of the sequence where they become binaries. Making the difficult separation a binary with the least temperature difference means the least heat degradation. Thus the vapour condensing at the top of the column (i.e at the condenser) is almost equivalent in usefulness to the steam at the bottom. The potential for heat integration is thus enhanced.

To examine this proposal, two feedstocks are chosen having relative volatilities corresponding to the values used in some of the triangular diagrams. The feed compositions for these feedstocks are taken at points where the proposed BDTVL method picks an optimum sequence that differs from that picked by the cost analysis. For the first feedstock of Trans-2-butene(A), Cis-2-butene(B) and Hexane(C), the feed composition chosen is 0.70, 0.20 and 0.10; and for the second feedstock of Propane(A), Trans-2-butene(B) and Cis-2-butene(C) the feed composition is 0.34, 0.33 and 0.33. For the first feedstock,

$\alpha_{AB} = 1.08$

$\alpha_{BC} = 8.33$

and for the second feedstock

$\alpha_{AB} = 3.53$

$\alpha_{BC} = 1.08$

The results are shown in Tables 6.2 and 6.3 and in Figures 6.12 to 6.15 which are plots of temperature (in Kelvin) against Q (in KJ/hr). For the first feedstock, the area under the curve, Q ΔT, for the indirect sequence is significantly smaller than for the direct sequence (Figures 6.12 and 6.13) even though in terms of the total annual cost, the direct sequence is less expensive. Refering to Figure 6.13 for example. For heat exchange to be possible the temperature interval XY has to be overcome in order to get the condenser temperature of column 1 higher than the reboiler temperature of column 2. This interval is smaller compared with the interval that has to be overcome in Figure 6.12 in order to get the condenser temperature of column 2 higher than that of column 1. This shows that the indirect sequence which is picked by the BDTVL method is more "integratable" than the direct sequence.

TABLE 6.2 : T-Q data for three-component feedstock 1 of Trans-2-butene, Cis-2-butene and Hexane.
(α_{AB} = 1.08; α_{BC} = 8.33)

	DIRECT			INDIRECT		
Variable	Col. 1	Col. 2	Total	Col. 1	Col. 2	Total
T_D	325.17	326.49		324.85	325.17	
T_B	342.04	404.01		404.01	328.02	
ΔT	16.87	77.52	94.39	79.16	2.85	82.01
Q_c	27229667	11795	27341462	295501	27270441	27565942
Q_r	28546935	431284	28578219	1416182	28648623	30064805
TAC	3081793	39733	312526	133293	3017184	3150478
V_B	16.1639	0.2491	16.4130	1.0637	14.9175	15.6812
$Q_c\ \Delta T$	459426819	8666732	468093551	23392258	77768123	101160381

TABLE 6.3 : T-Q data for three-component feedstock 2 of Propane, Trans-2-butene, and Cis-2-butene.
(α_{AB} = 3.53; α_{BC} = 1.08)

	DIRECT			INDIRECT		
Variable	Col. 1	Col. 2	Total	Col. 1	Col. 2	Total
T_D	323.84	380.21		357.61	323.84	
T_B	383.54	384.26		384.26	381.52	
ΔT	59.70	4.05	63.75	26.65	57.67	84.32
Q_c	614616	16943014	17557180	16610939	418928	17029867
Q_r	1227852	17849932	19077784	17837089	869705	18706794
TAC	109804	1823828	1933632	1821441	78226	1899668
V_B	0.8152	10.5362	11.3514	16.1339	0.6584	16.7923
$Q_c\Delta T$	36391500	68603776	105295276	442726404	24161667	466888071

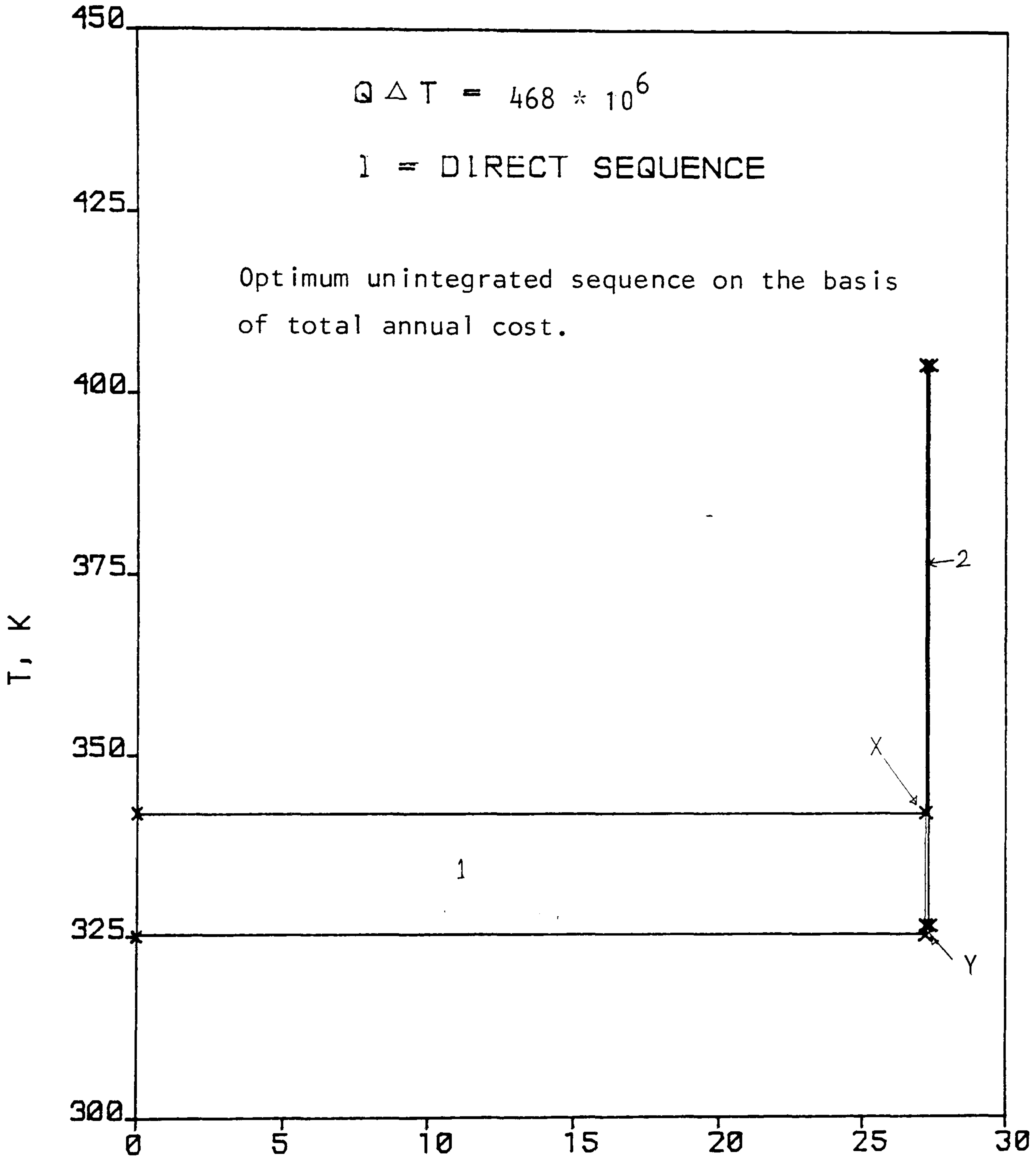

FIG: 6.12 T-Q DIAGRAM FOR A THREE-COMPONENT MIXTURE
(Trans-2-butene/Cis-2-butene/Hexane)

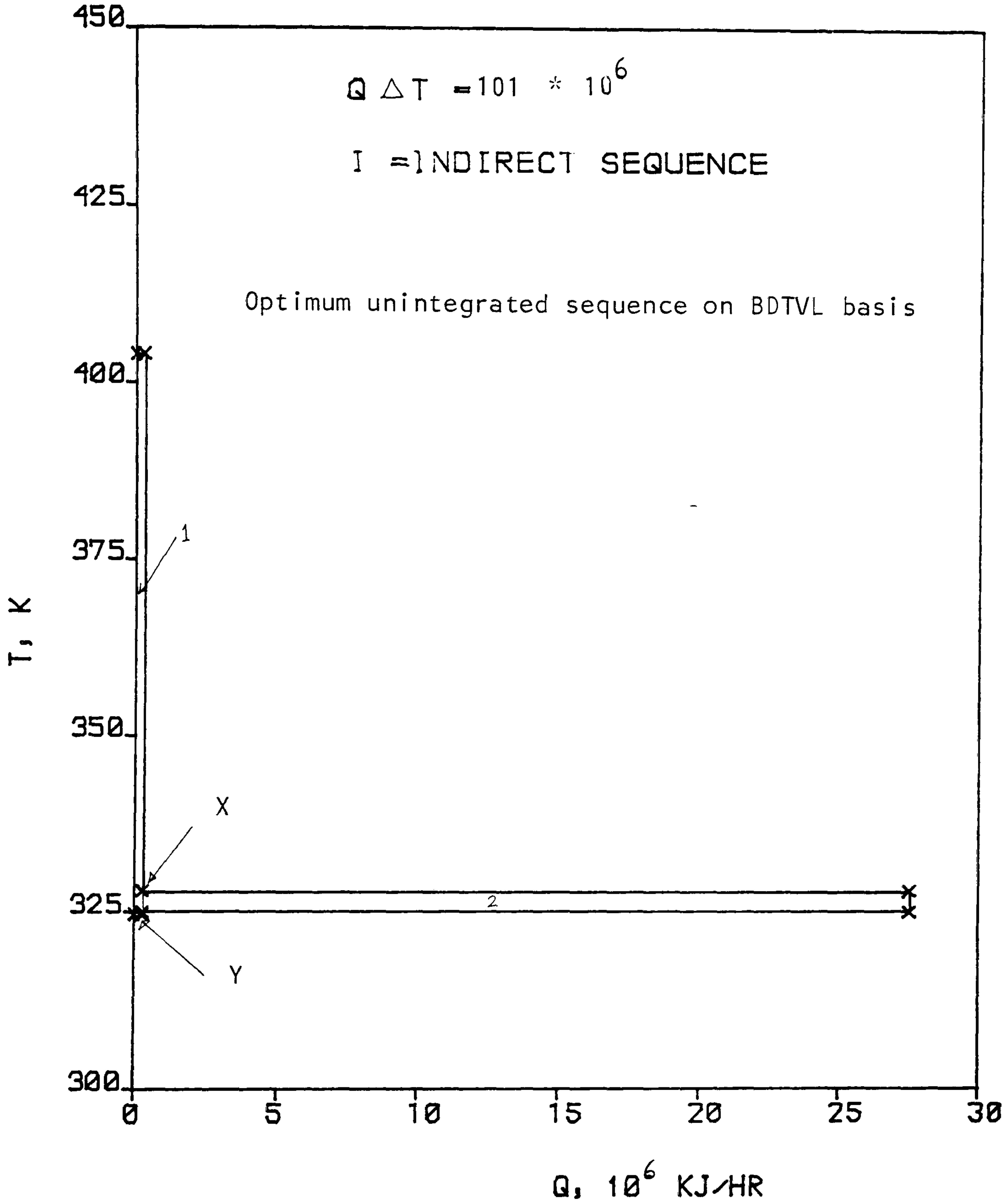

FIG: 6.13 T-Q DIAGRAM FOR A THREE-COMPONENT MIXTURE

(Trans-2-butene/Cis-2-butene/Hexane)

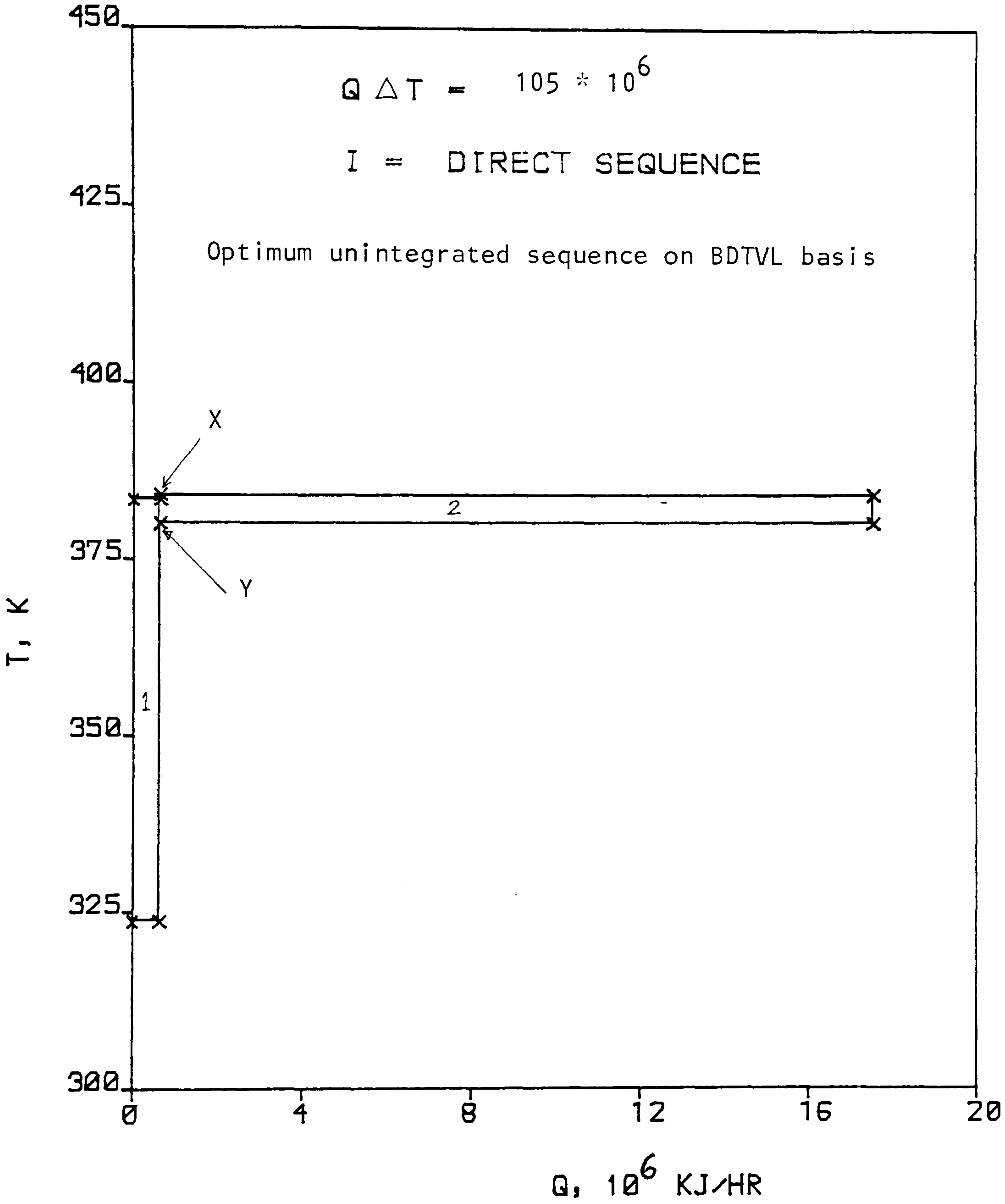

FIG: 6.14 T-Q DIAGRAM FOR A THREE-COMPONENT MIXTURE
(Propane/Trans-2-butene/Cis-2-butene)

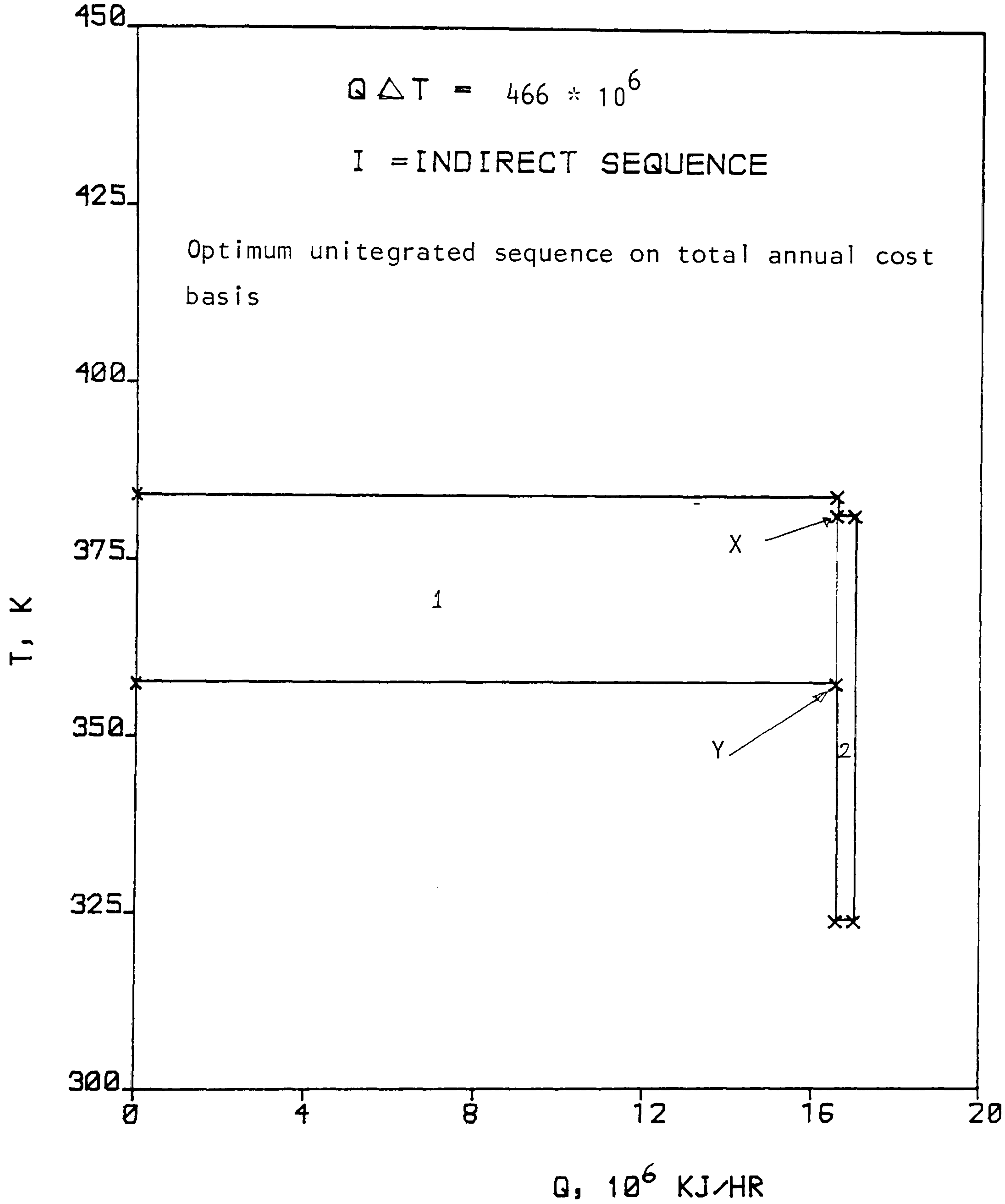

FIG: 6.15 T-Q DIAGRAM FOR A THREE-COMPONENT MIXTURE
(Propane/Trans-2-butene/Cis-2-butene)

Similarly in the second feedstock, the area under the curve for the direct sequence (Figure 6.15) is smaller than for the indirect sequence (Figure 6.16) even though the total annual cost of the former is larger than the latter sequence. Following the same arguement above, the direct sequence picked by the BDTVL method is more integratable in this case than the indirect sequence.

All these examples support the fact that though the proposed method may pick a wrong sequence (relative to cost) as being optimum, the sequence picked is generally more integratable than any other sequences for the given feedstock.

Nevertheless, caution should be exercised in using the proposed method if, for example in a three component feedstock, the relative volatility for a pair of adjacent components is very small (close to 1.0) compared with the next or previous adjacent pair. A wrong sequence may be picked as being optimum. Even for this case, however, the magnitude of the differences in cost between the sequences has been shown to be reasonably small. And this optimum picked by the method possesses better or larger potential for heat integration than any other sequences. It shows that the decomposition "that the single best (in terms of cost) unintegrated sequence will always lead to the single best integrated sequence", may not always apply.

CHAPTER SEVEN

APPLICATIONS OF THE BDTVL METHOD TO EXTRACTIVE DISTILLATION I:

[A REVIEW OF PREVIOUS WORK, VAPOUR LIQUID EQUILIBRIA AND AN EVALUATION OF SELECTIVITY FOR SOLVENT SCREENING.]

7.1 Introduction

In this chapter and the next, we take a new look at the analysis of the extractive distillation process. We extend the BDTVL method developed in chapter five to an extractive distillation with the aim of applying it to

(a) screening of solvents for an extractive distillation process, and

(b) determining the viability of an extractive distillation in replacing the ordinary distillation process.

Extractive distillation is an important separation process which can be used to separate components exhibiting close boiling points and is often considered as an alternative to ordinary distillation. In the presence of a solvent, the relative volatility of the components to be separated increases, thereby making the otherwise difficult separation an easy one.

The generally accepted definition of extractive distillation was that given by Benedict and Rubin(1945) and is defined as " a distillation in the presence of a substance which is relatively nonvolatile compared to the components to be separated and which, therefore, is charged continuosly near the top of the distilling (extraction) column so that, an appreciable concentration is maintained on all plates of the column." Implied in this definition is the restriction that the solvent introduces no new azeotropes in the mixture.

A number of experimental and theoretical studies have been reported in the literature on the extractive distillation operation [Drickamer and Hummel(1945), Dunn et al(1945), Tassions(1972), Halslund(1969), Dongen et al(1985), Levy et al(1985), Doherty and Caldarola(1985)]. Two problems which continue to receive attention are the determination of when an extractive distillation will be cheaper than ordinary distillation, and the identification of the best solvent from several candidate solvents.

At the heart of an extractive distillation process is the selection of suitable solvent capable of enhancing the relative volatility of the two key components to be separated. How well the selection is made depends on the approach or method used. Traditionally, the screening of solvents is usually done by ranking the solvents in the order of their selectivity at infinite dilution [Kyle and Leng(1965), Gerster et al(1960), Kolbe et al(1979), Bastos et al(1985)]. This is based on the understanding that the selectivity at infinite dilution is a good indication of the relative costs of the extractive distillation process. The solvent with the highest selectivity being the most promising solvent for the given separation. How good and reliable is this understanding? This is our focus in this chapter. The basic principles established in this chapter leads us to the next chapter.

Our investigations include

(1) to determine the solvent selectivity at infinite dilution of some common components of extractive distillation with the aim of screening the most promising solvent for the given separations.

(2) to determine the optimum solvent feed rate for an extractive distillation process.

(3) to determine the relationship between solvent selectivity and the total annual cost of an extractive distillation process.

All these investigations are necessary; for they provide the background information and data on solvent screening and the reliability of selectivity as compared with cost.

It should be pointed out that apart from (1) above, very little or, in some cases, no information is available in the literature on these areas.

The state of the art on the Vapour Liquid Equilibrium (VLE) is in the prediction of activity coefficient using the molecular structure of the components present in the mixture. It may well turn out in the future that solvents might be designed from their molecular group to achieve specified separation properties. It is with this broad objective in mind that a brief review of literature on the screening of solvents for an extractive distillation using the UNIFAC (UNIQUAC Functional-Group Activity Coefficient) group contribution method [Fredenslund et al(1975), Gmehling et al(1982)] is first made. This is the method employed in this study for the prediction of the liquid phase activity coefficients at infinite dilution, γ^{∞}. Next we consider the basic flowsheet of an extractive distillation process in order to give us an overview of the process itself; and then treat our investigations in the order listed above. The results and discussions are presented at the end of the chapter.

7.2 Previous Works.

The important parameter for consideration in the screening of solvents is selectivity at infinite dilution and this is usually defined as [Kolbe et al(1979)]

$$\int^{\infty} = \frac{\gamma_1^{\infty}}{\gamma_2^{\infty}} \qquad \ldots\ldots\ldots\ldots(7.1)$$

where γ_1^{∞} and γ_2^{∞} are the activity coefficients of component 1 and 2 at infinite dilution in the solvent. Thus, the problem of screening solvents for an extractive distillation turns out to be that of determining the activity coefficients of the key components in the solvents.

Over the years, numerous articles have appeared in the literature on the determination of activity coefficient and screening of solvents both experimentally and using theoretical prediction methods. It is not our intention to embark on the review of literature on this rather wide and general topic. We found it necessary to limit ourselves to the group contribution method of UNIFAC and the authors that have used it in the screening of solvents for an extractive distillation. But as an introduction, we mention some of the works on the experimental determination of the activity coefficient as a parameter for solvent screening. Here, the works of Benedict and Rubin(1945), Hess et al(1952), Gerster et al(1960), Deal and Derr(1964), Hanson and Van Winkle(1967), Null(1970), Leroi et al(1977), Eckert et al(1982) and Thomas et al(1982a,b) are worth mentioning.

The sucess of an earlier work on solution-of-group method of Derr and Deal(1969) and Abrams and Prausnitz(1975) encouraged Fredenslund et al(1975) to attempt a correlation which, in principle but not in detail, is similar to the ASOG (Analytical

Solution of Groups) method. Upon combining the concept of functional groups with the analytical results of the UNIQUAC (Universal Quasi-Chemical), they arrived at the UNIFAC method. The method takes into account not only the differences in molecular sizes as given by the group volumes but also the differences in molecular form presented by the group surface area.

In UNIFAC, the combination part of the UNIQUAC activity coefficient is used directly. Only pure component properties enter into the equations. Parameters r_i and q_i are calculated as the sum of the group volume and area parameters, R_k and Q_k. [The rest of the derivations, the advantages and limitations of the UNIFAC are given in Appendix C-2].

Only few articles have appeared in the literature on the screening of solvents for an extractive distillation process using UNIFAC.

Kolbe et al(1979) used the UNIFAC method to search for a good and, if possible, the best extractive solvent for the given mixture of Benzene and Cyclohexane from a number of possible solvents which show a marked selectivity. Also, in studying the effects of functional groups on selectivity, the authors compiled a list of a few solvents from different classes of organic compounds on the basis of functional groups defined in the UNIFAC method. Inspection of the selectivities at infinite dilution showed that the highest effects are produced by the following groups: ester (COOC), aromatics amine ($ACNH_2$), nitrile (CCN), aliphatic nitro (CNO_2), and aromatic nitro ($ACNO_2$). Surprisingly, phenol showed a rather low selectivity, which is in contrast to the reported use of phenol in an extractive distillation process for the separation of aliphatics and aromatics. Common functional groups which are known to produce selective effects for the separation of aromatics from aliphatics did not appear in the list. This, according to the authors, was due to inability to determine the interaction parameters for these groups at that time.

The agreement with the experimental data was just fair. Nonetheless, it was still suggested that the UNIFAC method is an effective tool in selecting solvents for the extractive distillation process.

Sucksmith(1982) on comparing some design and operating parameters of extractive distillation with ordinary distillation used the UNIFAC method to choose a good solvent for the extractive distillation process. The binary components were n-heptane and Toluene; and about five solvents were investigated from which phenol was chosen as the best. The UNIFAC method was used to predict the liquid activity coefficients at infinite dilution for the mixtures from which the selectivity at infinite dilution is obtained from Equation (7.1).

Bastos et al(1985) reported a collection of experimental values for activity coefficients at infinite dilution, γ^{∞}, for systems with potential application in the extractive distillation process, and a comparison of these data with those obtained using the group contribution methods for the prediction of activity coefficients at infinite dilution. This, however, depended on the availability of interaction parameters between the different functional groups which are present in the mixtures considered since the methods employed were UNIFAC and ASOG. They reported to have established a computerized data bank containing information referring to 2097 experimental values of infinite dilution activity coefficient.

Differences between the experimental and calculated values of the activity coefficients at infinite dilution were assessed in terms of

$$DD = \left| \frac{\gamma^{\infty}_{exp} - \gamma^{\infty}_{cal}}{\gamma^{\infty}_{exp}} \right| * 100 \qquad ....(7.2)$$

where DD is the mean deviation error.

The results obtained for some binary mixtures can be summarised as follow:

(1) significant differences between the experimental values for the activity coefficients obtained by different authors for the same mixtures were observed.

(2) mean deviation in the range of 24 - 91% were obtained for the different classes of solutes between the experimental and predicted activity coefficient at infinite dilution.

(3) best results were obtained with UNIFAC with a total mean deviation of 37%.

In conclusion, the authors noted that while the deviations for results obtained with the UNIFAC are not small, the method can be useful as a guide for solvent selection.

7.3 The Basic Extractive Distillation flowsheet.

Fundamentally, a flowsheet for accomplishing an extractive distillation process is shown in Figure 7.1. The solvent is added at the top of the first column, the extraction column. Since the solvent is much less volatile that either of the components A an B, it flows down the column to leave with the bottom products. While in the column, the solvent increases the volatility of A with respect to B, and thus makes the separation easier. The second column is the solvent recovery column which removes B from the solvent. This is always an easy separation because the solvent is much less volatile than B.

Usually, the solvent is fed a few stages below the top plate in order to reduce the solvent concentration in the ascending vapour to a negligible amount before the overhead product is

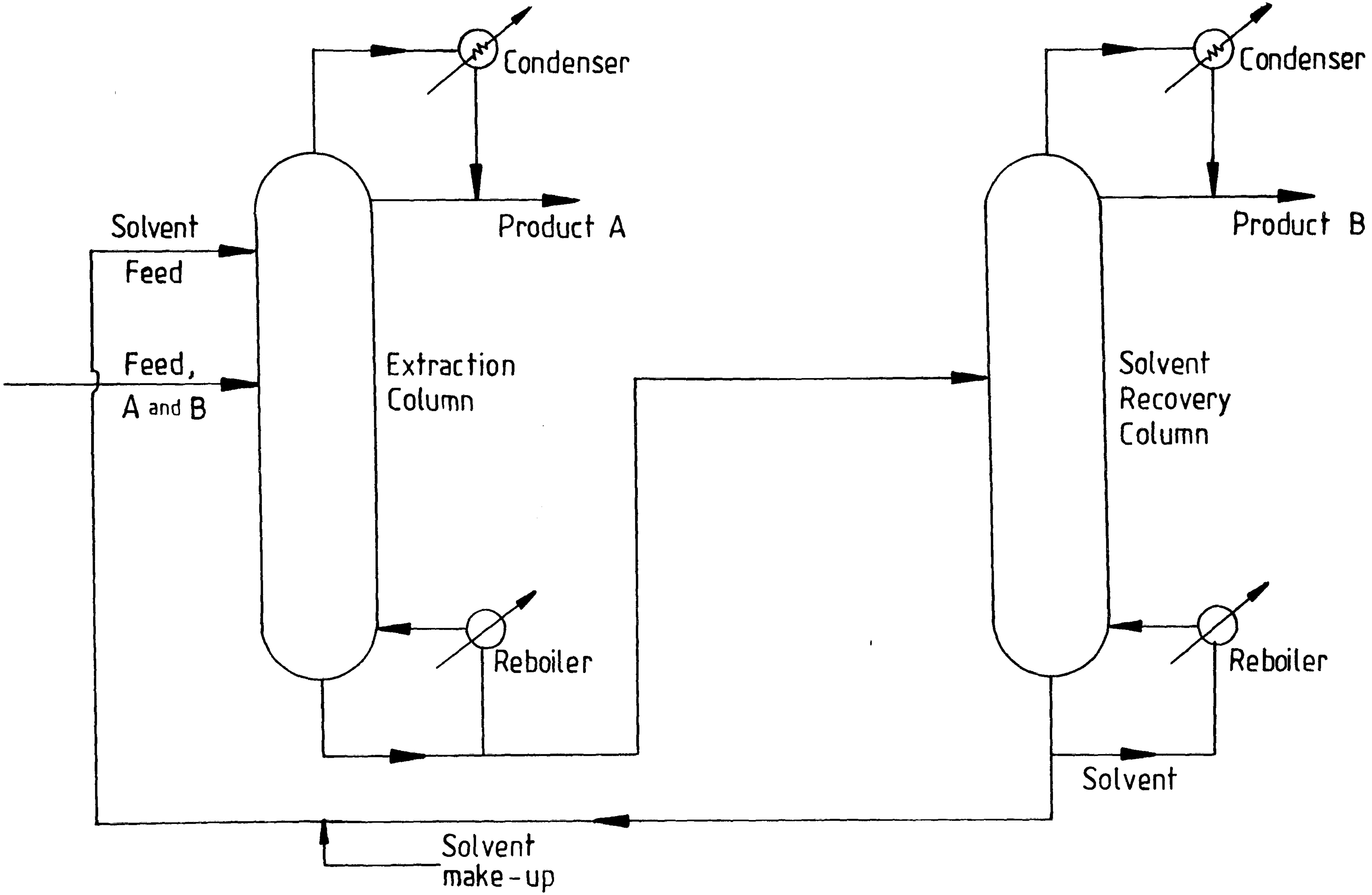

FIG. 7.1 TYPICAL EXTRACTIVE DISTILLATION PROCESS

withdrawn. The overflow rate of liquid solvent from plate to plate is relatively constant because of its low volatility. The actual concentration of the solvent will change abruptly at the component feed introduction point if a liquid feed is used.

High solvent concentration on the plates are usually desirable to maximises the difference in volatility between the binary components being separated. However, the solvent flow rate is generally a compromise between improved separability with increasing solvent concentration and the increasing cost of solvent recovery at increased flow rate.

7.4 Solvent Selectivity.

As already mentioned, the selection of the most promising solvents capable of enhancing the relative volatility of the key components to be separated presents a major problem in extractive distillation process. Typically, certain physical prerequisites should be satisfied [Treybal(1980), Dongen et al(1985)]. The solvent

(1) must have a low latent heat since part of the solvent stream will be vaporised in the reboiler. This maintains high concentration in the liquid.

(2) has to be thermally stable.

(3) must be non-reactive with the components in the mixture for which it is to be added.

(4) must be non-corrosive.

(5) must be non-toxic.

(6) has to be available and in-expensive.

(7) has to be easily separated from the component with which it associates, and

(8) must be miscible with both components over the full concentration range.

Apart form these physical properties, solvents are usually selected based on their selectivity at infinite dilution. Selectivity is a measure of the effect of the solvent on the relative volatility of the key components and thus the ease of separation.

Quantitatively, selectivity is defined as the ratio of the relative volatility of the key components in the mixture which are to be separated in the presence of the solvent, to their relative volatility before the addition of the solvents [Winkle(1967)]. Thus, for key components, i and j and solvent S, selectivity, $\mathcal{S}_{ij}$, is

$$\mathcal{S}_{ij} = \frac{\alpha_{ijS}}{\alpha_{ij}} \qquad \ldots\ldots\ldots(7.3)$$

But the relative volatility of component i with respect to j (i.e. α_{ij}) is the ratio of their Vapour Liquid Equilibrium (VLE) ratios. This is expressed as

$$\alpha_{ij} = \frac{y_i / x_i}{y_j / x_j} = \frac{\gamma_i \, f_i^o \, \theta_j}{\gamma_j \, f_j^o \, \theta_i} \qquad \ldots\ldots\ldots(7.4)$$

At low to moderate pressures and temperatures the standard state fugacity, f_i^o, can be approximated by pure-component vapour pressure (p_i^o) and the ratio of the vapour-phase fugacity coefficient, θ_i, is usually close to 1.0. The Equation (7.4) becomes:

$$\alpha_{ij} = \frac{\gamma_i \, p_i^o}{\gamma_j \, p_j^o} \qquad \ldots\ldots\ldots(7.5)$$

Since the vapour pressure ratio can be expected to remain relatively constant for a given separation, the most effective way of changing the relative volatility is to alter the ratio of the liquid-phase activity coefficients, γ . Therefore, the primary effect of adding a solvent a solvent to the original mixture is to alter the value of the activity coefficient ratio. This is the basis of an extractive distillation. It is then possible to estimate the effectiveness of a solvent by estimating values of the activity coefficients of the solutes in the presence of the solvents.

As the activity coefficients depend on phase compositions and the role of the solvent tends to increase with an increase of its concentration, it is common practice to consider the situation of infinite dilution. Then the definition of selectivity at infinite dilution becomes, from Equation (7.5)

$$S_{ij}^{\infty} = \frac{\gamma_i^{\infty}}{\gamma_j^{\infty}} \qquad \ldots\ldots(7.1)$$

The values of these activity coefficients can be predicted or obtained from experimentally determined observations. Very often, engineers have no experimental data at all or not enough for the mixtures being considered, and they have to rely on some generalised method for the prediction of the required information. Group contribution methods are examples of such methods like the UNIFAC which is employed in this work in the prediction of the activity coefficients.

Having established these basic principles, we now report on the investigations carried out in this work. In brief, the solvent selectivity at infinite dilution of some common key components used in extractive distillation processes are determined; and the solvents are then ranked in the order of their selectivity at infinite dilution for a particular given mixture. This ranking is then compared with the available experimental data, and with the total annual cost of the extractive distillation process - the design and costing are as explained below in section 7.6. This brings into focus the reliability of the use of selectivity as a criterion for solvent screening.

The key component mixtures considered include

n-Butane and Trans-2-butene.

n-Hexane and Benzene

n-Pentane and 1-Pentene

2-Methyl-1-butene and Isoprene.

But before embarking on the above, there is the need to establish the optimum solvent feed rate as this is necessary for obtaining the total annual cost of an extractive distillation process.

7.5 Optimum Solvent Feed Rate

The solvent feed rate is generally a compromise between improved separability with increasing solvent concentration and increasing cost of solvent recovery at increased flow rate. An increase in rate generally increases the relative volatility of the key components to be separated, thus decreasing the number of plates required. The solvent recovery costs, the initial solvent cost, and the reboiler steam requirements are also increased at the higher rate. These factors have to be balanced to yield an optimum solvent feed rate.

Some workers [Souder(1964), Nath and Mortad(1981)] have used a solvent feed rate of about two times the feed rate of the mixture to be separated. Knicle(1982) suggested three times the feed rate of the components. In the work of Kumar et al(1972) an exceptionally high solvent rate was used: 0.85 to 0.90 mole fraction of solvent concentration at the solvent feed plate. This may amount to about 5 to 9 times the feed rate of the components. They considered the effects of selectivity and activity coefficients on the cost of the propane-propylene extractive distillation process.

We note that these values of optimum solvent feed rate are normally picked arbitrarily as rules of thumb. Except for the work of Kumar et al(1972) already mentioned, we could find nothing in the literature on the economic design of extractive distillation regarding the optimum solvent feed rate.

In this work, calculation of the capital and operating costs for an extractive distillation is performed as explained below in section 7.6. The calculation is done for a particular case of a mixture of n-Butane/Trans-2-butene using Acetone as the solvent. The solvent rate is varied from 50 to 500 kmole per 100 kmoles of the feed rate of the key component mixtures. Three levels of concentration are examined. These are 25/75, 50/50 and 75/25. For example, 25/75 means 25kmoles of n-Butane to 75 kmoles of Trans-2-butene. The results are given in Table 7.1 and displayed in Figure 7.2. Comments on this table and figure are made under the results and discussions of section 7.7.

TABLE 7.1 The optimum solvent feed rate for n-Butane/Trans-2-butene/Acetone extractive distillation process.

Feed rate of the key components = 100 Kmoles/hr.

Solvent feed rate, S Kmole/hr	Total Annual Cost in dollars		
	25/75 kmoles of A & B	50/50 Kmoles of A & B	75/25 Kmoles of A & B
50	1214838	1363128	1496938
100	1056369	1162803	1256066
200	990286	1074161	1141773
300	1010741	1091297	1152759
400	1074988	1152980	1204275
500	1134438	1227878	1271732

7.6 Economic Evaluations of Extractive Distillation for the Comparison of Solvents.

The economic evaluations of the extractive distillations are carried out using many different solvents for separating three different binary mixtures. These are n-Butane/Trans-2-butene, 2-Methyl-1-butene/Isoprene and n-Hexane/Benzene. For each case, we did a complete design and costing of the extractive distillation process using our cost estimating computer programs. The UNIFAC method is used to establish the Vapour Liquid Equilibrium (VLE) data for the components. By using the same UNIFAC predicted VLE data in both the complete costing and in the determination of the selectivity at infinite dilution, a valid comparison of solvent ranking in terms of the total annual cost and selectivity at

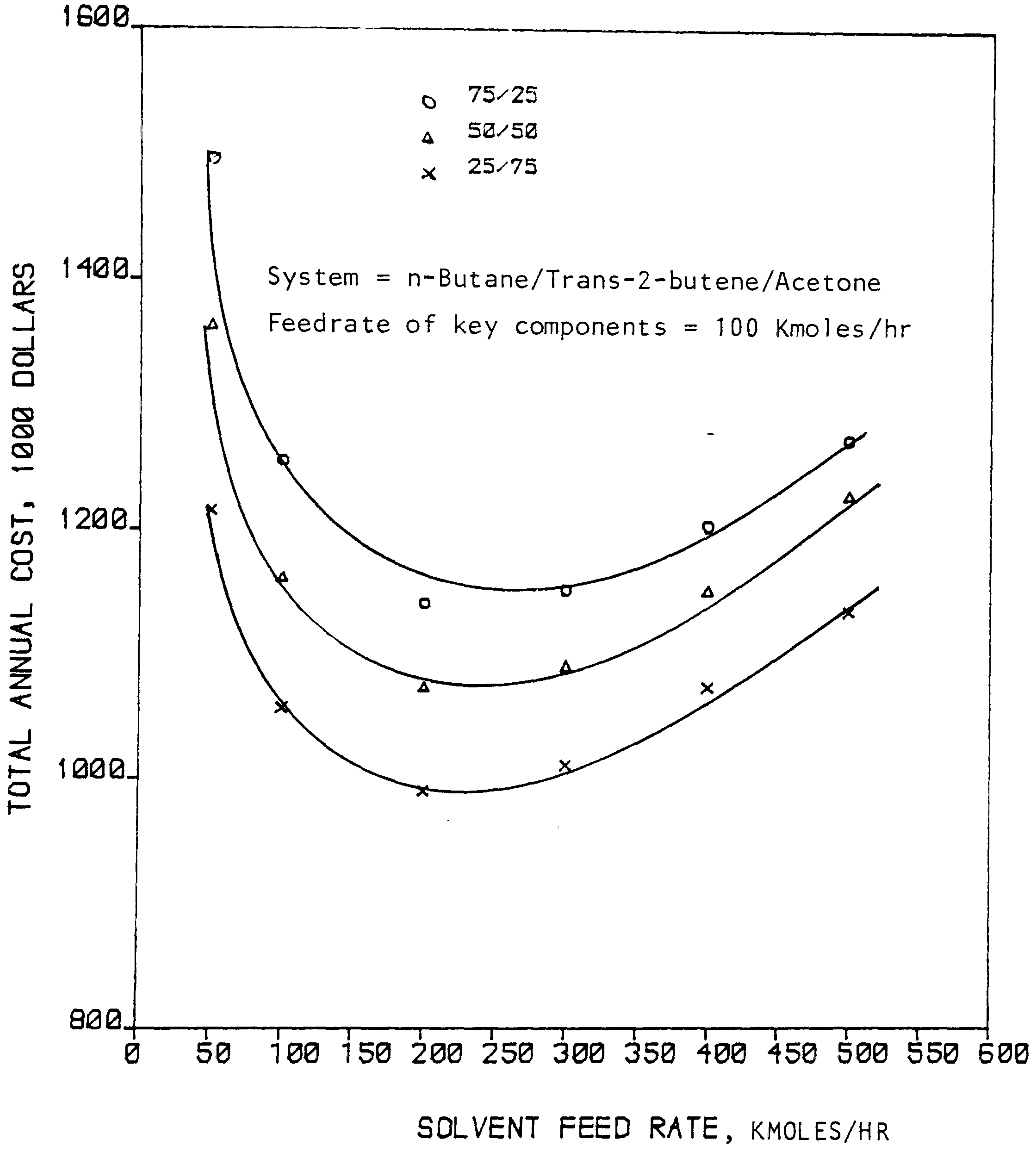

FIG. 7.2 OPTIMUM SOLVENT RATE FOR AN EXTRACTIVE DISTILLATION

infinite dilution is possible. The design calculation steps make use of known equations and a rigorous method of Naphtali and Sandholm(1971) to obtain the number of plates, column height and diameter; and the heat loads at the condensers and reboilers. Then the heat transfer areas of the condensers and reboilers are obtained. All these are used to obtain the capital and the energy (or operating) costs of the extractive distillation process. The capital costs involve two columns, two condensers and two reboilers. The energy costs include the cost of condensers' cooling water and the reboilers' steam cost. The other necessary details on the sizing and costing analysis are given in Chapter Nine and in Appendices B and C.

The cost of the solvents is assumed constant at the optimum solvent rate and therefore not considered in the calculations of the total annual cost. This optimum solvent rate is taken from the results obtained in Section 7.5 and it is two times the feed rate of the key component. The heat transfer duty of the solvent-cooler (if any) and the cost of solvent are always considered negligible compared with the steam and cooling water cost [Kumar et al(1972)].

The entering feed stream to the extraction column is taken to be 50/50 molar composition of the key component mixtures A and B.

7.7 Results and Discussions.

Figures 7.3 to 7.5 and Tables 7.2 to 7.4 show the graphical and numerical values of the experimental solvent selectivity obtained from published works [Hess et al(1952), Gerster et al(1960), Tassios(1972)], and those predicted in this work using the UNIFAC group method. A discussion on the accuracy of the collected results from literature is certainly difficult as the authors do not indicate either the purity of the chemicals used or the experimental errors to be expected.

Differences between the experimental and predicted values of selectivity at infinite dilution are assessed in terms of an equation similar to that of Equation 7.2

$$DD = \left| \frac{S^{\infty}_{exp} - S^{\infty}_{pred}}{S^{\infty}_{exp}} \right| * 100 \qquad \ldots\ldots(7.6)$$

where 'exp' connote experimental and 'pre' predicted values.
DD is the percentage mean deviation error.

The mean deviations calculated in terms of Equation (7.6) above are summarized below in Table 7.6 for the mixtures of n-Butane/Trans-2-butene, n-Pentane/1-Pentene and n-Hexane/Benzene whose experimental data are readily available.

TABLE 7.2 Comparison between Experimental and Predicted selectivities at infinite dilution in solvents for the separation of n-Butane/Trans-2-butene at 25°C.

Solvents	Experimental		Predicted			
	S^{∞}_{exp}	Order	γ^{∞}_1	γ^{∞}_2	S^{∞}_{pre}	Order
Nitromethane	1.60	1	7.942	4.826	1.645	1
Acetonitrile	1.49	2	12.353	7.574	1.631	2
Butyronitrile	1.42	3	3.091	2.177	1.420	3
Morpholine	1.41	4	2.731	1.940	1.408	4
Cyclohexanone	1.32	5	1.858	1.440	1.290	6
Methyl Isobutyl Ketone	1.23	6	1.821	1.387	1.312	5
1-Butanol	1.21	7	2.525	2.283	1.1060	10
2-Butanol	1.20	8	2.530	2.284	1.1062	9
Ethyl Butyrate	1.17	9	1.190	1.017	1.168	7
Ter-Butyl alcohol	1.16	10	2.520	2.280	1.1064	8

exp = denote experimental results.
pre = denote predicted results.

= Selectivity at infinite dilution

= Activity coefficient.

TABLE 7.3 Comparison between Experimental and Predicted selectivities at infinite dilution in solvents for the separation of n-Hexane/Benzene at 25°C.

Solvents	Experimental		Predicted			
	S^{∞}_{exp}	Order	γ^{∞}_1	γ^{∞}_2	S^{∞}_{pre}	Order
Dimethyl Sulfoxide	22.00	1	41.572	3.180	13.073	1
Nitromethane	15.00	2	14.109	3.598	3.921	6
Dimethyl formamide	12.50	3	13.685	1.550	8.830	2
Aninile	12.20	4	8.187	1.832	4.468	4
Furfural	10.90	5	10.605	2.003	5.296	3
Propionitrile	6.50	6	6.473	1.692	3.825	7
Phenol	6.00	7	7.793	1.802	4.325	5
Pyridine	5.20	8	3.763	1.277	2.946	8

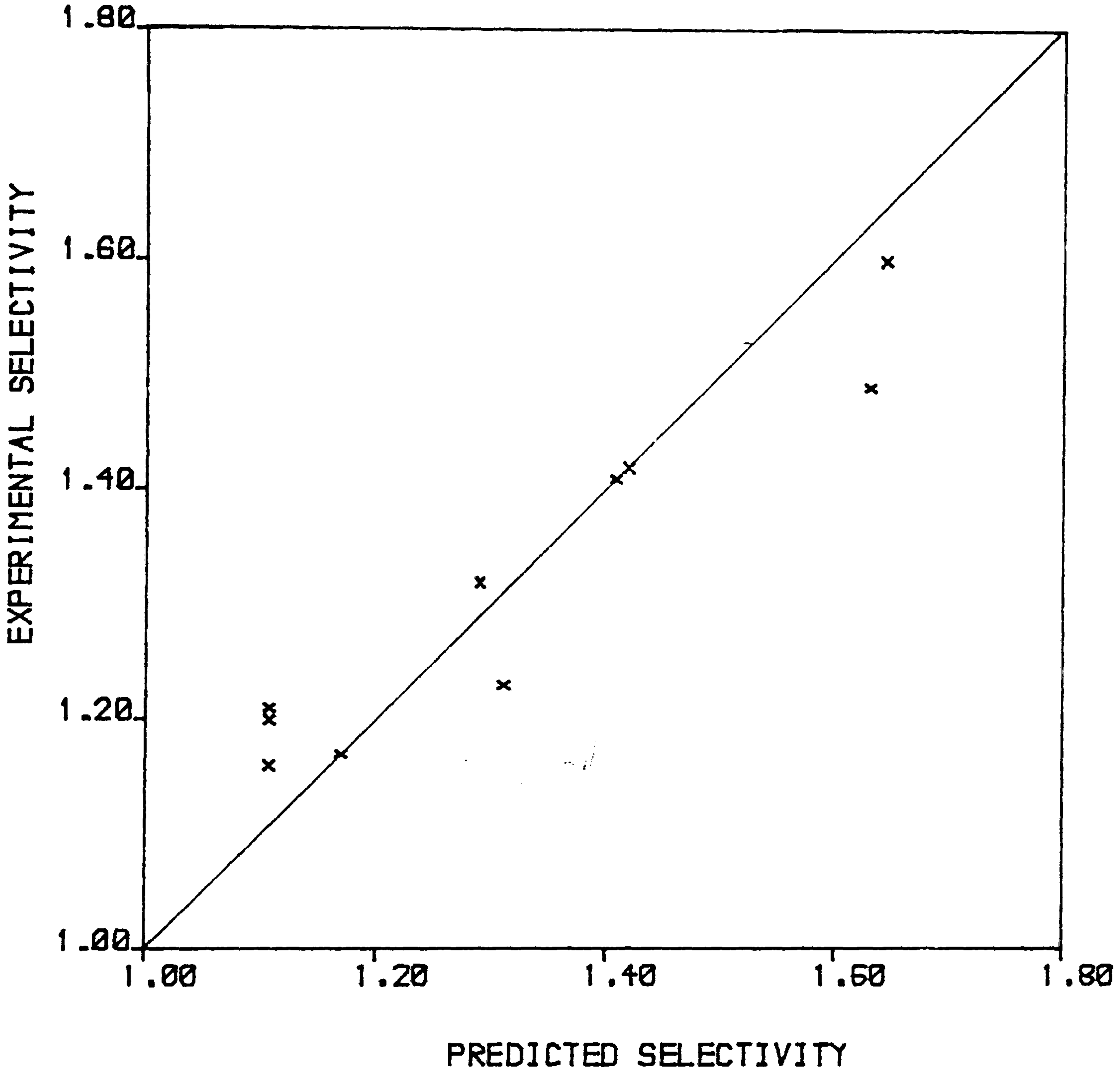

FIG. 7.3 SOLVENT SELECTIVITY FOR THE MIXTURE OF N-BUTANE/TRANS-2-BUTENE

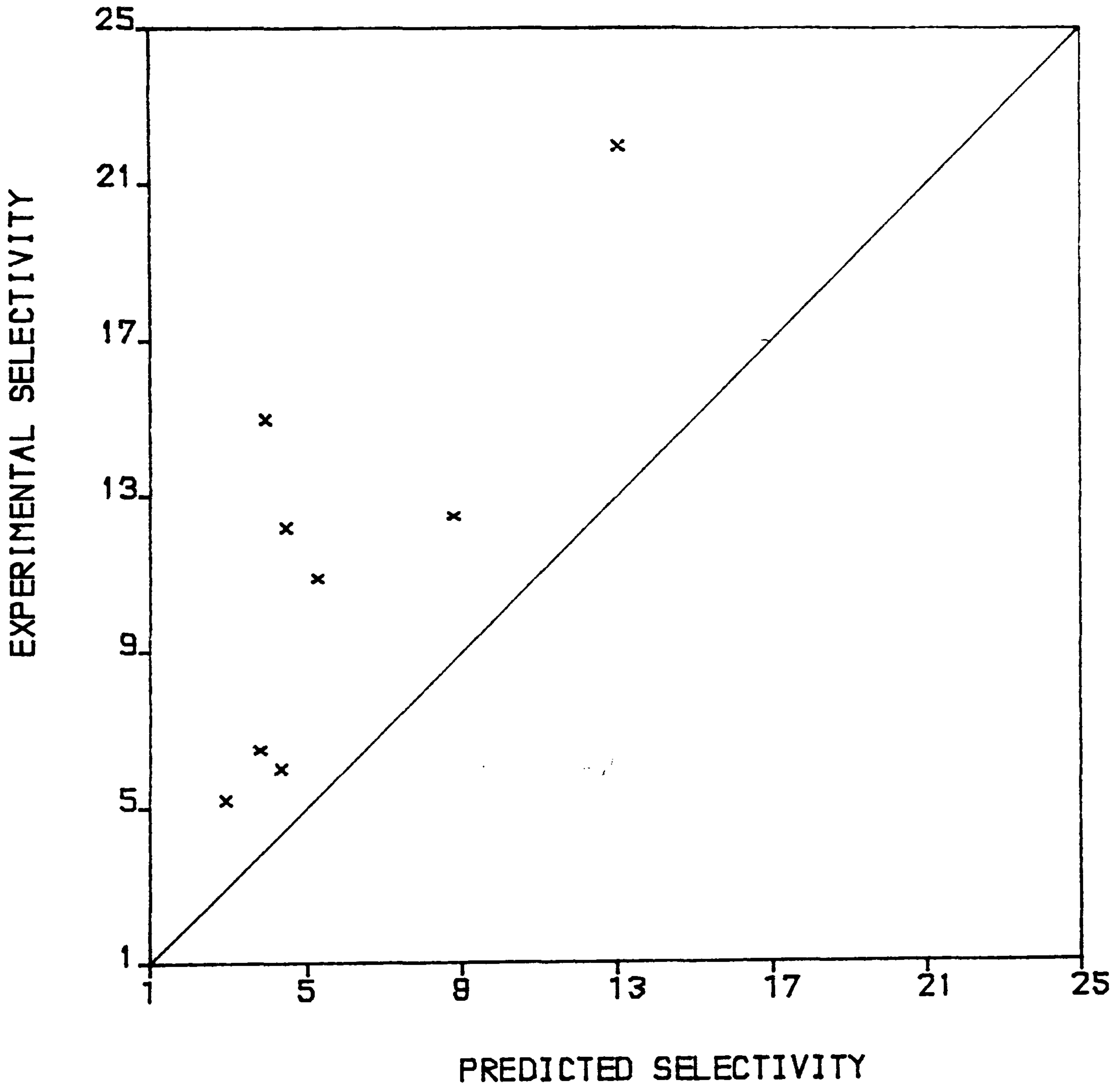

FIG. 7.4 SOLVENT SELECTIVITY FOR THE MIXTURE OF N-HEXANE/BENZENE

TABLE 7.4 Comparison between Experimental and Predicted selectivities at infinite dilution in solvents for the separation of n-Pentane/1-Pentene at 25°C.

	Experimental				Predicted			
Solvents	γ_1^∞	γ_2^∞	S_{12}^∞	Order	γ_1^∞	γ_2^∞	S_{12}^∞	Order
Nitromethane	53.50	21.50	2.49	1	10.74	5.83	1.84	6
-Butyrolacetone	26.99	12.44	2.17	2	7.38	4.02	1.82	7
Acetonitrile	20.40	9.45	2.16	3	17.24	9.36	1.84	5
Pyrrolidone	33.49	16.80	1.99	4	7.89	3.83	2.06	2
n-Methylpyrrolidone	10.74	5.48	1.96	5	3.25	2.07	1.57	11
Acetonylacetone	10.50	5.63	1.87	6	6.22	3.29	1.89	4
Dimethylacetamide	9.16	4.95	1.85	7	4.04	2.40	1.69	9
Propionitrile	8.28	4.42	1.85	8	5.34	3.30	1.62	10
Ethylene chloohydrin	24.00	13.40	1.79	9	8.40	6.28	1.34	16
Methylcarbitol	13.70	7.98	1.72	10	6.20	4.84	1.28	18
Pentanedione	4.74	2.75	1.72	11	10.70	4.83	2.22	1
Methylcellosolve	14.50	8.60	1.69	12	9.11	7.58	1.20	19
Acetone	5.28	3.16	1.67	13	4.74	2.75	1.72	8
Acetophenone	5.15	3.13	1.65	14	3.48	2.22	1.57	12
Cyclopentanone	4.79	2.91	1.65	15	2.61	1.83	1.43	15
Tetrahydrofurfuryl alcohol	11.15	6.89	1.62	16	4.49	3.81	1.18	20
Butyronitrile	5.35	3.30	1.62	17	3.79	2.48	1.53	14
Methyl Ethyl Ketone	3.42	2.11	1.62	18	3.38	2.17	1.55	15
Methanol	27.00	17.70	1.53	19	14.43	7.60	1.90	3
Diethyl Ketone	2.56	1.79	1.43	20	2.00	1.51	1.33	17
Tetrahydrofuran	1.72	1.22	1.41	21	1.81	1.55	1.17	21

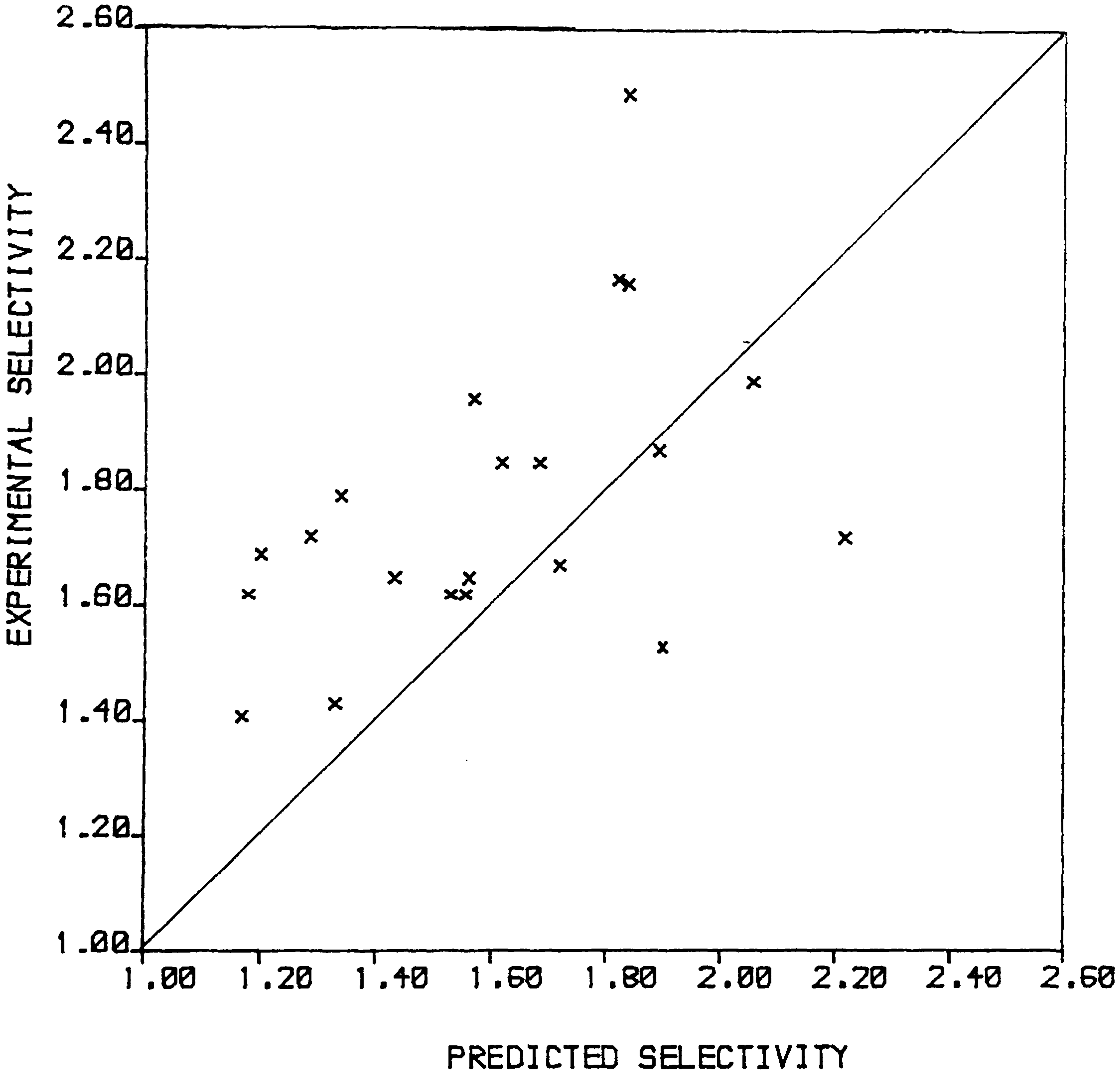

FIG. 7.5 SOLVENT SELECTIVITY FOR THE MIXTURE OF N-PENTANE/1-PENTENE

TABLE 7.5: Calculated activity coefficients and Selectivity at infinite dilution for some key component mixture.

Solvents	Formular	n-Butane/Trans-2-butene			n-Pentane/1-Pentene			n-Hexane/Benzene		
		γ_1^∞	γ_2^∞	S_{12}^∞	γ_1^∞	γ_2^∞	S_{12}^∞	γ_1^∞	γ_2^∞	S_{12}^∞
Acetone	C_3H_6O	3.8467	2.4816	1.550	4.7390	2.7514	1.722	5.6744	1.7264	3.286
Methyl Ethyl Ketone	C_4H_8O	2.7946	1.9486	1.434	3.3789	2.1748	1.554	3.9707	1.2929	3.071
Diethyl Ketone	$C_5H_{10}O$	1.7503	1.3789	1.269	2.0020	1.5089	1.327	2.2255	0.9372	2.375
Acetonitrile	CH_3CN	11.9900	7.2410	1.656	17.2377	9.3621	1.841	24.0864	3.0987	7.773
Propionitrile	C_2H_5CN	4.2782	2.8868	1.482	5.3379	3.3033	1.616	6.4731	1.6922	3.825
Butyronitrile	C_3H_7CN	3.0906	2.1770	1.420	3.7867	2.4778	1.528	4.5092	1.4001	3.221
Nitromethane	CH_3NO_2	7.9420	4.8262	1.646	10.7373	5.8246	1.843	14.1089	3.5982	3.921
Methanol	CH_3OH	10.6677	6.3479	1.681	14.4341	7.5978	1.900	18.9819	6.1907	3.066

TABLE 7.6 Comparison between the experimental and Predicted values of Selectivity at infinite dilution.

Components Mixtures	Mean Deviation	No. of data points
n-Butane/Trans-2-butene	4.256	10
n-Pentane/1-Pentene	15.144	21
n-Hexane/Benzene	37.100	8

Though the number of data points are relatively few, the percentage deviation obtained may not differ for a larger number of data points. For example, Bastos et al(1985) used a larger number of data points (109 data points were reported) and obtain a percentage deviation of 37% for the n-Hexane/Benzene mixture which is the same value given in Table 7.6.

For these key component mixtures, list of solvents are ordered in terms of experimental selectivities at infinite dilution. This is compared with those ordered in terms of the predicted selectivities at infinite dilution. The agreement is only fair. In most cases, the experimental selectivity values are higher than those predicted using the UNIFAC method. This is difficult to explain as the accurancy of the experimental data cannot be evaluated. Nevertheless, for most solvents, the percentage error is reasonably small except for the component mixture of n-Hexane/Benzene.

Inspection of the activity coefficient values, say, for 1-Pentene [Table 7.4] shows that for any solvent the values of γ_2^∞ is smaller in magnitude than the corresponding values of γ_1^∞. According to Gerster et al(1960), the 1-Pentene molecule permits greater interaction to exist between olefin and solvent molecules than between paraffin and solvent molecules, and the volatility of the olefin is reduced accordingly. From our results, similar observation can be made for the trans-2-butene in n-Butane/Trans-2-butene and for Benzene in n-Hexane/Benzene mixtures.

As for the magnitudes of the first key component of the various mixtures, two generalizations can be made for simpler types of solvents - those consisting a single functional group attached to the methyl or methylene groups. Results in Table 7.5 are used for these illustrations.

(1) γ_1^∞ decreases as the number of methylene group in the solvent increases. For example, the value of γ_1^∞ for solvents like acetonitrile, propionitrile and butyronitrile are 11.9900, 4.2782 and 3.0906 for n-Butane/Trans-2-butene; 17.2377, 5.3379 and 3.7867 for n-Pentane/1-Pentene; and 24.0864, 6.4731 and 4.5092 for n-Hexane/Benzene separations. A similar trend is observed for Acetone, Methyl ethyl ketone and Diethyl ketone. As Gerster et al also noted for their case of n-Pentane/1-Pentene, the effectiveness of the polar group in promoting non-ideality is "diluted" as the number of methylene group increases.

(2) The magnitude of γ_1^∞ depends, for a given number of methylene or methyl groups in the solvent molecule, upon the nature of the functional or polar group. For example, γ_1^∞ in the presence of Acetone is 3.8467, 4.7390 and 5.6744 respectively for n-Butane/Trans-2-butene, n-Pentane/1-Pentene and n-Hexane/Benzene separations while in the presence of propionitrile it is 4.2782, 5.3379 and 6.4731 respectively for the three types of mixtures.

A similar trend is observed for the solvent selectivities, S^∞

These two generalizations have been expressed for the n-Pentane/1-Pentene separation which was experimentally considered by Gerster et al(1960). It is interesting that these generalizations can be extended to some other key component mixtures as is done here. These observations also lend some support to the use of UNIFAC in predicting activity coefficients of liquid mixtures.

Now to the result of the optimum solvent feed rate investigation. For the three levels of concentration of the key component mixture shown in Figure 7.2, the optimum solvent feed rate lies between 200 and 300 kmole/hr for 100 Kmoles/hr of the feed rate of the key mixtures. That is, the optimum solvent feed rate is two to three times the feed rate of the key component mixtures. This is in agreement with values that have been suggested in the literature. A solvent feed rate of two times the feed rate of the key components is considered appropriate to be used in further analysis. This keeps the solvent recovery cost in the second column to the minimum.

Figures 7.6, 7.7 and 7.8 and Tables 7.7, 7.8 and 7.9 show the effects of solvent selectivity at infinite dilution on the total annual cost (TAC) of an extractive distillation for 2-Methyl-1-butene/Isoprene, n-Butane/Trans-2-butene and n-Hexane/Benzene mixtures respectivily.

As the solvent selectivity increases, the total annual cost decreases. The decrease is sharp at lower selectivity, but the slope of the curve flattening out at higher selectivity of about 1.40 for 2-Methyl-1-butene/Isoprene; above 9.0 for n-Hexane/Benzene and 1.60 for n-Butane/Trans-2-butene mixtures. The reason for the shape of the curve is clear. Higher selectivity yields higher relative volatility. A higher selectivity therefore results in a smaller reflux ratio and fewer equilibrium number of plates required for the given separation in the extraction column. The lower reflux rate corresponds to a lower vapour flow rate and a thinner column. This could result in the overall decrease in the cost of the utilities used, which constitute the major cost of an

TABLE 7.7 : Relationship between the total annual cost (TAC) and Selectivity at infinite dilution (S^{∞}).
(2-Methyl-1-butene/Isoprene)

Solvents	TAC in Dollars	Order	S^{∞}	Order
Nitromethane	769306	1	1.6339	2
Acetonitrile	847002	2	1.6319	3
Propionitrile	1124459	3	1.4323	6
Dimtheyl acetamide	1198127	4	1.4945	5
Methanol	1204804	5	1.6839	1
Butyronitrile	1297594	6	1.3545	7
Morpholine	1450704	7	1.3408	9
Methyl Ethyl Ketone	1480248	8	1.3770	8
Acetone	1504035	9	1.5266	4
Ethylene Chlorhydrin	1533817	10	1.1854	14
Cyclopentanone	1722085	11	1.2665	10
Methyl Isobutyl Ketone	1917681	12	1.2237	11
Cyclohexanone	2144885	13	1.1976	12
Diethyl Ketone	2237229	14	1.1760	15
Ethyl Butyrate	2247301	15	1.1954	13
Tetrahydrofuran	4742780	16	1.0374	16

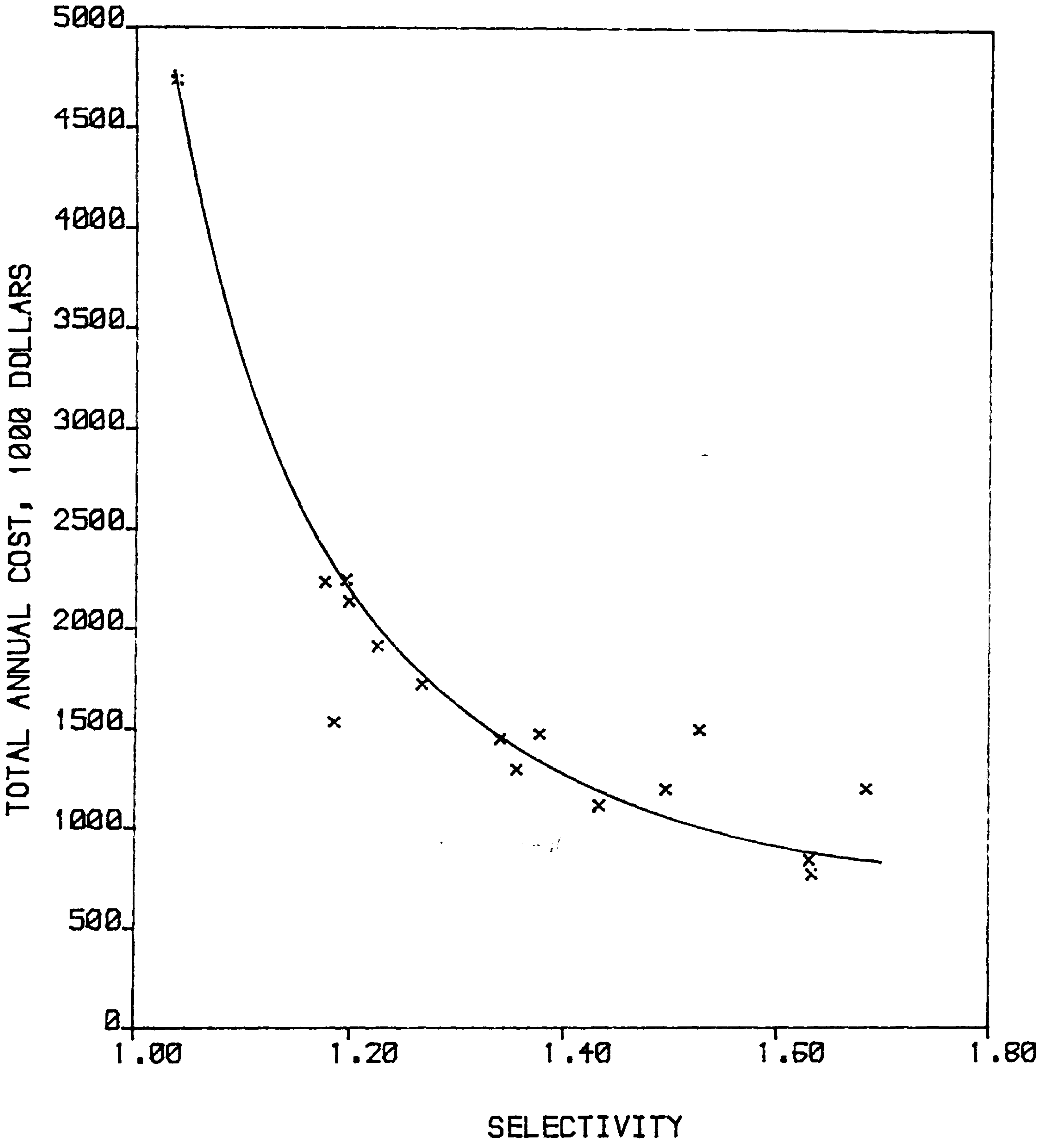

FIG. 7.6 EFFECT OF SOLVENT SELECTIVITY ON TOTAL ANNUAL COST OF EXTRACTIVE DISTILLATION OPERATION (2-METHYL-1-BUTENE/ISOPRENE)

TABLE 7.8 : Relationship between the total annual cost (TAC) and Selectivity at infinite dilution (S^{∞}).
(n-Butane/Trans-2-butene)

Solvents	:TAC in Dollars	:Order:	S^{∞}	:Order
Nitromethane	682607	1	1.6456	1
Acetonitrile	701752	2	1.6310	2
Acetone	1074161	3	1.5501	3
Butyronitrile	1124365	4	1.4197	4
Methyl Ethyl Ketone	1196157	5	1.4342	5
Morpholine	1395364	6	1.4084	6
Ethyl Butyrate	1421495	7	1.1683	11
Methyl Isobutyl Ketone	1566696	8	1.3124	8
Styrene	1710129	9	1.3265	7
Cyclohexanone	1936142	10	1.2902	9
Toluene	2038691	11	1.1796	10
Ethylbenzene	2485082	12	1.1488	13
1-Butanol	2571445	13	1.1060	15
2-Butanol	2651390	14	1.1062	14
Tetrahydrofuran	2654324	15	1.1489	12

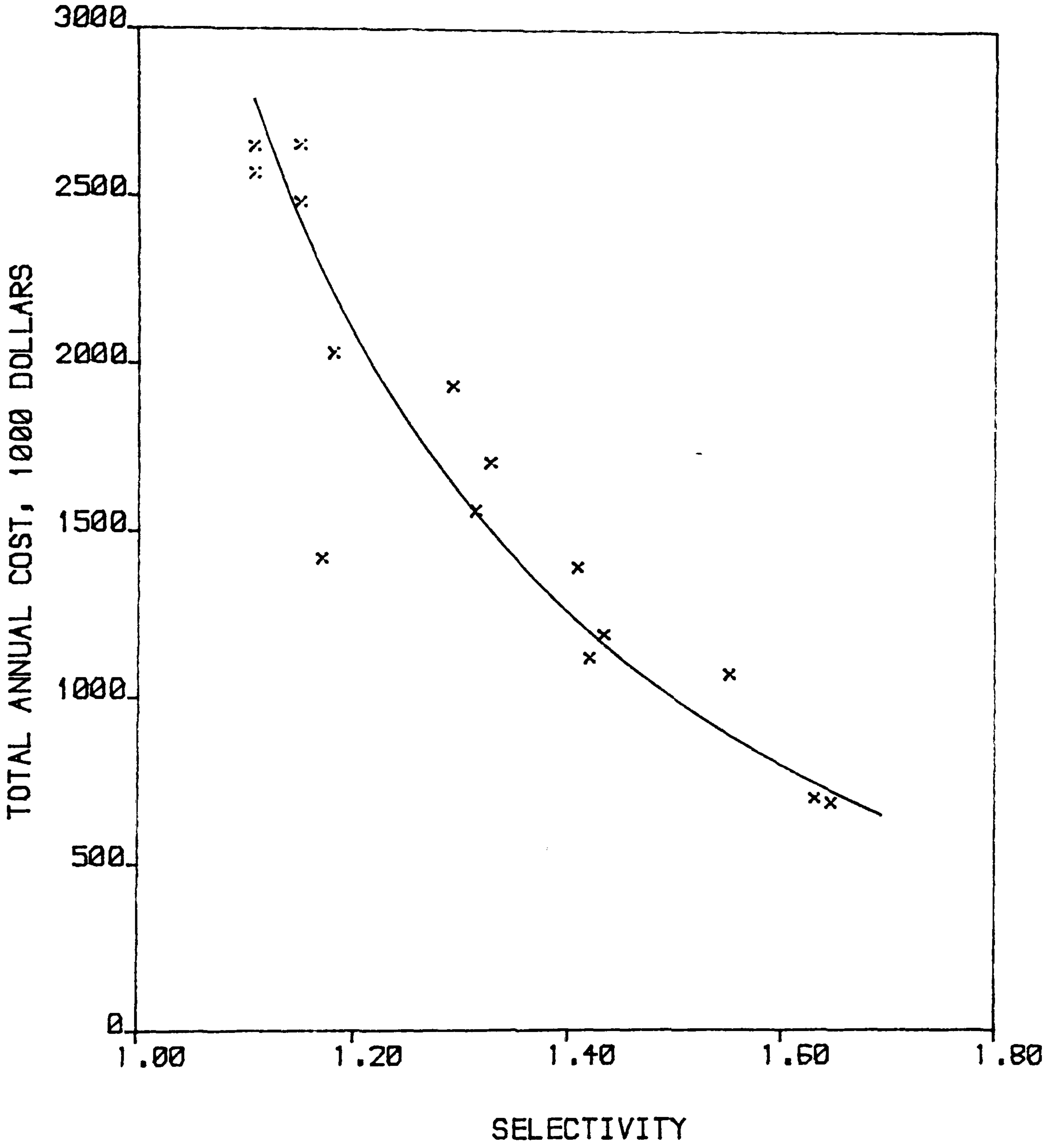

FIG. 7.7 EFFECT OF SOLVENT SELECTIVITY ON TOTAL ANNUAL COST OF EXTRACTIVE DISTILLATION OPERATION (N-BUTANE/TRANS-2-BUTENE)

TABLE 7.9 : Relationship between the total annual cost (TAC) and Selectivity at infinite dilution (S^{∞}). (n-Hexane/Benzene)

Solvents	:TAC in Dollars	:Order:	S^{∞}	:Order
Dimethyl sulfoxide	563200	1	13.0703	1
Dimethyl formamide	568304	2	8.8296	2
Furfuran	740255	3	5.2960	3
Phenol	845267	4	4.3250	5
Aniline	897585	5	4.4680	4
Styrene	1100363	6	1.9900	9
Pyridine	1159731	7	2.9462	8
Nitromethane	1168126	8	3.9211	6
Ethyl benzene	1206677	9	1.5115	11
Toluene	1398022	10	1.6508	10
Propionitrile	1777788	11	3.8253	7

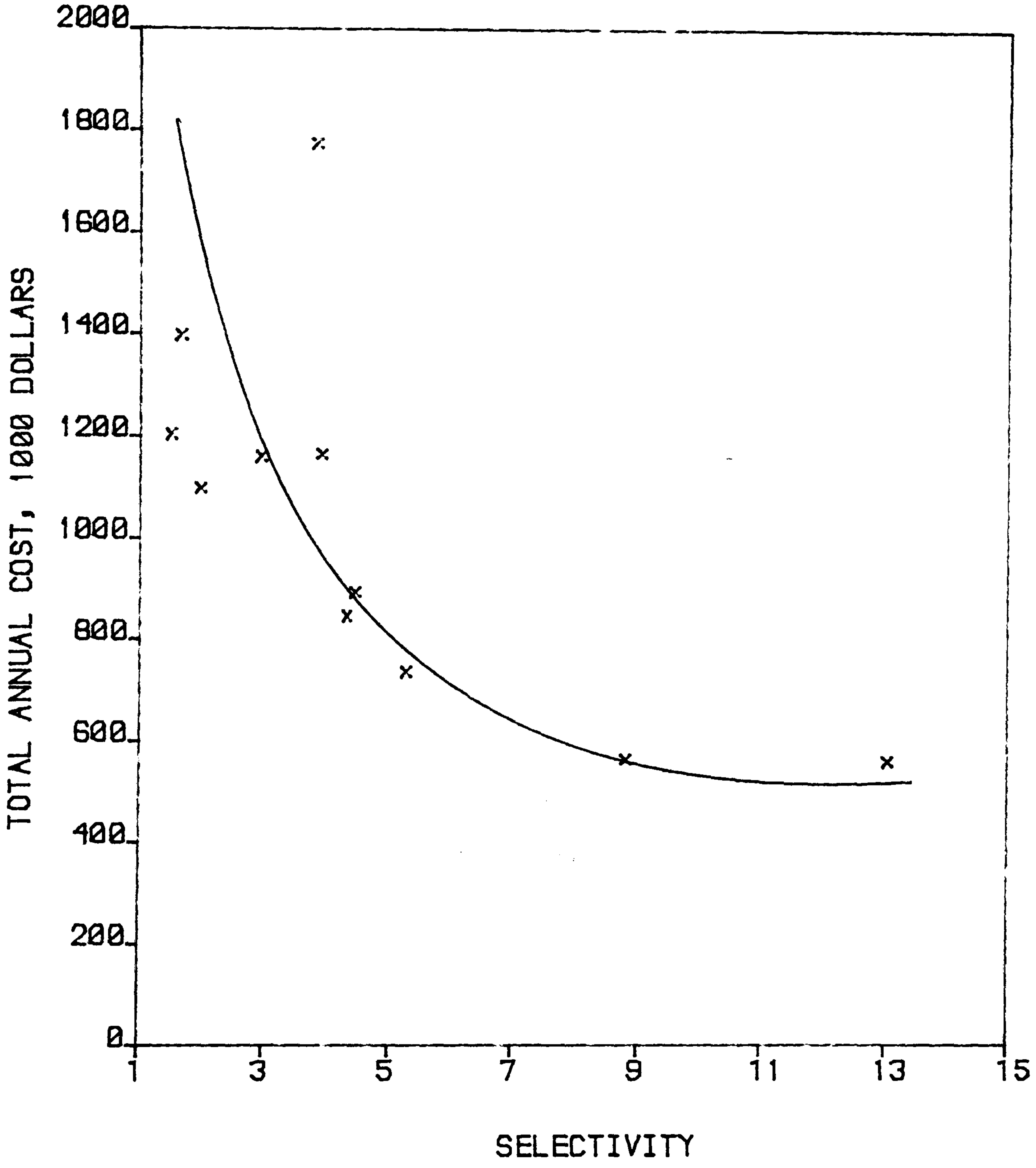

FIG. 7.8 EFFECT OF SOLVENT SELECTIVITY ON TOTAL ANNUAL COST OF EXTRACTIVE DISTILLATION OPERATION (N-HEXANE/BENZENE)

extractive distillation process. The change in the total annual cost resulting from a change in selectivity is higher at low selectivity than at high selectivities. The total annual cost then becomes controlled mainly by the almost constant cost of the recovery column as the selectivity increases to very high values. Most of the analyses reported here are on the basis of an equal molar composition of the original key component mixtures in the feed. The trends and patterns of the results are most unlikely to be affected by using other feed concentrations.

In conclusion, we observe that selectivity is still a useful tool in screening solvents for an extractive distillation process. But matching selectivity with the total annual cost does not produce a good correlation. This may not be too surprising. Choosing solvents on the basis of selectivity alone tends to emphasis more the cost of the extractive column in which the difficult separation takes place; whereas for good solvents the cost of the second column (i.e the solvent recovering column) is sometimes significant and in some cases may control the cost of the process. This leads us to the subject of the next chapter.

CHAPTER EIGHT

APPLICATIONS OF THE BDTVL METHOD TO EXTRACTIVE DISTILLATION II:

[A MORE ACCURATE METHOD OF SELECTING SOLVENTS.]

8.1 Introduction

In the last chapter, we determined the solvent selectivity of some common key component mixtures for various solvents in an extractive distillation process; the optimum solvent feed rate; and the relations between the solvent selectivity and the total annual cost. We concluded that although selectivity at infinite dilution is still a useful tool in screening potential solvents for an extractive distillation process, matching selectivity with the total annual cost did not produce a good enough correlation.

Furthermore, the solvent with the a highest selectivity at infinite dilution for a key component mixture may not necessarily have the appropriate or best relative volatility with the heavy component of the mixture for the solvent recovery column. An equation or expression that takes both the extraction and the solvent recovery columns into account will provide a better evaluation of solvents for an extractive distillation process.

Therefore, in this chapter, we present a two-term equation which permit a more accurate selection of potential solvents for an extractive distillation process. And this equation also lend itself to a simple approach for a preliminary decision on when an extractive distillation may be better economically than ordinary distillation. This was one of the problems introduced earlier in the previous chapter.

In the equation, the first term relates to the first column (i.e the extraction column) and the second term to the second (i.e the solvent recovery) column.

First, we derive the equation and then consider its applications to screening of solvents and economic comparison of the extractive distillation with the ordinary distillation.

8.2 Derivation of the BDTVL Equation for an Extractive Distillation Process.

The equation is derived from the Binary Distillation Total Vapour Load (BDTVL) method for distillation sequence evaluations which has been described in Chapter Five. This, simply, is an attempt to extend the method to an extractive distillation process.

The following assumptions are made:

(a) The assumptions of the BDTVL method in section 5.2.1 hold.

(b) Assume solvent is non-volatile which usually is a design specification. If a relatively non-volatile solvent is fed to the top of the column, then all the solvent flows down the column and appears in the bottom stream.

(c) Constant molar overflow, and

(d) The solvent feed is pure.

Assumptions (b-d) are those typically made in shortcut methods [Van Winkle(1967), Knickle(1982)] for an extractive distillation design.

The schematic diagram to be referred to in the derivation is shown in Figure 8.1.

It has been shown in Chapter Five that for a sharp separation, the Fenske(1932) equation for minimum reflux ratio becomes:

$$R_m = (x_{D,LK}/x_{F,LK}) \frac{1}{(\alpha_{LH} - 1.0)} \qquad \text{......(8.1)}$$

and

$$V = (1 + R_f R_m) D \qquad \text{.......(8.2)}$$

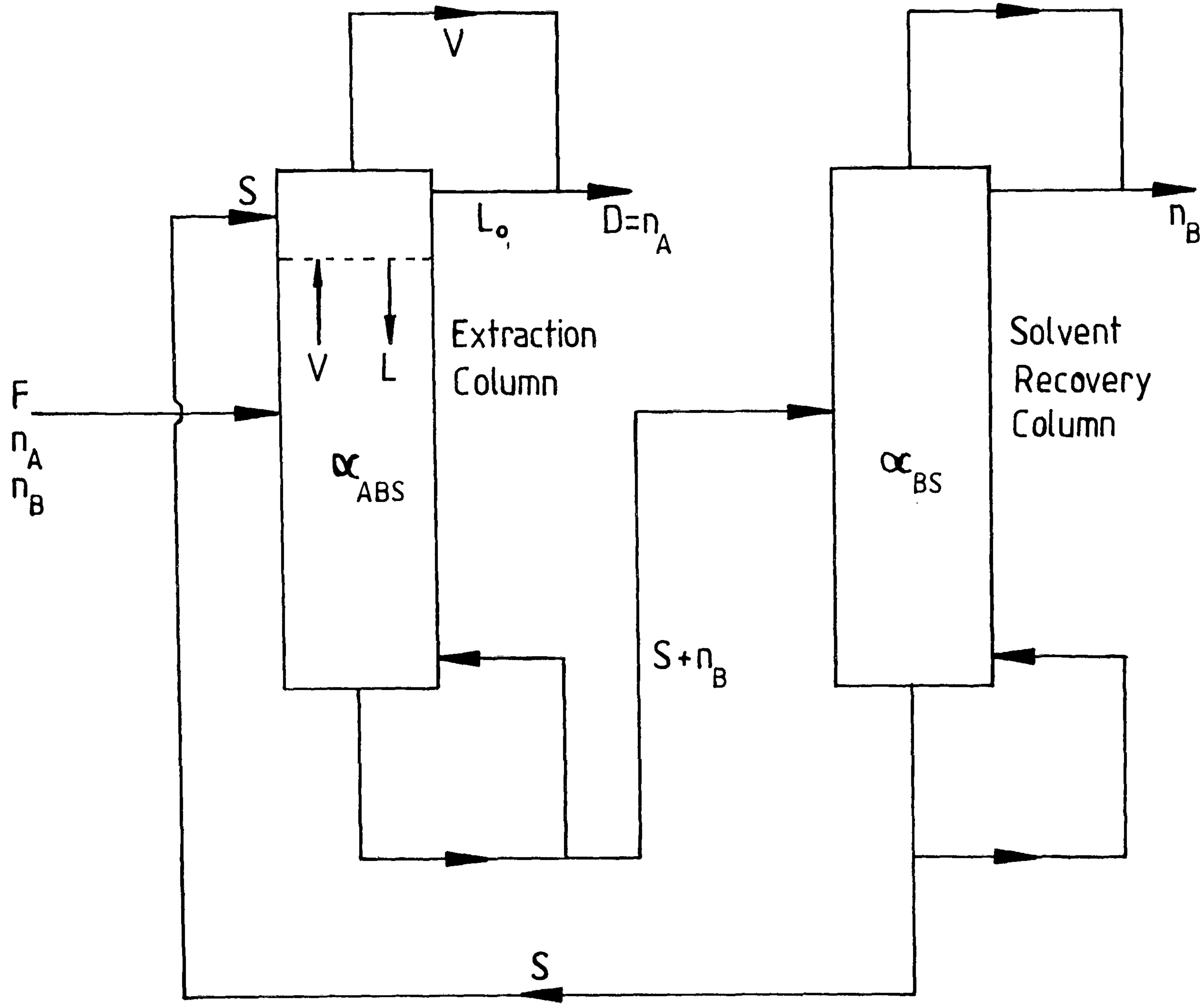

FIG. 8.1 SCHEMATIC DIAGRAM OF AN EXTRACTIVE DISTILLATION

$x_{D,LK}$, $x_{F,LK}$ are the mole fractions of LK (Light Key) component in the distillate and feed stream respectively.

α_{LH} is the relative volatility between the light and Heavy Key(HK) components.

In an extractive distillation, taking the total material balance through the rectifying sections of the extraction column at a point where the composition of the solvent is relatively constant yields,

$$V = L + D - S \qquad \text{..........(8.3)}$$

But $L = L_o + S$ ....(8.4)

Therefore,

$$V = (1 + R_f R_m) D \qquad \text{..........(8.5)}$$

Consider the extraction column and for components A, B and solvent S,

$$X_{D,A} = n_A/n_A = 1.0 \qquad \text{...........(8.6)}$$

$$X_{F,A} = \frac{X_A}{X_A + X_B + X_{FS}} \qquad \text{.............(8.7)}$$

$$D = n_A \qquad \text{..........(8.8)}$$

Note,

X_A, X_B, X_{FS} = mole fractions of components A, B and solvent S in the feed plate.

The X_{FS} can be specified or obtained by specifying the slope of the operating lines in either the rectifying or stripping sections of the column. The reasonable practical values of X_{FS} and that of the slope of the operating line in the stripping section of the column are 0.45 and 1.8 respectively [Smith(1963), Knickle(1982)].

F and S = component and solvent feed rate, Kmol/hr.

n_A and n_B = number of moles of component A and B respectively in the original feed stream.

At the feed plate, the composition of the components must match the feed stream composition [Coulson et at(1983)]. In other words,

$$\frac{X_A}{X_B} = \frac{x_A}{x_B} \qquad \text{...........(8.9)}$$

where x_A and x_B are the mole fractions of components A and B in the original feed stream.

$$\text{But } X_A + X_B + X_{FS} = 1 \qquad \text{........(8.10)}$$

$$x_A + x_B = 1 \qquad \text{........(8.11)}$$

From Eqn. (8.9)

$$X_B = \frac{x_B}{x_A} X_A$$

Substituting in Eqn. (8.10), we have

$$X_A = (1 - X_{FS})x_A \qquad \text{.........(8.12)}$$

Similarly,

$$X_B = (1 - X_{FS})x_B \qquad \text{..........(8.13)}$$

Therefore,

$$X_F = (1 - X_{FS})\ x_A = (1 - X_{FS})\frac{n_A}{F}$$

and

$$R_m = \frac{1}{(\alpha_{ABS} - 1)} \left[\frac{F}{(1 - X_{FS})\ n_A}\right] \qquad \text{......(8.14)}$$

Substuting for R_m in Equation (8.5)

$$V_{ABS} = n_A \left[1 + \frac{R_f}{(\alpha_{ABS} - 1)} \cdot \frac{F}{(1 - X_{FS})\ n_A)}\right]$$

$$= n_A + \frac{R_f}{\Delta_{ABS}} \cdot \frac{F}{(1 - X_{FS})} \qquad \text{.......(8.15)}$$

V_{ABS} = total vapour flow for the extraction column.

$\Delta_{ABS} = (\alpha_{ABS} - 1)$

Now,

Consider the solvent recovery column. In a similar approach to the above derivation, the vapour flow in the column is

$$V_{BS} = n_B + \frac{R_f}{\Delta_{BS}} (S + n_B) \qquad \ldots\ldots\ldots\ldots(8.16)$$

Therefore, the total vapour load for the two columns is given as

$$V_T = V_{ABS} + V_{BS}$$

$$= \left[n_A + \frac{R_f}{\Delta_{ABS}} \cdot \frac{F}{(1 - X_{FS})} \right] + \left[n_B + \frac{R_f}{\Delta_{BS}} (S + n_B) \right] \quad .(8.17)$$

The total vapour load per mole of feed is

$$V_{EXT} = \left[x_A + \frac{R_f}{\Delta_{ABS}} \cdot \frac{1}{(1 - X_{FS})} \right] + \left[x_B + \frac{R_f}{\Delta_{BS}} (S/F + x_B) \right] \quad .(8.18)$$

[Based on the results of the previous chapter, the value of S/F is taken as 2.0. The relative volativities are obtained from the vapour liquid equilibrium data.]

For an ordinary distillation column, the total vapour load per mole of feed has been shown to be equal to

$$V_{DIS} = x_A + \frac{R_f}{\Delta_{AB}} (x_A + x_B) \qquad \ldots\ldots\ldots(8.19)$$

where $\Delta_{AB} = (\alpha_{AB} - 1.0)$

8.3 Application to Screening of Solvents.

As has been mentioned, the screening of solvents for a given separation process has been by ranking the solvents in the order of their selectivity at infinite dilution. This is considered to be a good indication of the relative costs of the resulting plant. The correlation between the total annual cost and selectivity has been shown in the last chapter to be not good enough. We then decide to apply Equation (8.18) to the selection of solvents for an extractive distillation process by observing the correlation between the proposed method and the total annual cost, as compared with selectivity at infinite dilution and the total annual cost.

It can be seen from the equation that experimental VLE data are required for the evaluation of α_{ABS} and α_{BS} in order to evaluate the equation experimentally. An examination of the literature shows that sufficient experimental data are rarely available for the complete design of an extractive distillation process for the many solvents considered in this work. We therefore resort to using the UNIFAC method to predict the activity coefficients of the various components/solvents involved from which α_{ABS} and α_{BS} are obtained using equation of the form (7.4)

Although we have observed and reported in the last chapter that where experimental data is available to check the UNIFAC predictions of activity coefficients/selectivity, the agreement is only fair, nevertheless, by using the same UNIFAC predicted values of α_{ABS} and α_{BS} in both the complete costing and the BDTVL equation, a valid comparison of the proposed methods of solvent ranking is possible.

The procedure is as follows:-

First, the vapour flow rate per mole of feed is calculated for the examples of the key component mixtures (50/50 molar composition) and for the various solvents using Equation (8.18).

Second, a complete design and costing of the extractive distillation process using our cost estimating computer program is undertaken. Much has been said on sizing and costing of columns in the previous chapters and full details are given in Chapter Nine and in Appendix B-11. It may not be necessary to repeat them here.

Third, the solvents are then ranked in th order of: (a) the total annual cost, (b) the vapour flow obtained by the BDTVL Equation (8.18), and (c) the predicted selectivity at infinite dilution.

The results are given in Tables 8.1 to 8.3. Part of these results have been given in Tables 7.7 to 7.9 of Chapter Seven. In the tables (Tables 8.1 to 8.3) the total annual cost and the order are shown in col. 2 and col. 3 respectively; the corresponding values of vapour load by BDTVL equation are in col. 4 and 5; and the selectivity at infinite dilution in col. 6 and 7. Figures 8.2

to 8.4 show the correlation between the total annual costs and the BDTVL vapour flow rates. [Each point in the figures corresponds to a particular solvent in the accompanying Tables 8.1 to 8.3 respectively.] These figures are to be compared with Figures 7.6 to 7.8 of Chapter Seven which show the correlation between the total annual costs and selectivity at infinite dilution for the same mixtures.

Further discussions on the results are given under section 8.5

8.4 Extractive and Ordinary distillations Compared.

If an extractive distillation is to be considered as a viable alternative to ordinary distillation, a substantial improvement in the relative volatility of the key components to be separated must be accompanied by the addition of a solvent. The relative volatility of the key components has a direct relation to the solvent selectivity, with a higher selectivity yielding a higher relative volatility of one component to another. An increasing

TABLE 8.1 : Relationship between the total annual cost (TAC), the BDTVL vapour load (V_B) and Selectivity at infinite dilution (S^∞).
(2-Methyl-1-butene/Isoprene)

Solvents	TAC in Dollars	Order	V_B	Order	S^∞	Order
Nitromethane	769306	1	4.7690	1	1.6339	2
Acetonitrile	847002	2	5.1941	2	1.6319	3
Propionitrile	1124459	3	6.7803	4	1.4323	6
Dimtheyl acetamide	1198127	4	6.1219	3	1.4945	5
Methanol	1204804	5	7.3601	5	1.6839	1
Butyronitrile	1297594	6	7.5481	6	1.3545	7
Morpholine	1450704	7	8.4082	7	1.3408	9
Methyl Ethyl Ketone	1480248	8	8.4471	8	1.3770	8
Acetone	1504035	9	8.4903	9	1.5266	4
Ethylene Chlorhydrin	1533817	10	9.4376	10	1.1854	14
Cyclopentanone	1722085	11	10.3062	11	1.2665	10
Methyl Isobutyl Ketone	1917681	12	10.8929	12	1.2237	11
Cyclohexanone	2144885	13	12.2859	13	1.1976	12
Diethyl Ketone	2237229	14	13.2802	14	1.1760	15
Ethyl Butyrate	2247301	15	13.6192	15	1.1954	13
Tetrahydrofuran	4742780	16	27.7844	16	1.0374	16

The BDTVL vapour rate for the ordinary distillation is 17.268 and the total annual cost is 3276024 dollars.

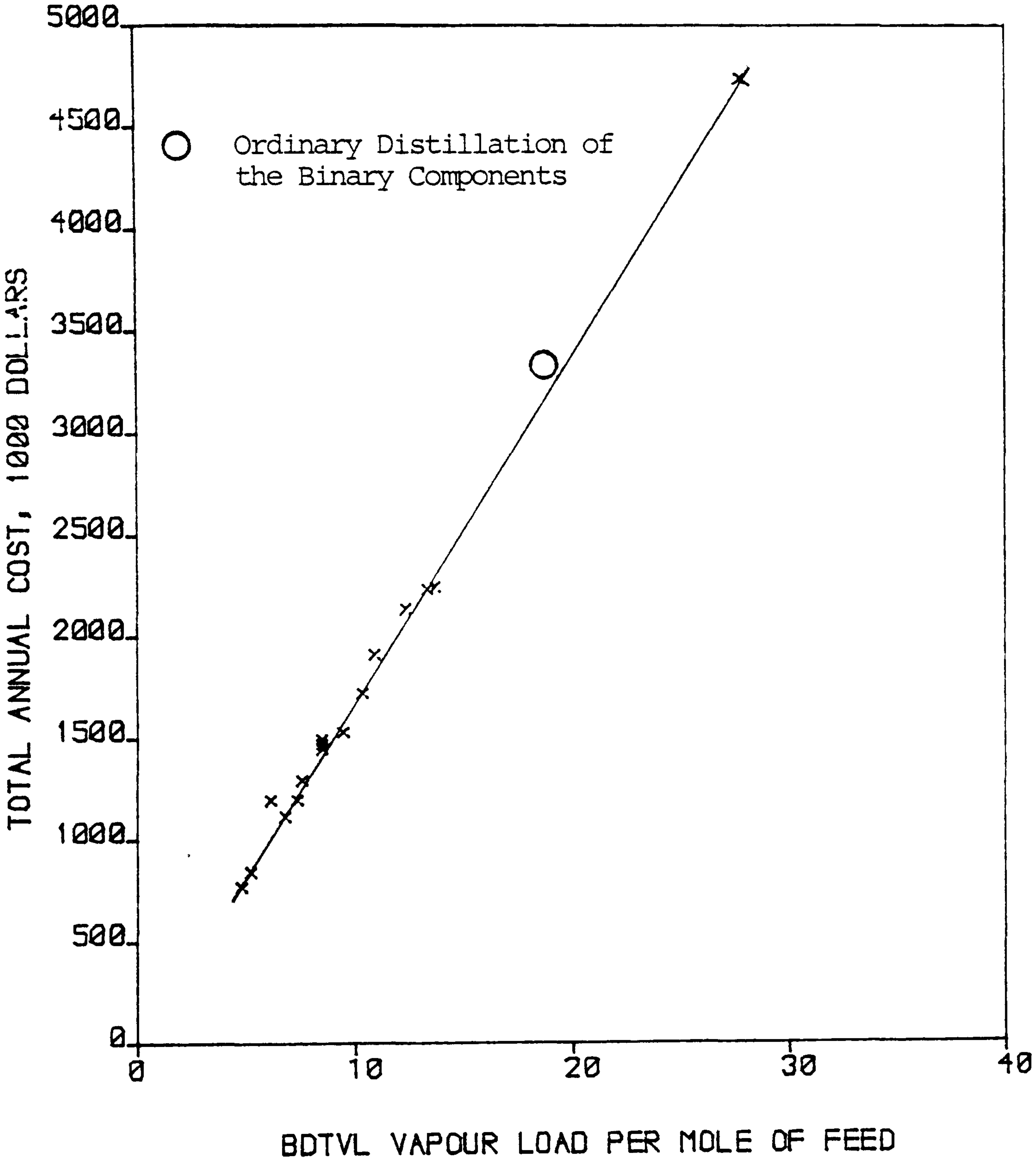

FIG. 8.2 EFFECT OF VAPOUR LOAD ON TOTAL ANNUAL COST OF EXTRACTIVE DISTILLATION OPERATION (2-METHYL-1-BUTENE/ISOPRENE)

TABLE 8.2 : Relationship between the total annual cost (TAC), the BDTVL vapour load (V_B) and Selectivity at infinite dilution (S^{∞}).
(n-Butane/Trans-2-butene)

Solvents	TAC in Dollars	Order	V_B	Order	S^{∞}	Order
Nitromethane	682607	1	5.8068	1	1.6456	1
Acetonitrile	701752	2	5.9520	2	1.6310	2
Acetone	1074161	3	8.3862	4	1.5501	3
Butyronitrile	1124365	4	7.8573	3	1.4197	4
Methyl Ethyl Ketone	1196157	5	8.9184	5	1.4342	5
Morpholine	1395364	6	9.3670	6	1.4084	6
Ethyl Butyrate	1421495	7	10.0662	7	1.1683	11
Methyl Isobutyl Ketone	1566696	8	10.1789	8	1.3124	8
Styrene	1710129	9	10.2182	9	1.3265	7
Cyclohexanone	1936142	10	11.3504	10	1.2902	9
Toluene	2038691	11	14.5087	11	1.1796	10
Ethylbenzene	2485082	12	16.3435	12	1.1488	13
1-Butanol	2571445	13	19.8386	13	1.1060	15
2-Butanol	2651390	14	19.8627	14	1.1062	14
Tetrahydrofuran	2654324	15	20.2857	15	1.1489	12

The BDTVL vapour rate for the ordinary distillation is 46.525 and the total annual cost is 10820431 dollars.

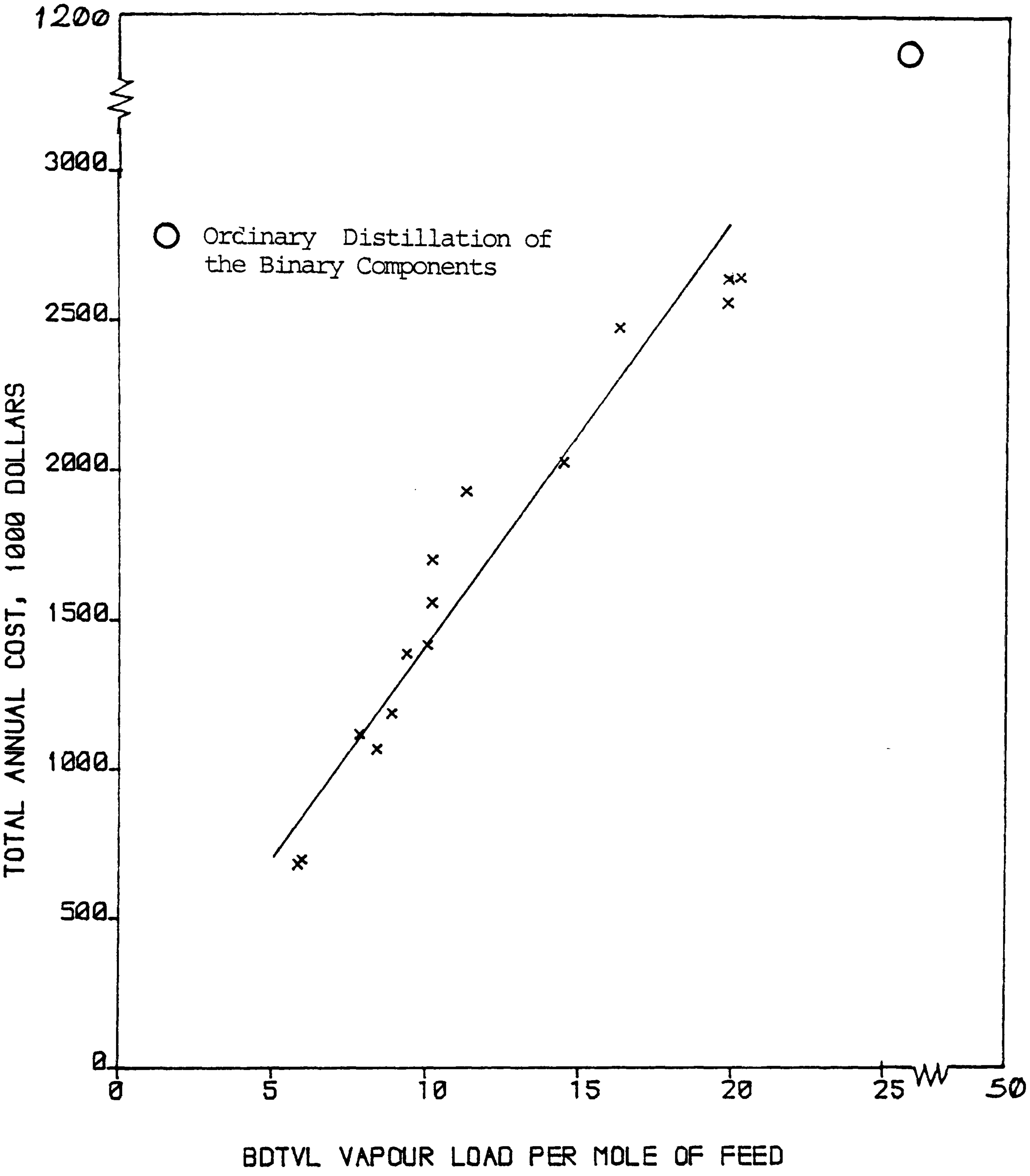

FIG. 8.3 EFFECT OF VAPOUR LOAD ON TOTAL ANNUAL COST OF EXTRACTIVE DISTILLATION OPERATION (N-BUTANE/TRANS-2-BUTENE)

TABLE 8.3 : Relationship between the total annual cost (TAC), the BDTVL vapour load (V_B) and Selectivity at infinite dilution (S^{∞}).

(n-Hexane/Benzene)

Solvents	TAC in Dollars	Order	V_B	Order	S^{∞}	Order
Dimethyl sulfoxide	563200	1	1.4571	1	13.0703	1
Dimethyl formamide	568304	2	1.6781	2	8.8296	2
Furfuran	740255	3	1.7837	3	5.2960	3
Phenol	845267	4	2.0795	5	4.3250	5
Aniline	897585	5	1.9594	4	4.4680	4
Styrene	1100363	6	3.0441	6	1.9900	9
Pyridine	1159731	7	3.3460	7	2.9462	8
Nitromethane	1168126	8	4.0045	9	3.9211	6
Ethyl benzene	1206677	9	3.7006	8	1.5115	11
Toluene	1398022	10	4.4957	10	1.6508	10
Propionitrile	1777788	11	5.9173	11	3.8253	7

The BDTVL vapour rate for the ordinary distillation is 3.0688 and the total annual cost is 899249 dollars.

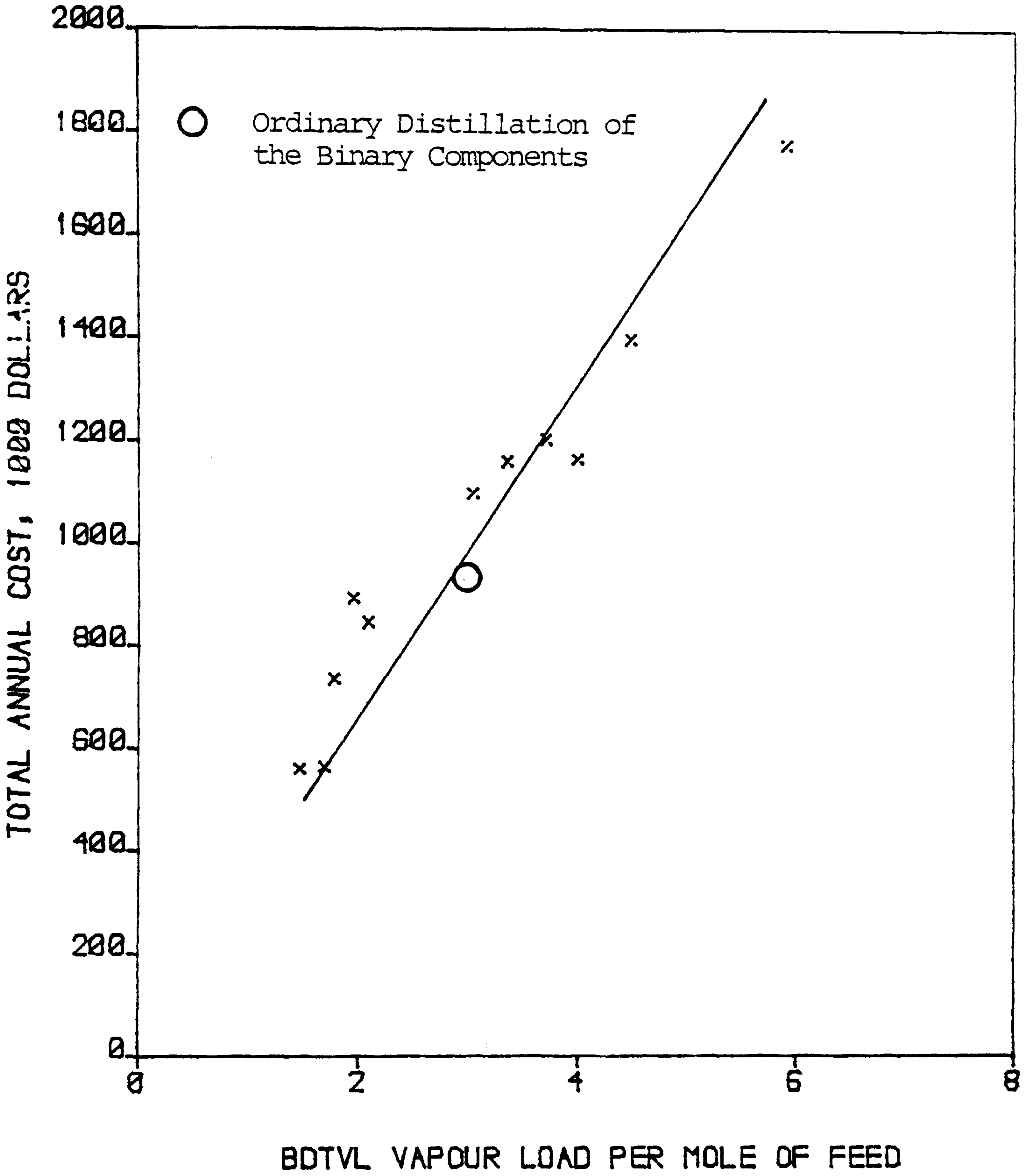

FIG. 8.4 EFFECT OF VAPOUR LOAD ON TOTAL ANNUAL COST OF EXTRACTIVE DISTILLATION OPERATION (N-HEXANE/BENZENE)

selectivity, therefore, will result in a smaller reflux ratio and fewer number of equilibrium plates. The lower reflux ratio corresponds to a lower vapour flow rate in the extraction column and hence a thinner column. The overall total annual cost should decrease. With the total annual costs plotted against the BDTVL vapour flow rates, it is possible that at a particular value of BDTVL vapour flow rate, the extractive distillation process may be better economically than the ordinary distillation for a given mixture. We set out to investigate the value of the BDTVL vapour flow a solvent should have so as to make the extractive distillation economically better than the corresponding ordinary distillation process for the given mixture.

The circular symbols in Figures 8.2 to 8.4 show the BDTVL vapour rate and the total annual cost (TAC) for the ordinary distillation separating the two components in the absence of any solvent. The results implies that all the solvents represented by points below the circular symbol (i.e. below the ordinary distillation calculated BDTVL vapour flow rate and the TAC), are those that will make an extractive distillation cheaper than the ordinary distillation when added to the mixture. In other words, any solvent with the BDTVL value less than its (BDTVL) value without a solvent is a good one for separating the given component mixture. [The BDTVL vapour flow rate and the total annual cost for the ordinary distillation column for each of the binary mixtures are given at the bottom of Tables 8.1 to 8.3.] Using such a solvent will make the extractive distillation cheaper than the ordinary distillation. In short, the lower the value of the BDTVL vapour rate the better the solvent. Above the circular symbol (i.e for the BDTVL vapour load of the extractive process greater than its value for the ordinary distillation), the reverse arguement holds. If the extractive distillation is desired to be cheaper than the ordinary distillation, the solvents with a BDTVL vapour rate greater than the corresponding ordinary distillation column should not be used. They represent no improvement in the total annual cost of separation by extractive distillation over the ordinary distillation column. For example, all the solvents (except one) listed in Table 8.1 when added to the key mixture of 2-Methyl-1-butene/Isoprene are capable of making the extractive distillation cheaper than the ordinary distillation of the key components. For the key component mixture of n-Butane/Trans-2-Butene, all the solvents listed in Table 8.2 are capable of enhancing the relative volatility of the components so as to make the extractive distillation cheaper than the ordinary distillation of the key components. For the third key component mixture, only the first five solvents listed in Table 8.3 may be used if an extractive distillation is to be cheaper than the ordinary distillation of the key components. This third mixture is a much easier separation than the first two.

It can be concluded that a good guide for comparing the extractive and ordinary distillation processes is on the basis of the vapour flow rate produced by the BDTVL method. Any extractive distillation process with a BDTVL vapour rate higher than its value for the ordinary distillation may not be cheaper than the ordinary distillation of the key component mixture. From the results both the ordinary distillation BDTVL vapour flow and the corresponding total annual cost are higher than the TAC of any of the extractive distillation processes with a lower BDTVL vapour rate. However, a closer inspection of the result shows that for the third mixture (n-Hexane/Benzene in Table 8.3) the TAC of the ordinary distillation is lower than one of the extractive distillation processes whose BDTVL vapour rate (3.0441) is lower than the BDTVL vapour rate (3.0688) of the ordinary distillation of the key components. This key component mixture is of a much higher relative volatility ($\alpha > 1.40$) than the other two key component mixtures whose relative volatility is quite smaller than 1.10. Generally, it is a common obervation that the decrease in cost produced as a result of addition of a solvent to a key component mixture is less pronounced for mixtures with a high relative volatility than those with a very low relative volatility. This may have accounted for this slight deviation in the result. Nevertheless, the BDTVL method is still a better guide for comparing extractive and ordinary distillation processes than selectivity at infinite dilution.

8.5 Further Discussion of the Results on Screening of Solvents.

For the screening of solvents, the results show that the BDTVL method puts solvents in the order of cost much better than selectivity at infinite dilution. And there is a better and more perfect correlation between the total annual cost of the extractive distillation process and the BDTVL vapour flow rate [Figures 8.2 to 8.4] than it is between selectivity at infinite dilution and the total annual cost [Figures 7.6 to 7.8].

This is an interesting and useful result. It suggests than the screening of potential solvents for a given separation mixture can be easily and more accurately done by estimating the total vapour flows [Equation 8.18] of the extractive distillation for the various solvents under consideration. This is a more representative of the relative total annual cost of an extractive distillation than selectivity at infinite dilution. The solvent with the lowest vapour load has the potential of being the optimum or near optimum solvent for the given separation mixture.

Based on the approach evolved in this chapter, the promising solvents, for example, for n-Butane/Trans-2-butene are Acetone, Acetonitrile, Methyl Ethyl Ketone; for n-Hexane/Benzene mixture are Phenol, Furfuran, Dimethyl Sulfoxide, Dimethyl formamide and Aniline. These solvents conform with those already considered by several authors [Sucksmith(1982), Chilton(1957), Ewanchyra and Ambridge(1958)] as being viable for the same given mixtures. Infact, as observed from the analysis, most of the solvents listed in the Tables 8.1 and 8.2 may make the extractive distillation processes of n-Butane/Trans-2-butene and 2-Methyl-1-butene/Isoprene more economically viable to use than the corresponding ordinary distillation processes.

On the whole, the results obtained from this work on the screening of solvents and the viability of extractive distillation in replacing an ordinary distillation process look very promising. They may provide a basis from which other separation processes and the inclusion of these processes in the sequence of separation processes will be evaluated in the future.

CHAPTER NINE

DESIGN METHODS AND THE COMPUTER PROGRAMS.

9.1 Introduction

This chapter deals with the design methods employed in the sizing and costing of the distillation columns; and the computer programs developed during the course of this research.

In the process design and costing analysis procedures, the standard known equations/methods are employed to size and cost the various aspects of the columns. Part of the objective of this work was to be able to develop computer programs for sizing and costing distillation sequences of three-, four-, five- and six-component mixtures. This had been successfully carried out. The programs are able to handle extractive distillation columns and columns with sidestreams as well (sidestream columns are not investigated anyway)

The programs are developed into a form of a package using the menu-driven technique. The package, however, includes a few existing programs which are modified for our use.

The programs are written in FORTRAN 77 language and performed on the HARRIS mainframe computer of the University of Aston. They are developed such that they would, as much as possible, be independent of the machine/hardware used.

In this chapter, only the essential details of the design procedures and the essential features of the computer programs are given. Except in few cases, the necessary equations and details of the program data and features are reserved for the Appendices.

9.2 Column Design and Procedures.

The actual number of trays in each column is first determined from the Hengstebeck-Geddes(1958) - Fenske(1932) - Underwood(1948) - Erbar-Maddox(1961) shortcut method using 1.1 (or a variable variable that balances the energy and the capital cost of the column) times the minimum reflux ratio.

The Hengstebeck-Geddes(1958) as expressed and modified by Yaw et al(1979) or Chang(1980) is used for the estimation of the distribution of components between the top and bottom products.

The minimum number of plates, N_m, and the minimum reflux ratio, R_m, are obtained respectively by the Fenske equation and the Underwood equation. The trial-and-error solution of finding the root, O, of the Underwood equation is done using the Bisector (Half-Interval) numerical method [James et al(1977)].

The feed-point location is estimated by using the empirical equation of Kirkbride(1944).

The theoretical number of plates is then estimated by the Erbar-Maddox(1961) correlation which relates the number of theoretical plates required for a given separation, at a given reflux ratio, to the number at total reflux reflux and the minimum reflux ratio. Using the graph of Figure 9.1, we fitted the curve into a correlation suitable for computer use. The Erbar-Maddox correlation is now generally considered to give reliable estimates of the theoretical number of plate [Barna and Ginn(1985), Coulson et al(1983)].

A rigorous multicomponent steady state simulation involving material, energy and equilibrium balances is then used to get the values for energy consumptions. The results from the shortcut methods serve as part-input to the rigorous method. The rigorous method employed is the multicomponent column design techniques developed by Naphtali and Sandholm(1971). This same method has also been used by Fredenslund et al(1977). The advantages of the method as stated by the original authors are numerous. Some of these are:-

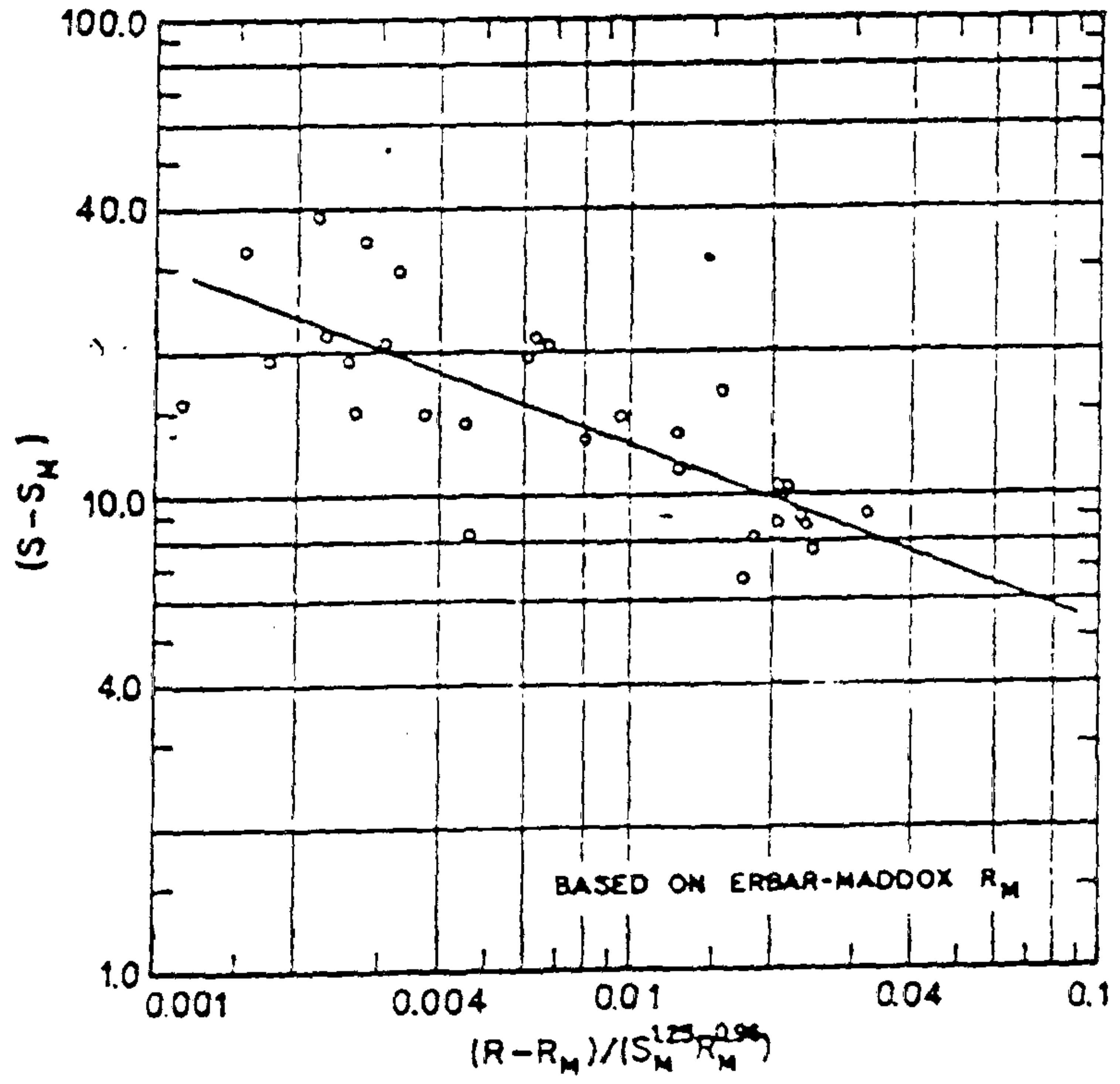

FIG. 9.1 CALCULATED DATA IN THE FORM OF MASON'S CORRELATION WHEN THE REFLUX IS COMPARED BY THE METHOD OF ERBAR AND MADDOX
[ERBAR AND MADDOX (1961)]

(1) Component volatility ranges do not affect the convergence.

(2) The presence of nonideal solutions and plate efficiecies are taken into account in a rigorous manner. In most of the analysis done here, the overall tray efficiency is maintained constant at 100%. Prevous workers [Cheng and Luyben(1985), Morari and Faith(1980), Chang and Luyben(1985), Freshwater and Henry(1975), etc.] have used constant and 100% overall plate efficiency in their analysis. Since, for most of the cases examined here, the capital costs constitute less than 20 percent of the total annual costs of the distillation column sequences, using the variable efficiency [calculted by some correlation] may not have a significant effect on the relative costs of the sequences obtained.

(3) Temperature, key component composition or rates, reflux ratio, recovery, or any other functions of condenser or reboiler flows can be used as specifications.

(4) The method is flexible: the same algorithms may be used for distillation, extraction, absorption; and any number of feed and sidestreams may be used.

(5) The method converges rapidly as the solution is approached.

The equations of conservation of mass, energy and phase equilibrium are set up for each component and each plate. The resulting set of equations has a block-tridiagonal structure which permit rapid solutions by Newton-Raphson iteration.

The primary disadvantage of the method however is its high requirement of storage space and computer time particularly for problems with a large number of theoretical plates.

9.2.1 Calculation Steps for the Rigorous Method.

The calculation steps may be outlined as follows [Fredenslund et al(1977)].

(1) Read input (pure-component data, thermodynamic data for the mixtures, and detailed column specifications such as feed plates, reflux ratio, etc.)

(2) Guess initial temperature and component flow profiles.

(3) Determine all K-factors, stream enthalpies, and their derivatives with respect to temperature and composition.

(4) Set up the discrepancy functions, F(x).

(5) Determine the elements of the Jacobian matrix and solve the block-tridiagonal system of the equations.

(6) Determine the corrections to the temperature and component vapour and liquid flow profiles. Determine the new profiles.

(7) Are the corrections smaller than a specified value? If no, go to 3 with the newly determined profile. If yes, go to 8.

(8) Print final output and return to the program for costing.

Input to the rigorous column calculations can be classified as follows:-

(1) The user should specify
the number of plates
plate efficiencies or overall column efficiency.
feed and sidestream (if any) locations
feed composition, flow rates, and thermal states.
distillate flow rate
reflux ratio.
sidestream (if any) phase condition and flow rates.
column pressure, and
initial estimate of the temperature of the top and bottom of the column.

These specifications are taken from the results of the shortcut method.

(2) Physical properties (e.g Antoine parameters, constants in the ideal-gas heat capacity equation, etc.) are to be known for each component. These are supplied from the data bank generated in the course of this work.

(3) The vapour phase nonideality is calculated using the virial equation of state with second virial coefficients obtained from the Hayden and O'Connel(1975) correlation.

(4) The activity coefficients of component i infinitely dilute in component j, is calculated for all possible i-j pairs in the multicomponent system using the UNIFAC group method. These calculations are carried out at two temperatures T_1 and T_2, the boiling point temperatures of the least and most volatile components.

These activity coefficients at infinite dilution form the basis for a trial-and-error estimation of the UNIQUAC parameters which are used in the distillation calculations; and the temperature dependent parameter τ_{ji} is linearized as follows:

$$\text{UNIQUAC:} \quad \tau_{ij} = A^{(o)}_{ji} + A^{(1)}_{ji} \cdot T \qquad ....(9.1)$$

where $A^{(o)}_{ji}$ and $A^{(1)}_{ji}$ are assumed to be independent of temperature T.

In order to achieve convergence, the Newton-Raphson procedure requires that reasonable guesses be provided for the values of all output variables. These guessed values are generated from the shortcut values of temperature, T, vapour flow, V, and liquid flow rate, L, for the bottom and top plates. The remaining guessed values of T_n, V_n and L_n (i.e. for each plate) are readily obtained by linear interpolation. Then the calculation can now proceed.

Other further details are not discussed as these are available in some standard textbooks [Fredenslund et al(1977), Henley and Seader(1981) and in the original paper of Naphtali and Sandholm(1971)].

The results from the column design procedures are taken into the costing stage of the package. The calculations involved in this stage are discussed in details in Appendix B-11.

We now give some essential features of the computer programs developed and those modified for our use.

9.3 Computer Programs.

The programs developed for sizing and costing the distillation sequences of three-, four-, five- and six-component mixtures are in the form of a package using the menu-driven techniques.

9.3.1 Program MAIN

The package consists of an executive main program from which other subprograms can be accessed. The command options available in the main-menu include:

COMPonent.

SEQuence-2 for a two-component mixture.

SEQuence-3 for a three-component mixture.

SEQuence-4 for a four-component mixture.

SEQuence-5 for a five-component mixture.

SEQuence-6 for a six-component mixture.

EXIT to exit from the main-menu.

At the end of execution of any command option (except EXIT) the main-menu is displayed ready for any other choice.

On entering the package, it is necessary to first choose the first option (COMPonent). This option displays all the components available in the data bank from where a choice of components required for a particular problem is made by the code number attached to the desired component(s). About 84 components are available in the bank.

Any of the other options could then be chosen in whatever order the user desires.

The program MAIN incorporates the choice of either using the approach of Chang(1980) in applying the Hengstebeck-Geddes equation or that of Yaw et al(1979). If an extractive distillation is to be used, the choice is made in the MAIN program.

Throughout the package, prompts are signalled before each READ statement. This tells the user what variable is to be read in.

9.3.2 DATA BANK

As many as 84 components are included in the data bank. For each of the components, data are given for the basic physical and thermal properties. These properties are:

Antoine constants, A, B, and C.

Boiling point temperature, T_b, in Kelvin.

Molecular Weight , M_w.

Liquid density, ρ_L, g/cm^3, at boiling point temperatures.

Heat of vapourisation at normal boiling point, λ_b, cal/gmol.

Critical temperature (T_c, K), pressure (P_c, atm.), volume (V_c, cm^3/gmol) and complexibility factor (Z_c).

Liquid molar volume at superscripted temperature, V_L, ^{o}C cm^3/gmol.

Hilderbrand's solubility parameter at 25^{o}C (δ , (cal/cm^3)$^{0.5}$).

Dipole moments, DMU, debyes.

Association parameters, ETA

Constants in ideal-gas specific heat equation, with C_p in cal/gmol K and T in K [$C_p = a + bT + cT^2 + dT^3$], and

Pitzer's accentric factor, ω .

All these are either obtained from various textbooks [Reid et al(1977), Henley and Seader(1981), McClellan(1963), Yaws(1977)] or calculated using the basic equations found in them.

These basic data enumerated above are generally required for the design and costing of separation columns. From these data, other derived quantities may be obtained: e.g vapour pressure, relative volatility, etc.

Attached to each component is the code or identification number by which it is known or called. On specifying a particular code number, all the desired data are "mapped" with it.

9.3.3 Programs SEQ2, SEQ3, SEQ4, SEQ5, SEQ6 and EXTRACT.

Each of these subprograms gives the process topology for the given number of components. In other words, each program gives the interconnection of process streams of all the sequences of three-, four-, five- and six-component mixtures.

There are a few data that have to be supplied to any of these programs whenever it is called. These include, the feed rate, feed vaporisation factor, condenser temperature, pressure drop in the condenser and along the column, and the relative volatility between the components (if to be supplied).

For the program EXTRACT (for the extractive distillation), the nonideal average relative volatility is taken as the geometric mean of the values at the rectifying and the stripping sections of the column. The component feedstream and the solvent stream enter the column at their bubble temperature.

For each column in the sequence to be designed a call is made to the program DISCOL.

9.3.4 Program DISCOL.

This program makes use of the Hengstebeck-Geddes-Fenske-Underwood-Erbar-Maddox-Kirkbride equations to estimate

the distribution of components between the top and bottom products for a recovery fraction of 99% (or any other specified value).

the minimum number of plates.

the minimum reflux ratio.

the actual number of plates.

the feed-point location.

the distillate flowrate and reflux ratio.

the column pressures and temperatures, and

the vapour and liquid enthalpies.

The BDTVL and the Underwood vapour flow rates may be calculated by this program for each column and summed up for each sequence for any given number of components being investigated.

9.3.5 Programs BUBPT, BUBPP, DEWPT, DEWPP

The relative volatilities between the components in the feed are required at the feed conditions. The bubble point temperature is calculated using the program BUBPT. The criterion is to find the temperature at which the expression

$$\sum_{i}^{M} K_i x_i - 1 = 0 \qquad \ldots\ldots\ldots\ldots(9.3)$$

where

K_i is the K-values for the component i at a particular temperature. x_i is the component feed composition. M is the number of components.

The Equation (9.3) can be expressed in a functional form

$$f(x_i) = \sum_{i}^{M} K_i x_i - 1 \qquad \ldots\ldots\ldots(9.4)$$

and solved using the Newton-Raphson numerical method. The tolerance set limit is 0.001.

This equation (9.4) is also useful for calculating the bubble pressure at any specified temperature in the program BUBPP.

Similarly the dew point criterion used for the programs DEWPT and DEWPP is

$$\sum_{i}^{M} y_i/K_i = 1.0 \qquad \text{.........(9.5)}$$

The nonidealities are incorporated in the determination of the K-values.

9.3.6 Program COLPRE

This program, incorporating the programs mentioned in section 9.3.5 is a systematic way of determining the column operating pressure and type of condenser. The algorithm is as described by Henley and Seader(1981) and shown in Figure 9.2. The figure is self-explanatory.

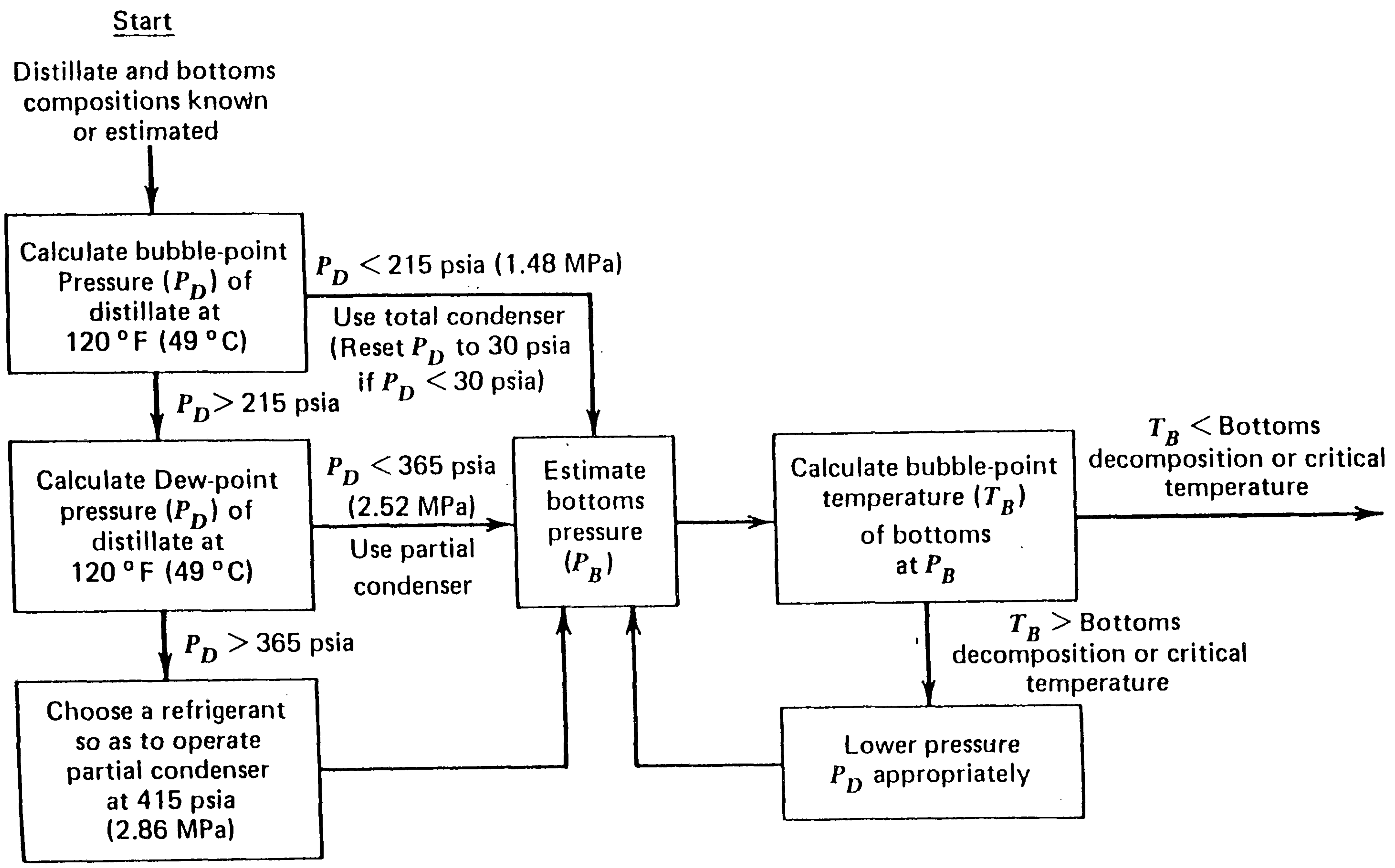

FIG. 9.2 ALGORITHM FOR ESTABLISHING DISTILLATION COLUMN PRESSURE AND TYPE CONDENSER [HENLEY AND SEADER (1981)]

9.3.7 Program RDISCOOL

This is the program that incorporates the rigorous multicomponent column design techniques developed by Naphtali and Sandholm(1971). The input data are taken both from our data bank and from the shortcut calculations. The program follows the calculation steps outlined in Section 9.2.1. The balance equations and the UNIFAC group-contribution method for the calculations of the activity coefficients are given in Appendix C-1 and C-2.

Some of the features of this program, which correspond to that of Fredenslund et al(1977), are those used in the Chemical Engineering Department of this University. However, we carried out some modifications of the program so as to make it suitable for our purposes.

Some of the advantages of the modifications carried out include:

(i) The program can now handle up to a maximum of 200 actual number of plates and six feed components instead of the 30 plates and five components it was designed for.

(ii) The UNIFAC subroutine has been extended to cover 76 subgroups presently known.

The major outputs variables from this program are the condenser and reboiler heat loads for each column in the sequence.

9.3.8 Program REF

The program solves the derived Equation 3.35 for the determination of the optimum reflux ratio of a distillation column. The Newton-Raphson numerical method of finding the roots of a nonlinear equation is used in the solution.

9.3.9 Program COST

The output from the column design programs are fed into the program COST for the costing purposes.

The equations employed in the cost analysis are those described in Chapter three.

The calculations include:

the vapour and liquid densities.

the log mean temperature differences.

superficial vapour velocity (using the Fair's graph), diameter and height of the column.

the condenser and reboiler heat transfer areas, etc.

The costs considered considered in the program for each column include

the capital cost of the columns

the capital cost of the condensers and reboilers.

the condenser cooling water cost, and

the reboiler steam cost.

The specifications and assumptions made including the cost factors used, are discussed in Appendix B-11.

The total annual cost is the addition of the depreciated capital costs of the columns, condenser and reboilers; and the energy cost of the condenser cooling water and the reboiler steam costs. These are summed up for each sequence for the given number of components in the mixture.

9.4 Summary.

The major features of the design methods employed and the computer programs developed in the course of the research are given.

All the results from the various subprograms are finally summarized in the main program from where the results may be printed out when required. There are a large number of variables being calculated in the package. All of them may not be printed out. The values for any variable required may be obtained by inserting a print statement at the appropriate position in the package.

All the programs are run interactively but could be run as control point jobs by punching the required information on a file which can be accessed. Information is transferred between subprograms using common blocks and/or arguments. Comments are given where necessary for clarity purposes.

There are many other on-the-spot programs which are written that are not considered necessary to be described in this thesis.

CHAPTER TEN

GENERAL DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK.

Although most of the discussions have been done at the end of each of the chapters, it is appropriate to give a summary in this chapter.

The problem of sequencing of separation processes is a complex one. The task of selecting the least expensive separation sequence for a given multicomponent mixture often represent a formidable combinatorial problem. Examination of the literature reveals that most of the work done on the sequencing of separation processes is on ordinary distillation column trains. This is probably not surprising as distillation is the most widely used separation process in the chemical industry. Methods of finding the optimum sequences of distillation columns have reached such a complex state that it seems unlikely that the introduction of other separation methods into the sequence will be possible without some simplifications. The complex and tedious techniques that have been used hitherto have not helped the situation. They reveal little or nothing about why a particular sequence is the best. It is with this in view that the development of simple procedures which can lead to a greater understanding of the total problem is necessary.

The initial stage of the work deals with the examination of the concept of energy flow per unit area of distillation column. This is an idea developed from the work of Porter and Jenkins(1979). It is a common observation that for the conditions of practical distillation, the major determinant of both the physical properties and throughput is the operating pressures. It was thus to be expected that the total annual cost per mole of distillate and the optimum reflux ratio would change with operating pressure and that a correlation against the flow parameter would be achieved. Making the relative volatility between the components a variable showed that the contribution of the capital cost to the total annual cost of a distillation column at low relative volatilities is very large compared with the cases of high relative volatilities. From the results, the capital cost contribution to the total annual cost of distillation operation varies from about 10% at a relative volatility of 3.00 to about 50% at a relative volatility of 1.05 for atmospheric pressure and above. Unexpected as this result may seem, it provides explanations for some of the results observed in other chapters. This variation of the ratio of capital cost to the total cost implies that the energy cost only dominate the total annual cost of distillation column when the relative volatility is not in the neighbourhood of 1.00.

Moving on to the optimum sequencing of distillation column (i.e separations consisting of more than one distillation column) which is the main thrust of the work, we first investigated the variation of the cost and order of sequences resulting from changes in some system parameters, e.g. feed compositions, relative volatilities between the components in the feed, etc. The result is then used to evaluate the use of heuristics as a technique for determining the optimum sequences of distillation columns. As far as is known, this is the most comprehensive and extensive exercise of this nature. Thirteen feedstocks of three-, four- and five-component mixtures at different feed compositions are examined. This gives 463 number of sequences and 1497 number of distillation columns that have been evaluated. This far exceeds the number in the previous work; and covers a wider spectrum of components with varied relative volatilities. On the whole, the analysis suggests that the feed composition and the relative volatility influences the order of sequencing much more than any of the other variables examined. The order of sequences as given by the energy cost is in most cases the same as that by the total annual cost. In support of the results in chapter three, it was observed too that the capital cost becomes significant as the relative volatility of the feed components becomes nearer to 1.0. In this case, the order of sequences as given by the energy cost is in most cases not the same as that by the total annual cost.

Although the heuristics examined in Chapter Four are useful in the sequencing of distillation column, they are not infallable.

The rules of thumb sometimes contradict each other. Nevertheless, their development has provided a first breakthrough towards the solution of the problem of sequencing. They will continue to play a prominent role in the sequencing of separation processes. Quantitative expressions of the heuristic rules will be valuable in strengthening their applications to the sequencing problems. Therefore, a new and simple equation (which we referred to as the Binary Distillation Total Vapour (BDTVL)), based on the binary total vapour rate, for choosing between different sequences of distillation column is derived. The equation uses only the mole fraction of the components in the feed and the volatility of one component relative to another. The method represents a quantitative expression for the most powerful heuristics rules found in the literature. The results from the equation are checked against examples (up to a six-component mixture) which have been solved previously in the literature using other methods. It identifies the optimum sequences for all the various examples. Some other real mixtures were used to further test the applicability of the method. This consists of 10 different feedstocks each at five different feed compositions giving 160 number of sequences and 420 number of columns. There is a good agreement between the order of results obtained by the BDTVL method and those by the Underwood total vapour flow and by the total annual cost of the sequences. It is surprising that the method does so well in view of the simplifications used in the derivation particularly the assumption that the minimum reflux ratio may be calculated as for a binary mixture in terms of the relative volatility of the key components only. Although it has not been rigorously proved as to why it works, the numerous case studies carried out have shown it does.

The method may fail in some cases of relative volatility. Even here it is shown that sequences predicted to be optimum by the BDTVL equation are likely to be those most suitable for energy integration. This will form the basis for future work. For such cases, the percentage error incurred in picking a wrong sequence to be optimum (from the point of view of cost) is reasonably low. The main probable reason for its failure is due to the large contribution of capital cost to the total annual cost as the relative volatility of any pair of adjacent components approaches 1.0. Correction factors which might be derived from the correlations of cost against the flow parameter and relative volatility of chapter three may be inserted or added to the BDTVL equation to make it capable of sequencing distillation columns for these cases.

The possibility of extending the BDTVL method to other separation processes is investigated. Only the extractive distillation is analysed here. A simple two-term equation which results from extending the BDTVL to an extractive distillation permits a more accurate selection of solvents for a given separation than selectivity at infinite dilution. The equation is also useful in determining when an extractive distillation becomes cheaper than an ordinary distillation. It is anticipated that the extension of the BDTVL method to other separation processes could be a possibility. In particular, to determine the optimum position for the use of other separation processes in addition to an ordinary distillation in any sequence is of future importance.

For all the case studies, it is important that realistic design and cost methods (as far as is possible within the academic environment of the university) be employed. The design procedures and the computer programs illustrated in Chapter Nine, although conventional, were quite demanding because of the complexity of the problem. The computer package is capable of sizing ordinary distillation sequences of three-, four-, five- and six-component mixtures is developed. It uses the menu-driven technique and the programs written in FORTRAN 77 language which were performed on the HARRIS mainframe computer of the University of Aston. The programs, while sizing the columns also evaluate the total annual cost of each of the possible number of sequences for a given number of components. A rigorous multicomponent design procedure is employed. The results from the package were shown to agree reasonably with published results.

It should be noted that like other workers, factors relating to the operability of a plant, such as flexibility, controllability, reliability, and safety are not considered in the analyses carried out in this work.

The optimal sequencing of separation process problem is in no doubt a complex one. It cannot be said to have reached an advanced stage yet. As stated in section 2.4, there are still many areas to be considered. For example, non-sharp problems, the non-ideal mixtures and even the use of other separation methods other than ordinary distillation have not received any adequate attention. And although some recent works are giving attention to sequencing with heat integration, much is still to be done. The algorithms for sequencing of distillation columns so far developed in the literature are complex and require large computational time and special mathematical skills even with simplifying assumptions usually employed. It seems unlikely that further progress can be made on the more complex problem of sequencing of separation processes without some simplifications. The simple concepts and equations developed in this work may help. We believe that such efforts should continue since they provide invaluable insight which is lacking at the moment into the sequencing problem and separation processes themselves. This may in future lead to further breakthrough in the energy integration problem and sequences of separation processes as a whole.

CONCLUSIONS

The main conclusions from this work can be summarised as follows:.

(1) A concept of energy flow per unit area of distillation column is introduced and this resulted in a simple equation for determining the optimum reflux ratio, number of plates and optimum cost of distillation process per mole of distillate.

The results have shown that the optimum reflux ratio, the total annual cost (TAC) per mole of distillate and the TAC per energy cost of distillation process can be correlated against the operating pressure and the total reflux flow parameter. The optimum reflux ratio to minimum, R/R_m and the TAC per mole of distillate decreases as the operating pressure or the total reflux flow parameter increases. In recent years' cost, a value between 1.05 and 1.10 is obtained for the optimum reflux ratio to the minimum. For a condition of zero-energy, a much higher value is obtained.

(2) The energy cost dominates the cost of distillation operation in the ranges of relative volatilities equal or greater than 1.50. However, for the lower values of relative volatilities this is not so. The contribution of capital cost to the total annual cost of distillation becomes significantly increased. In this case the energy cost cannot be said to dominate the cost of distillation anymore.

(3) The effects of system parameters on the total annual cost of distillation sequences, and the evaluation of heuristics as a technique for determining the optimum sequence of distillation column are investigated. Thirteen feedstocks of 3-, 4- and 5-component mixtures at different feed compositions are examined. This gives 463 number of sequences and 1497 number of distillation columns that have been evaluated. It was found that the total annual cost and/or order of sequences is(are) sensitive to each of the parameters examined; and the degree of sensitivity however varies from one parameter to another. The heuristics examined are found to be very useful in the sequences of distillation column. They sometimes contradict each other.

In most of the cases, the ordering of the sequences in terms of the total annual cost is the same as that in terms of the energy cost. It means that finding the optimum sequence of distillation column may be done by considering only the energy aspect of the total annual cost.

(4) A new and simple equation based on the total vapour rate for choosing between different sequences of distillation column is derived. The equation represents a quantitative expression for most of the powerful heuristics. It identifies the optimum sequences for all of the examples which have been solved previously in the literature using other complex methods. Even when the method fails (compared with the total annual cost of sequences) to predict the optimum sequence in certain cases, the

sequences predicted to be the optimum by the method are likely to be those most suitable for energy integration.

(5) In extending the BDTVL method to an extractive distillation process, a simple two-term equation results which permits a more accurate selection of solvents for a given separation.

(6) A computer package capable of sizing and costing ordinary distillation sequences of three-, four-, and five-component mixtures is developed. A rigorous multicomponent design procedure is employed. The results from the package agree reasonably with published results.

RECOMMENDATIONS FOR FUTURE WORK

The following recommendations are made to extend and improve on the applications of the work presented in this research.

(1) Correction factors may be inserted or added to the BDTVL equations to make it more capable of sequencing distillation columns for cases where one of the relative volatilities is in the neighbourhood of unity and the others large. These might be derived from the correlations of cost against flow parameters and relative volatility of chapter three.

(2) The examination of the optimum position(s) at which alternative methods of separation can be introduced into a sequences so as to cause the sequence to become more economical than separation by ordinary distillation columns alone is of future primary concern. A start may be made by using the methods proposed in this work to identify the optimum position for extractive distillation in a distillation sequence.

(3) The possibility of extending the derivation of the method to other separation processes, for example, liquid-liquid extraction, gas absorption, etc. can be considered.

(4) Furthermore, the application of the method to energy integration so as to generate useful rules of thumb and design procedures that will allow for a greater understanding of the problem may also be considered.

(5) On the basis of the approach developed here for selecting solvents for an extractive distillation processes, the design of solvents from their molecular structures could be investigated.

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