I agree that the above thesis/dissertation shall be available for reading in accordance with the regulations governing the use of University of Surrey theses.

Author's Signature

USER'S DECLARATION

I undertake not to reproduce any portion of, or to use any information derived from, this thesis without first obtaining the permission, in writing, of the Librarian of the University of Surrey.

<table>
<thead>
<tr>
<th>Date</th>
<th>Signature</th>
<th>Address</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
UNIVERSITY OF SURREY

Regulations for Higher Degrees: Copyright

Preamble

Dissemination of knowledge is one of the objects of the University. Therefore Members of the University and others who submit theses/dissertations for higher degrees are expected to relinquish to the University certain rights of reproduction and distribution.

Moreover it is recognised that applicants owe a duty to their Departments of study, the Academic Staff and sponsoring bodies for their respective contributions to the research. Within the limits of these requirements, the author's copyright is safeguarded.

Regulations

1. When submitting a thesis/dissertation for the purposes of a higher degree the applicant shall sign an irrevocable authority in prescribed form appointing the Librarian his attorney with the right to reproduce the thesis/dissertation by photocopy or in microfilm and to distribute copies to those institutions or persons who in the Librarian's opinion require them for academic (as distinct from commercial) purposes.

2. The Librarian in consultation with the appropriate Department of study or sponsoring body shall have the right to refuse to provide copies, or to impose such conditions as he thinks fit on the provision of copies, with the object of safeguarding the applicant's copyright and the interests of the University and the sponsoring body.

3. These Regulations are subject to requirements of any body under whose sponsorship the research project giving rise to the thesis/dissertation is carried on.
OPTIMUM PROCESS DESIGN USING A SEARCH TECHNIQUE

A Thesis submitted for the degree of Doctor of Philosophy

by

Shashikant Vasudeo Dharmadhikari

Department of Chemical Engineering
University of Surrey
Guildford

February 1971
SYNOPSIS

The work consists of an optimization study of the design of a complete chemical plant. The process chosen is the manufacture of acetic anhydride by thermal cracking of acetone. There are involved fourteen design variables, two major recycles and six iterative, computational loops. The process includes the most important unit operations of chemical engineering.

Emphasis is placed in two areas: developing computer procedures which perform the design of individual items of plant in considerable detail and in producing an optimization program for the integrated plant.

An improved version of the Pattern Search method is presented, known as MOSP, and it is shown to be competitive with the best Direct Search techniques available. A new approach is offered for achieving global rather than local optima.

The results show clearly the feasibility of optimization in process design and give quantitative information, for the chosen example, of the optimum conditions.
(3)

TO

LATE FATHER AND MOTHER

FOR

THEIR DEDICATED LOVE AND ENCOURAGEMENT
ACKNOWLEDGMENTS

The author is most grateful to Dr. R.W. Goulcher who suggested the problem and supervised the work.

The author also wishes to thank the University of Surrey for the award of a University Studentship.

The help of the following persons for sending their unpublished materials is sincerely appreciated.

M. J. Box, (Central Instrument Laboratory, I.C.I. Limited).
P. A. Hawkins, (Mond Division, I.C.I. Limited).
R. R. Hughes, (The University of Wisconsin, U.S.A.).

Sincere thanks are also due to Mrs. N. Devereux for her neat and accurate typing.
## CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 1</td>
<td>General Introduction</td>
<td>7</td>
</tr>
<tr>
<td>Chapter 2</td>
<td>Process Design Optimization</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>2.1 The process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.2 Process flowsheet</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>2.3 Optimization criterion</td>
<td>12</td>
</tr>
<tr>
<td>Chapter 3</td>
<td>Process Flowsheet Analysis</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>3.1 Previous related work</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.2 Information flowsheet of acetic anhydride process</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>3.3 Process variables</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>3.4 Constraints on process variables</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>3.5 Selection of design variables</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>3.6 Recycle computations</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>3.7 Organization of the process model</td>
<td>55</td>
</tr>
<tr>
<td>Chapter 4</td>
<td>Univariable Search Methods</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>4.1 Terminology</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.2 Sequential search methods</td>
<td>69</td>
</tr>
<tr>
<td>Chapter 5</td>
<td>Multivariable Search Methods I</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>5.1 General considerations</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.2 Transformation techniques</td>
<td>80</td>
</tr>
<tr>
<td>Chapter 6</td>
<td>Multivariable Search Methods II</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>6.1 Direct search methods</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.2 Gradient methods</td>
<td>119</td>
</tr>
<tr>
<td>Chapter 7</td>
<td>Mathematical Programming Methods</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>7.1 Linear programming</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.2 Geometric programming</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>7.3 Dynamic programming</td>
<td>131</td>
</tr>
<tr>
<td>Chapter 8</td>
<td>Proposed Modified Pattern Search Methods</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>8.1</td>
<td>Reasons for the choice of the Pattern Search method</td>
<td></td>
</tr>
<tr>
<td>8.2</td>
<td>Need for improvement</td>
<td></td>
</tr>
<tr>
<td>8.3</td>
<td>Modified method I</td>
<td></td>
</tr>
<tr>
<td>8.4</td>
<td>Modified method II</td>
<td></td>
</tr>
<tr>
<td>8.5</td>
<td>Modified method III</td>
<td></td>
</tr>
<tr>
<td>8.6</td>
<td>Location of alternate optima</td>
<td></td>
</tr>
<tr>
<td>8.7</td>
<td>Comparison with other direct search methods</td>
<td></td>
</tr>
<tr>
<td>8.8</td>
<td>Conclusions</td>
<td></td>
</tr>
<tr>
<td>Chapter 9</td>
<td>Optimization Calculations</td>
<td></td>
</tr>
<tr>
<td>9.1</td>
<td>Incorporation of costs</td>
<td></td>
</tr>
<tr>
<td>9.2</td>
<td>Optimization procedure</td>
<td></td>
</tr>
<tr>
<td>9.3</td>
<td>Computations</td>
<td></td>
</tr>
<tr>
<td>9.4</td>
<td>Optimization results</td>
<td></td>
</tr>
<tr>
<td>9.5</td>
<td>Sensitivity analysis</td>
<td></td>
</tr>
<tr>
<td>9.6</td>
<td>Remarks</td>
<td></td>
</tr>
<tr>
<td>Chapter 10</td>
<td>Discussion</td>
<td></td>
</tr>
<tr>
<td>Chapter 11</td>
<td>Conclusions</td>
<td></td>
</tr>
<tr>
<td>Bibliography</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appendix A</td>
<td>General Flowchart for Standard Pattern Search Procedure</td>
<td></td>
</tr>
<tr>
<td>Appendix B</td>
<td>Detailed Process Model</td>
<td></td>
</tr>
<tr>
<td>Appendix C</td>
<td>Application of Dynamic Programming to Acetic Anhydride Process Flowsheet</td>
<td></td>
</tr>
<tr>
<td>Appendix D</td>
<td>Computer Program for Process Design Optimization</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 1

General Introduction

The application of computer techniques to chemical engineering problems has increased rapidly in the past decade. Classical design problems were first programmed e.g. heat transfer, distillation, absorption etc. In recent years, more attention has been given to the problems of total process optimization. (44, 49, 116) However, the published process design examples are often oversimplified and do not demonstrate chemical engineering principles in detail. It is the scope of the present project to consider a fairly complex design problem and to study it in details for optimum return.

The use of a computer model of the chemical plant as the central tool of a process design is discussed in the context of a specific project for the manufacture of acetic anhydride by thermal cracking of acetone. The reasons for the selection of the particular process are as follows:

(1) A detailed design report of the process is available (52)
(2) Most of the unit operations of chemical engineering are present in the process flowsheet.
(3) The process design involves the selection of a problem having 14 design variables, two major recycles and about 6 iterative loops. The design analysis of such problem is capable of revealing the stability of the chosen optimization method.

The central feature of the present approach is the use of a computer program representing the process as a whole as a medium for exploring the design. The computer program contains the appropriate chemical engineering design methods, the equipment costing and finally the optimization procedure.
Most designs do not reduce simply to the solution of a set of simultaneous equations but rather to that of a mathematical programming problem. The design variables must be chosen to minimize the selected objective function and at the same time satisfy the constraints imposed by the specifications and the process model equations. The careful selection of the design variables often avoids recycles, which otherwise add considerable complexity. The solution of the groups of units linked by the recycles have to be carried out iteratively, guessing unit input variables in recycle streams so as to reduce the computation to a simple sequence. Recently, various procedures have been proposed to solve these difficulties (89). In the present work, the procedures of Rudd et al (52) have been applied for process analysis. Such an analysis is very useful before carrying out process optimization.

In addition to the optimization of the process, there is one more problem to be considered (87), that is optimizing the method used for optimization. The optimum conditions can be eventually located by almost any reasonable optimization method, but the important question that must be considered is which method of optimization makes the most efficient use of the process engineer's time? There should be a practical compromise between the methods which are easy to implement and slow to converge and the methods which are quick to converge but troublesome to implement. It is also particularly important that the optimization method should take proper account of constraints both explicit and implicit, as these are essential in a chemical process study to ensure that any flowsheet considered is both flexible and safe. Explicit constraints which demand that the values of the design variables stay in the feasible region, are relatively easily dealt with. Implicit constraints impose limitations on the values of the dependent variables, and their violation may not be known until the evaluation of the design itself is under way. A further requirement of the optimization method is that it should not require the evaluation of derivatives of the objective function with respect to the decision variables in order to make progress.
Since the objective function is usually in practice undifferentiable and finite difference approximation to the derivative may be inaccurate, the Pattern Search method of Hooke and Jeeves (50) has many of the properties desired. However, it has been experienced that the Pattern Search strategy needs some improvements and the efforts in this direction yielded a better search procedure. This modified Pattern Search method is used in the present work for the optimization study.

The Dynamic Programming method proposed by Bellman (11) has been used fairly widely in certain design optimization problems. The main reason for this is its easy adoption to a series of stages where the numbers of streams and stage variables is limited. The theoretical analysis of the application of dynamic programming to the acetic anhydride process is presented in this work.

Once the optimal conditions have been found, it is necessary to analyse the sensitivity of the optimal solution to changes in the design variables, without resolving the problem for each new value of the design variables. Such sensitivity analyses provide insight into the structure of the problem which cannot be gained by examining only the optimal solution. The sensitivity analyses of the optimal solution of the process is computed and critically examined.

Thus, to summarise, the present project illustrates the detailed optimization study of a particular process design. Such a study is necessary and very useful both from the design and economic points of views. The modified optimization method used is completely general and can be used in a large variety of design problems.
CHAPTER 2

Process Design Optimization

The objective of optimum process design is the establishment of equipment specifications and operating variables that maximize some economical function, e.g., annual profit. The approach to the design optimization of a process is rather methodical. First of all, a design arrangement is chosen. An optimization technique is of no use until such an arrangement is finalized. Secondly, the proper performance objective function is selected and a satisfactory mathematical model constructed to describe the process. The choice of optimization technique is also kept in mind while the modelling is in progress.

In the present chapter, the process of the manufacturer of acetic anhydride is briefly described, with the flowsheet, and finally, the criterion for optimization is given.

2.1 The process

The process of manufacture of acetic anhydride by thermal cracking of acetone is briefly as follows:

Acetone is vapourised at about atmospheric pressure, preheated, and fed into a tubular reactor at 1200°F to 1500°F, where thermal cracking takes place.

\[ \text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_4 + \text{CH}_2;\text{CO} \quad \text{[Eqn No. 2.1]} \]

The ketene produced in the above reaction undergoes further reaction to ethylene and carbon monoxide.

\[ 2 \text{CH}_2;\text{CO} \rightarrow \text{C}_2\text{H}_4 + 2;\text{CO} \quad \text{[Eqn No. 2.2]} \]

Some acetone is more destructively decomposed to hydrogen carbon monoxide and a deposit of carbon. Thus
The gases leaving the cracking unit are quenched as quickly as possible to prevent the decomposition of the ketene by reaction (2, 2), by injecting recycle acetic acid-anhydride mixture from the acetone column. The shock cooled mixture is then passed to a packed quench tower over which a further quantity of recycle acetic acid-anhydride is passed. The quench liquor from this tower leaves via a continuous filter which removes suspended coke carried out of the reaction furnace. In the initial quenching by the sprays the gaseous reaction products tend to become saturated with acid and anhydride vapour whilst in the tower both acid and anhydride are condensed from the gas phase. This cooled mixture of reaction products, consisting of a number of non condensable gases together with the vapours of acetone, anhydride, acid and ketene pass to a shell and tube condenser where during condensation 90% of the ketene in the reactor effluent reacts with the acetic acid to form acetic anhydride. The remainder, with the permanent gases and a high concentration of acetone, passes to an absorption unit where the residual ketene is absorbed in recycle acetic acid to form acetic anhydride. Probably acetone is also absorbed in the acid. The liquor discharged from the absorber is pumped to a storage tank where it is mixed with the liquid condensate from the condensers. This mixture of acetone, acetic acid and acetic anhydride is fed to an acetone recovery unit, where acetone is recovered as distillate and recycled to the cracking unit. The bottom product of the acetone column is passed to a divided line which is automatically controlled to split the stream into the anhydride column feed and recycle to the quench unit.
The top product of the anhydride column consists of practically pure acetic acid and a bottom product of acetic anhydride of required purity. The acetic acid is recycled for reuse in the quenching and absorption units.

2.2 Process flowsheet

The essential features of a simplified flowsheet for this acetic anhydride process, are shown in schematic form in figure (2.1). The detailed flowsheet of course, contains various items such as pumps and heat exchangers which, for the sake of clarity, are not shown. They are included in the detailed process model, but do not affect the approach to the problem.

2.3 Optimization criterion

Pilot plant data is available in the literature (30). The major contribution of the pilot plant studies was to establish the yield-conversion relationship of the pyrolysis of acetone. The selectivity - acetone conversion relationship is linear and is given as

\[ S = (95-x)\% \]  

[Eqn No. (2.4)]

where \( x \) is the percentage of acetone converted, defined as 'the number of moles of acetone decomposed expressed as a percentage of the total number of moles of acetone fed to the reaction furnace', and \( S \) is the percentage of raw material converted into acetic anhydride.

Characteristic features of the process are the presence of recycles and also of different items of equipment with interacting tasks. The recycle computational problems are studied in detail in chapter (3.6).
Figure 2.1. Simplified process flowsheet.
The selectivity-conversion relationship given by equation (2, 4) indicates that operation of the reactor at lower conversion would result in an increased yield of anhydride. At the lower conversion, the separation problem becomes a major factor for overall economy. Because of these interactions, and many similar ones, it is impossible to arrive at the best process by specifying the performance of each item independently. There is a clear case therefore for the modelling of the complete process so that it can be explored and optimized systematically as a whole.

In the original reference (52), the requirement was to design a plant for the production of 20,000 long tons per annum of 95% w/w acetic anhydride in acetic acid. In the present optimization study, the production rate has been taken as a design variable rather than fixed, so that the plant design for any other production rate can be investigated easily. It means that for any specific production rate, optimum plant design can be obtained. Unfortunately, the cost data for acetic anhydride purity other than 98% was not available, so purity is taken as a fixed variable.

The optimization criterion chosen is to maximize the yearly profit, taking into account the annual operating cost (i.e. capital and running costs) and the cost of raw materials. The objective function to be optimized becomes

\[
\text{profit, £/annum} = \left[ \text{(annual product rate, lb/annum x value of the product, £/lb)} - \frac{\text{(annual capital cost, £) + (annual acetone required, £/annum, x cost of acetone, £/lb) + (annual acetic acid required, lb/annum, x cost of acetic acid, £/lb)}}{\text{(annual capital cost, £) + (annual acetone required, £/annum, x cost of acetone, £/lb) + (annual acetic acid required, lb/annum, x cost of acetic acid, £/lb)}} \right]
\]

[Eqn No. (2.5)]
CHAPTER 3

Process Flowsheet Analysis

In chemical engineering, there was a tendency to regard a process design as the use of crude and rather simple methods to obtained ad hoc solutions to specific problems. With the introduction of computers, the inadequacies of traditional methods have been revealed, and there has been a gradual realization that better techniques and a more systematic approach are necessary. In this chapter, some of the new techniques for improving the efficiency of the design program, by reducing complex design problems into simpler form, are briefly reviewed and some of the algorithms are applied to the present process flowsheet.

3.1 Previous related work

The solution of the design equations for a complex process often cannot begin unless values are assumed for certain variables and the recycle parameters. Process computations then proceed until new values of the recycle parameters are computed and iteration is then performed to force agreement to some specified tolerance of the assumed and computed values of them. Since the computational effort depends largely on the number of variables for which values must be assumed, there is an incentive to seek an order of computation which minimizes the number of recycle streams or the number of variables associated with them. Rubin (85) was the first to publish a procedure which was based on systematic interchanges, but he showed that this did not always find the global optimum. Sargent and Westerberg (90) have given an algorithm based on dynamic programming, together with some rules for initial reduction of the network.
Lee and Rudd (62) attacked the same problem as Rubin. They have developed an algorithm to determine the number of recycle parameters that must be assumed in order to render recycle calculations acyclic; i.e., so that no calculation recycle loops would be present. Recently, Christensen and Rudd (25) have developed algorithms for more complex systems. In order to apply the algorithm of Lee and Rudd, it is first necessary to locate the recycle loops. Norman (74) described a matrix method for determining nests of recycles of a directed graph. Lee, Christensen and Rudd (63) have given a systematic search procedure for selection of the design variables to reduce difficulties of iteration and thus save in computational labour associated with the process analysis.

Recently, the emphasis has been made on the development of programs which automatically combine the calculation of individual units to produce characteristics for the overall process. Sargent (88), Evans et al. (34) have reviewed the related work. The practical examples of some of these programs are given by Andrew (2), and by Forder and Hutchinson (42).

3.2 Information flowsheet for acetic anhydride process

Figure (3.1) is the information flowsheet for the acetic anhydride process. The unit operations, reaction, quenching, condensation, and so forth, are presented by blocks and the arrows trace out the direction of flow of material and energy between the blocks.
Figure 3.1. Information flowsheet of acetic anhydride process.
When the block represents a unit operation, there will be certain variables which can be said to be internal to it. These variables are usually termed as Independent Variables and are denoted by the full arrows. The input and output variables are denoted by the half arrows.

Notice that the direction of physical flow does not necessarily indicate the direction of information flow, e.g., the specification of the output product of the acetic anhydride column actually transfers information back into the system.

An extra unit viz. a feed make up unit has been considered to simplify the flowsheet analysis.

3.3 Process variables

Once the input variables and the independent variables* to a block are specified, the output variables can be solved for; this is the usual convention in a flowsheet calculation. Table (3, A,) shows the variables associated with each block. If the output from a block becomes the input to the next block and if there is no other output going out of the first block and no other input coming into the latter block, then, only the output stream of the first block is mentioned to avoid repetition.

* Quite often, independent variables are termed design variables. However, we will prefer to differentiate between these two terms, because some independent variables may not be design variables. The next section deals with the selection of design variables.
Table 3.A  
Variables associated with each unit of the process

<table>
<thead>
<tr>
<th>Unit</th>
<th>Input Variables</th>
<th>Output Variables</th>
<th>Independent Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace</td>
<td>Feed rate</td>
<td>Exit gaseous rate</td>
<td>% conversion</td>
</tr>
<tr>
<td></td>
<td>Feed composition</td>
<td>Exit gaseous comp.</td>
<td>Reaction temp.</td>
</tr>
<tr>
<td></td>
<td>Feed temperature $^c$</td>
<td>Exit gaseous temp.</td>
<td>Pressure in -</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>the tubes $^a$</td>
</tr>
<tr>
<td>Quench spray</td>
<td></td>
<td>Exit gaseous rate</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Exit gaseous comp.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Exit gaseous temp.</td>
<td></td>
</tr>
<tr>
<td>Quench tower</td>
<td>Make up acetic acid rate</td>
<td>Exit gaseous rate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Recycle rate</td>
<td>Exit gaseous comp.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Recycle composition $^b$</td>
<td>Exit gaseous temp.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Recycle temperature $^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Condenser</td>
<td></td>
<td>Gaseous product rate</td>
<td>Cooling water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gaseous product temp.</td>
<td>rate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gaseous product comp.</td>
<td>% ketene to be</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Liquid product rate $^b$</td>
<td>condensed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Liquid product temp $^b$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Liquid product comp.</td>
<td></td>
</tr>
<tr>
<td>Absorber</td>
<td>Gaseous feed rate</td>
<td>Liquid product rate</td>
<td>Water rate to</td>
</tr>
<tr>
<td></td>
<td>Gaseous feed comp.</td>
<td>Liquid product comp.</td>
<td>interstage cooler</td>
</tr>
<tr>
<td></td>
<td>Gaseous feed temp.</td>
<td>Liquid product temp.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Absorbent rate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crude product</td>
<td>Liq, ex-absorber rate</td>
<td>Feed to acetone colmn rate</td>
<td></td>
</tr>
<tr>
<td>storage</td>
<td>Liq, ex-absorber comp.</td>
<td>Feed to ac. column comp.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liq, ex-absorber temp.</td>
<td>Feed to ac. column temp $^b$</td>
<td></td>
</tr>
<tr>
<td>Unit</td>
<td>Input Variables</td>
<td>Output Variables</td>
<td>Independent Variables</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------------------------------------</td>
<td>----------------------------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>Acetone column</td>
<td></td>
<td>Furnace recycle rate</td>
<td>Reflux ratio</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Furnace recycle comp.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Furnace recycle temp. (^{(b)})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anhydride colm. feed rate</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anhydride colm. feed comp.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anhydride colm. feed temp. (^{(b)})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Quench unit recycle rate</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Quench unit recycle comp.</td>
<td>(^{(b)})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Quench unit recycle temp.</td>
<td>(^{(b)})</td>
</tr>
<tr>
<td>Anhydride column</td>
<td>Column feed rate</td>
<td>Top product rate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Column feed comp</td>
<td>Top product comp</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Column feed temp. (^{(b)})</td>
<td>Bottom product rate</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom product comp</td>
<td></td>
</tr>
<tr>
<td>Feed make up unit</td>
<td>Recycle (from acetone column) rate</td>
<td>Feed to furnace rate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Recycle' comp</td>
<td>Feed to furnace comp.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Recycle temperature (^{(b)})</td>
<td>Feed to furnace temp. (^{(c)})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fresh feed rate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fresh feed comp. (^{(b)})</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fresh feed temp.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes:  
(a) It is assumed that the furnace tubes operate at 5 atm. pressure.  
(b) This variable is neglected for flowsheet analysis because the effluent temperature requirement must be met by the accessory heat exchanges and how this is met is irrelevant to the rest of the system.  
(c) It is assumed that fresh feed is available at room temperature.
3.4 Constraints on process variables

It is very common that some of the independent and dependent variables have to satisfy certain limits. In such a situation, the constrained variables can be adjusted to range only within the constraints during the optimization. In the following paragraph, the various constraints present in the acetic anhydride process are discussed.

(i) % acetone conversion in the reactor

\[ 10 \leq \text{Acetone conversion, } \% \leq 25 \]

The pilot plant data are available in this range only.

(ii) Temperature of effluent gas to quench tower

\[ 800^\circ F \leq \text{Temperature} \leq 1000^\circ F \]

The rate of decomposition of ketene in this range is negligible.

(iii) Temperature of the stream leaving the quench tower

\[ 290^\circ F \leq \text{Temperature} \leq 310^\circ F \]

(iv) Cooling water rate of condenser cooler.
The water velocity through the condenser tubes should be sufficiently high to minimise the deposition of salts. McAdams(66) states that for most heat exchangers the suitable range for water velocity through the tubes is 2ft/sec - 4ft/sec, thus,

\[ 2 \leq \text{Water velocity through condenser tubes, ft/sec} \leq 4 \]

(v) Reflux ratio to distillation column.

Coulson and Richardson(28) recommend the optimum reflux ratio between 1.4 and 4 times minimum reflux ratio, therefore,

\[ 1.4 \times R_m \leq \text{Reflux ratio} \leq 4.0 \times R_m \]

(vi) Weight ratio of acetic acid to acetic anhydride in acetone column - quench unit recycle stream. A preliminary optimization study suggested the following range,

\[ 0.70 \leq \frac{\text{Acetic acid rate, lb/hr}}{\text{Ac. anhydride rate, lb/hr}} \leq 1.50 \]

(vii) Irrigation rate to quench tower.
The liquid flowing down the quench tower over the packing must confirm to the following requirements: (52)

(a) the quantity of liquid must be such that it is capable of carrying away the heat transferred from the gas without undue temperature rise.

(b) the liquid rate must exceed the minimum wetting rate.

(c) the liquid rate must be such that the tower operates below loading.

For the requirement (a), the heat load on the tower and temperature rise of the liquor are estimated and then a proposed liquor rate is determined.

For the calculation of the minimum wetting rate, the value given by Coulson and Richardson (28) for minimum wetting rate for 3" stacked rings, is used. The correlation presented by Leva (65) has been used to compute the tower loading.

3.5 Selection of design variables

The design variables are those variables which are to be adjusted in optimizing the process design and the state or dependent variables are those variables which are determined by the solution of the design equations. The selection of the design variables depend on the following criteria:
(i) The constraints do give a clue concerning the strategy of selecting design variables. If the constrained variables are chosen as the design variables, it is easier to keep them in the range during optimization. Also, if virtually all variables are constrained, then those whose constraints are most severe can be chosen.

(ii) The major purpose of design variable selection is to simplify process calculations e.g. in the distillation column, it is much more convenient to select reflux ratio as design variable and then calculate the number of plates than vice versa.

The above criteria suggest the selection of the following variables as potential design variables.

a) % acetone conversion
b) reaction temperature in furnace
c) temperature of the exit vapour from quench spray
d) temperature of the exit vapour from quench tower
e) weight ratio of acetic acid to anhydride in quench unit-acetone column recycle stream
f) % ketene to be condensed in condenser
g) cooling water rate to condenser
h) cooling water rate to 'interstage' exchangers of absorber
i) reflux ratio in acetone distillation column
The above selection of design variables is principally based on the detailed chemical engineering study of the process. Recently, Lee (63) et al. have given a systematic procedure for the selection of the set of design variables so as to assist in avoiding recycles and to minimize computational labour associated with the process analysis. In the following paragraphs, their algorithm is given and then applied to the flowsheet of the acetic anhydride process. Finally, the resultant set of design variables obtained is compared with that listed above.

3.5.1 The algorithm for the selection of design variables

The process design equations can be expressed in symbolic form as

\[ f_i(V_j) = 0 \]  \hspace{1cm} [Eqn No. (3.1)]

with \( i = 1, 2, \ldots, n \)

and \( V_j \) defined as the vector

\[ V_j = (v_1, v_2, \ldots, v_m) \]
The design equations tie together the process variables \( V_j \) through the material and energy balances, equipment design equations etc. In practice, for any value of \( i \), not all of the complete set of \( m \) variables will appear on the contrary, in most equations only a few will be present. In real cases, \( m > n \). For \( m = n \) there would be a unique solution to the process design problem, obtained by solving simultaneously the set (3.1). In fact this will never occur, nor the "over design" case of \( m < n \).

When \( m > n \), it is necessary to select \((m - n)\) variables from the total \( m \) and designate them as Design Variables. The number of such distinguished variables is equal to the degree of freedom of the system that being the excess of variables over equations.

\[
i.e. \quad F = m - n \quad [\text{Eqn No. (3.2)}]
\]

There are \( \binom{m}{F} \) ways of choosing a set of design variables. The algorithm proposed by Lee, et.al. is based on the criterion that a best set of design variables results in a structure in which the largest number of equations that must be solved simultaneously is minimised. A block in the process flowsheet may be thought of as embracing a number of design equations for an adequate description of that operation. For practical reasons, it may be preferred to have close control over certain variables, and such preferred variables may be elevated to the level of design variables regardless of the logical structure of the problem.
For example, in the present process design, the product purity have to meet some restrictions and it is desired to compute only designs which meet these restrictions. Such preferred variables are assigned prior to the use of the algorithm. The number of input arrows to a block equals the local degree of freedom there, a number that is preserved during the manipulations. With this interpretation, the algorithm of Lee, Christensen and Rudd can be given step wise as follows:

Step 1  Record the local degree of freedom for each block, and remove all heads from the arrows in the initial information flowsheet.

Step 2  Note for special considerations any variables which do not connect blocks in the system. Variables so distinguished are assigned an "outward" direction. This assignment is continued upto the point where the number of unassigned variables equals the local degrees of freedom for the block, at which time the block is deleted from the diagram.

Step 3  Repeat Step 2 on the reduced diagrams until no further reductions occur. The unassigned variables are the design variables.
Application of the algorithm to acetic anhydride process flowsheet

From a careful study of the process, the following set of preferred design variables is selected.

a) % acetone conversion
b) weight ratio of acetic acid to anhydride in quench unit - acetone column recycle stream
c) % ketene to be condensed in condenser
d) reflux ratio in acetone column
e) top product composition in acetone column
f) bottom product composition in acetone column
g) reflux ratio in anhydride column
h) acetic anhydride rate in anhydride column
i) acetic anhydride purity

With the initial selection of the preferred design variables and other specified design variables, the new information flowsheet becomes as shown in figure (3.2). In this figure, stream details are not shown and each unit is represented in alphabetical order. The preferred design variables and initially specified design variables are denoted by the crossed arrows and the full arrows respectively. The half arrows denote state or dependent variables. If a stream connecting two blocks is acting as a preferred design variable (or a specified design variable) for both blocks, then that stream is shown disconnected by a dotted line.
Figure 3.2. Information flowsheet of the process without stream details.

- Quench Tower (D)
- Quench Spray (C)
- Condenser (E)
- Absorber (F)
- Crude Product Storage (G)
- Acetone Column (H)
- Anhydride Column (I)
- Reactor (B)
- Feed Make-up Unit (A)
Figure (3.3) results from the application of step 1 of the algorithm. Notice that the heads from crossed arrows representing the preferred design variables are not removed. Figures (3.4A) to (3.4D) show the results of four passes through step 2 and 3 of the algorithm, resulting in the assignment of output variables for each block. The circle round a block indicates that the number of unassigned variables equals the local degrees of freedom for the block and thus, that block is deleted from the diagram. In a number of cases one choice of direction of information flow was made from several possible alternatives. The preferred direction to the information flow was made by using insight into the process and favouring 'easy direction of information flow through given blocks. For example in figure (3.4D), for block E, the degrees of freedom are five and the number of unassigned variables are four. To equalize them, any one of the assigned variables for the block E can be made an unassigned variable and thus, design variable. From the process study, it can be seen that it is preferred to choose the cooling water rate as the design variable.

Figure (3.5) shows the information flowsheet for the new assignment of design variables.
Figure 3.4.(A) - Application of steps 2 and 3 of the algorithm - Pass 1
Figure 3.4 (B). Application of steps 2 and 3 of the algorithm - PASS 2.
Figure 3.4. (C). Application of steps 2 and 3 of the algorithm - PASS 3
Figure 3.4. (D). Application of steps 2 and 3 of the algorithm - PASS 4
Figure 3.5. An information flowsheet resulting from the reassignment of design variables.
3.5.3 Comparison with the previously selected design variables

Figure (3.5) indicates that by the selection of the following set of design variables, the recycle loops can be eliminated.

a) % acetone conversion  
b) reaction temperature in the furnace  
c) total feed rate to the reactor (or furnace)  
d) temperature of the exit gases from quench spray  
e) weight ratio of acetic acid to anhydride in quench unit - acetone column recycle stream.  
f) temperature of the exit gases from quench tower  
g) % ketene to be condensed in condenser  
h) cooling water rate to the condenser  
i) cooling water rate to heat exchangers in absorber  
j) top product composition in acetone distillation column  
k) bottom product composition in acetone distillation column  
l) reflux ratio in acetone distillation column  
m) acetic anhydride (product) rate  
n) acetic anhydride (product) purity  
o) reflux ratio in anhydride column

By comparing the above set of design variables to the set preselected prior to the application of the algorithm, and given on page(24), it can be seen that only one design variable viz feed rate to the reactor, is additional to the above set.
However, this extra design variable is quite unnecessary, because once the product rate and % acetone conversion are specified, total feed rate to the reactor can be determined. (See also equation (3.5)). Thus, the feed rate to the reactor can be safely considered as a state variable.

Therefore, it can be concluded that the previously selected design variables are satisfactory and their selection promises an efficient computational scheme.

3.6 Recycle computations

In the past, a self consistent design for the recycle process was carried out in the following way:

i) the values of all recycle parameters were tentatively assigned,

ii) the remaining calculations, which contain no unspecified recycle parameters, were then performed step by step, yielding new values for the recycle parameters.

iii) the above step (i) and (ii) were repeated until the desired convergence was achieved.

The convergence of such a procedure is often slow and much time and effort is required, especially if the number of recycle parameters are large. Mathematically, the problem generated may be formulated as finding a solution to the set of equations (25).

\[ x^{r+1} = g(x^r) \]  

[Eqn No. (3.3)]
where, $X^r + 1$ is the $k$ dimensional set of recycle parameters and $g(X^r)$ is the set of new values of the recycle parameters generated by the solution of the design equations. Therefore the fewer the recycle parameters, $k$, the less is the difficulty of the iterative calculations.

Lee and Rudd (62) have developed procedures for determining the minimum number of recycle parameters that must be assumed to render cyclic calculations acyclic. Recently, Christensen and Rudd (25), and Sargent and Westerberg (90) have proposed algorithms on the same lines to find the simplest recycle set in a system of arbitrary complexity.

In the next paragraphs, the procedures of Lee and Rudd are outlined and then applied to the acetic anhydride process. Finally, the methods used in the present work, to solve recycle problems are given. These methods do not require any iterative calculation.

3.6.1 The procedures of Lee and Rudd (62)

Norman (74) described a matrix method to locate all recycles in a system. The cycle matrix $C$ can be represented as

$$C = \begin{pmatrix} c_{ij} \end{pmatrix} = \begin{cases} 1 & \text{if } S_j \text{ appears in cycle } i \\ 0 & \text{otherwise} \end{cases}$$  \[\text{Eqn No. (3.4)}\]

where, $S_j$ represents stream $j$
A cycle rank is defined as the number of streams involved in a cycle and equals the sum of the elements in a row of the cycle matrix. A stream frequency is the number of cycles in which a stream appears and equals the sum of column elements. If the frequency of column j is equal to or greater than that of column k and if the column j has non-zero elements in all of the rows where column k has non-zero elements, then column k is said to be contained in column j. A set of columns is said to be independent when no column is contained in any other column. Column k is said to be strictly contained in column j, if column k is contained in column j and the number of variables of stream k, Pk, is not less than those of stream j, Pj. If the column k is contained in a set of columns and if the variable number of stream k is not less than the sum of the variable numbers of the columns in the set, then the column k is said to be strictly contained in the set.

Based on the above definitions, figures (3.6A to 3.6D) show the flowcharts of the algorithms of Lee and Rudd, and figure (3.7) shows the flowchart of the application of these algorithms for estimation of the minimum number of recycle parameters.
(41)

Eliminate any cycle have rank one? yes Eliminate that cycle

Are all columns independent? no Eliminate all dependent columns

yes Algorithm 2

Select corresponding nonzero element as recycle variable and eliminate the corresponding column along with rows in which nonzero element of column appears

Does any independent column contains a row with only one nonzero element? no Algorithm 2

yes

Does any row remain? yes 1

no STOP

Figure 3.6 A: Algorithm I of Lee and Rudd
Is there any set of columns with total frequency less than number of cycles of the matrix? 

Eliminate column with the fewest stream frequency 

2

Figure 3.6. B: Algorithm 2 of Lee and Rudd
Find column $S_j$, with largest value of $P_j$

1. Delete rows which have a zero element in column $S_j$.
2. Delete columns which do not have at least one nonzero element in any one of the remaining rows.
3. Delete column $S_j$.

Does any row have only one nonzero element?

yes

Delete the column in which this nonzero element appears and rows in which other nonzero element(s) of this column appears.

Has any set which strictly contains column $S_j$ been found?

yes

Is there any strictly contd. column?

no

Eliminate the column

no

Algorithm 2

Are $P_j$'s the same?

no

Find column, say $S_k$, with largest $P_k$

Can this column be eliminated?

no

Algorithm 4

yes

Delete the column

Figure 3.6 C: Algorithm 3 of Lee and Rudd
Find column $S_j$, with largest value of $P_j$

Divide column $S_j$, into a number of pseudo columns such that at least one of the pseudo columns is strictly contained in some columns of the matrix

Eliminate the pseudo column

2

Figure 3.6. D: Algorithm 4 of Lee and Rudd
Figure 3.7: Application of the algorithms of Lee and Rudd
3.6.2 Application of the above procedures to the acetic anhydride process

Figure (3.8) shows the original acetic anhydride process flowsheet. There are two recycle streams present viz $S_9$ and $S_{10}$. Table (3.B) indicates the number of parameters necessary to characterize each stream.

Table 3.B

<table>
<thead>
<tr>
<th>Stream Number</th>
<th>Number of parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>1</td>
</tr>
<tr>
<td>$S_2$</td>
<td>3</td>
</tr>
<tr>
<td>$S_3$</td>
<td>3</td>
</tr>
<tr>
<td>$S_4$</td>
<td>3</td>
</tr>
<tr>
<td>$S_5$</td>
<td>3</td>
</tr>
<tr>
<td>$S_6$</td>
<td>3</td>
</tr>
<tr>
<td>$S_7$</td>
<td>3</td>
</tr>
<tr>
<td>$S_8$</td>
<td>2</td>
</tr>
<tr>
<td>$S_9$</td>
<td>1</td>
</tr>
<tr>
<td>$S_{10}$</td>
<td>2</td>
</tr>
<tr>
<td>$S_{11}$</td>
<td>2</td>
</tr>
</tbody>
</table>
Figure 3.8. The original acetic anhydride flowsheet with two recycle streams (S9 and S10)
It is possible to trace out all cycles in the process flowsheet without applying any procedure such as that of Norman(74). Table (3, C) lists the cycles present in the system.

<table>
<thead>
<tr>
<th></th>
<th>Cycles of the process</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$S_4, S_5, S_7, S_8, S_{10}$</td>
</tr>
<tr>
<td>B</td>
<td>$S_4, S_6, S_8, S_{10}$</td>
</tr>
<tr>
<td>C</td>
<td>$S_1, S_2, S_3, S_4, S_5, S_7, S_8, S_9$</td>
</tr>
<tr>
<td>D</td>
<td>$S_1, S_2, S_3, S_4, S_6, S_8, S_9$</td>
</tr>
</tbody>
</table>
Table (3, D) illustrates the augmented matrix with the cycle rank, stream frequency and stream variables, $P_j$.

**Table 3, D**

*Augmented cycle matrix of the process*

<table>
<thead>
<tr>
<th>Cycle matrix</th>
<th>$S_1$</th>
<th>$S_2$</th>
<th>$S_3$</th>
<th>$S_4$</th>
<th>$S_5$</th>
<th>$S_6$</th>
<th>$S_7$</th>
<th>$S_8$</th>
<th>$S_9$</th>
<th>$S_{10}$</th>
<th>$S_{11}$</th>
<th>Cycle rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>.</td>
<td>.</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>B</td>
<td>.</td>
<td>.</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>Stream frequency</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of variables of stream $P_j$</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

By applying algorithms 1 and 3 of Lee and Rudd, it can be seen that:
- columns $S_2, S_3, S_4, S_5, S_6, S_7$ are strictly contained in column $S_8$.
- columns $S_1, S_{10}$ are strictly contained in column $S_9$. Moreover, as there is no element in the column $S_{11}$, it is unnecessary to consider it.
Thus, column elimination results in the reduced matrix shown in Table (3, E)
Table 3.E
Reduced matrix of the process system

<table>
<thead>
<tr>
<th>C</th>
<th>S₈</th>
<th>S₉</th>
<th>Cycle rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>.</td>
<td>(1)</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>.</td>
<td>(1)</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Stream frequency

<table>
<thead>
<tr>
<th></th>
<th>Pj</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

Table (3, E) shows that rows A and B each have only one non zero element and thus, according to algorithm 1, the corresponding column is selected as the recycle stream. Elimination of column S₈ results in elimination of all rows, so the minimum number of recycle streams has been found. Recycle stream for the present system is S₈ and the minimum number of recycle parameters is 2. Figure (3.9) shows the resultant process flowsheet.
Figure 3-9. The process flowsheet with minimum number of recycle streams.
Methods adopted to carry out recycle computations

The result of the algorithms of Lee and Rudd when applied to the acetic anhydride process show that it is necessary to assume the values of two parameters to render recycle calculations acyclic. It is interesting to note that if these two parameters are chosen as design variables, the iterative calculations can be successfully avoided. The recycle computations are carried out on the same basis. As already stated before, there are four recycles in the acetic anhydride process; however, the major recycle streams which influence overall material balance are

i) reactor - acetone column recycle

and

ii) quench unit - acetone column recycle

Each of these recycle calculations is discussed individually in the following paragraphs.

i) reactor - acetone column recycle calculations

The material balance program for the feed make up unit gives the following relation

Feed to reactor = fresh feed + recycled feed from acetone column

and the overall material balance for total quantity of feed requirement shows that

The hourly fresh feed required

\[ = \frac{a \times m w_f}{102 \times x \times y} \]  

[Eqn No. (3.6)]

where,

\( a = \) hourly production rate of ac. anhydride
The purity of the fresh feed viz acetone is known, however the composition and the rate of the recycle feed is not known at this stage. So, to define the recycle flowstream, it seems that two recycle parameters viz. flow rate and composition, have to be specified for iteration calculation. However, if the top composition of the acetone column is specified to satisfy the required quality of recycle to the reactor, one of the recycle parameters can be omitted. In the present program, this parameter is treated as a preferred design variable and its value is specified to match the fresh feed i.e. nearly pure acetone. Though the iteration problem is simplified, it has not been avoided completely.

If the material balance for the feed make-up unit is avoided until the computations of the acetone distillation unit are completed, there will be no need for any iteration calculation at all. From equation (3, 6), the material balance for the reactor can be done to determine the total quantity of acetone feed required for the specified acetic anhydride hourly production rate. This information is stored in the machine. The computations of the acetone column reveal the flow rate of the recycle stream. So the difference between these two rates will give the quantity of fresh feed required. Thus, there is no need of any iteration calculation for the reactor-acetone column loop.
It is interesting to note that the algorithm of Lee, Christensen and Rudd\(^\text{63}\) has suggested the same optimum ordering of units in the process flowsheet to minimize computational labour (Figure 3, 5).

ii) **Quench unit - acetone column recycle calculations.**

The calculations of the quench unit - acetone column involve two parameters, the recycle rate and composition. The exit temperature of the gases leaving the quench tower has been specified; moreover the acetic acid and acetic anhydride contents in the exit gases will be known from the results of quench unit design calculations. Thus, if the composition of the recycle stream is known, the flow rate of the recycle stream can be determined. The excess acetic acid required can be obtained from the make-up unit. It means that to define the recycle flow stream it is only necessary to specify the composition of the recycle stream, and all other parameters follow by the mass balance.

In the present process model program, the composition of the quench unit - acetone column is treated as a preferred design variable. The weight ratio of acetic acid to anhydride in the recycle stream can only be determined by optimum process analysis. If this ratio becomes less than unity, fewer plates are required for separation in the acetone column whilst at the same time, more make-up acetic acid will be required, or vice versa. For practical purposes, this ratio is constrained and the range is chosen, based on intuition.
It has been shown in the preceding paragraphs that the algorithms of Lee and Rudd are extremely useful as the guidelines to render the cycle calculations acyclic, and using the information obtained and placing the insight into the process structure, it is possible to find the optimum order of calculation of units within a flowsheet such that only a forward feed of information occurs.

**Organization of the process model**

Once the design variables are chosen and iterative calculations are simplified, the computation of the process model program requires solution of the design equations. In this section, design equations relating the process variables for each unit are discussed briefly. The detailed design procedures are given by Jeffreys (52). The more detailed process model is described in Appendix B.

(a) **Furnace (or reactor)**

The furnace is represented in the process model by its heat duty. The design variables for this unit are % acetone conversion and temperature of cracking.

The datum temperature of the liquid acetone feed has been taken as 86°F and on this basis total heat duty of the furnace can be given by the following equations

(i) preheating the liquid acetone to its boiling point:

\[ \Delta H_1 = z \times sp \times (t_1 - 30) \times 1.8 \]  

[Eqn No. (3, 7)]
(ii) Vapourisation of the acetone:

\[
\Delta H_2 = \nu \times \lambda \times 1.8 \tag{Eqn No. (3, 8)}
\]

(iii) Superheating the acetone to the cracking temperature.

\[
\Delta H_3 = \frac{\nu \times \lambda \times 1.8}{58} \left[6.36 (t_2 - t_1) + \frac{2.185}{100} (t_2 - t_1)(T_2 + T_1) - \frac{3.65}{10^6} (T_2 - T_1)^2\right] \tag{Eqn No. (3. 9)}
\]

(iv) Provision of the heat of cracking:

\[
\Delta H_4 = \frac{\nu \times \lambda \times 1.8}{58} / 58 \tag{Eqn No. (3. 10)}
\]

(v) Heating residual acetone and reaction products:

\[
\Delta H_5 = \frac{\nu \times \lambda \times 1.8}{58} \left[a_m (t_3 - t_2) + \frac{b}{200} (t_3 - t_2)(T_3 + T_2) - \frac{8.4}{3.10^6} (T_3^3 - T_2^3)\right] \tag{Eqn No. (3. 11)}
\]

(vi) Preheating the acetone still feed stock:

As the feed rate to the acetone column is unknown at this stage; this heat requirement cannot be determined so, this heat duty will be calculated later on and the total heat duty of the furnace at this stage will be represented by the above five equations. This heat duty will be stored and the information can be used when the heat load on the furnace for preheating the acetone column feed has been determined.
The notations in the above equations are as follows:

- $z$: feed rate to the reactor (lb/hr)
- $sp$: mean specific heat of liquid acetone between datum temp and boiling point of acetone $(\text{cal/gm}°\text{C})$
- $t_1$: boiling point of acetone at the operating pressure of furnace tubes $(°\text{C})$
- $\lambda$: latent heat of vapourization of acetone $(\text{cal/gm})$
- $x$: specified % acetone conversion
- $ht$: heat of reaction $(\text{cal/gm mole})$
- $mw$: molecular weight of the total reaction mixture
- $am, bm, cm$: values of the constants for reaction heat capacity equation
- $t_3$: exit temperature of reaction products $(°\text{C})$

Note that the temperature shown in capital letters are temperatures in absolute degrees e.g. $T_2 = (t_2 + 273)°K\text{ etc.}$

(b) Quench Unit

The hot vapours leaving the furnace are rapidly cooled i.e. quenched to prevent decomposition of the ketene. This quench is carried out by injecting a fine spray of a mixture of acetic acid and acetic anhydride which can be obtained from the bottom product of the acetone column. The composition of the recycle stream is a chosen design variable for this unit. Daroux(30) has pointed out that a simple four jet unit can be conveniently employed. As the cost of this unit will be comparatively negligible, it is not necessary to include detailed design of this unit.
However, material and heat balances are necessary for flowsheet calculation. Besides the above mentioned design variable, the temperature of the process stream leaving the quench spray influences the mass and heat balance program. This latter design variable should be constrained in such a way that the rate of decomposition of ketene is negligible in the chosen range.

The heat balance equations can be given as:

(i) heat lost due to cooling of process stream:

$$\Delta h_1 = \frac{zm^1.8}{mw} \left[ a \frac{m}{200} (t_2-t_e) + \frac{b}{200} (t_2-t_e) (T_2+T_e) \right]$$

$$- \frac{8.4}{3 \times 10^6} (T_2^3 - T_e^3) \quad \text{[Eqn No. (3.12)]}$$

(ii) heat gained from acetic acid in the mixture:

$$\Delta h_2 = \left( X_{ac}RT_{ac}(Sp) \right) (t_4-63) \times 1.8 + \left( X_{ac}RT_{ac} \lambda ac \times 1.8 \right)$$

$$+ \left( \frac{X_{ac}RT}{60} \right) \times 1.8 \times 9.88(t_e-t_4) + \frac{2.68}{200} (t_e + T_4)$$

$$- \frac{5.89}{3 \times 10^6} (T_e^3 - T_4^3) \quad \text{[Eqn No. (3.13)]}$$

(iii) heat gained from acetic anhydride in the mixture

$$\Delta h_3 = \left( X_{an}RT_{an}(Sp) \right) \times (t_5-63) \times 1.8 + \left( X_{an} \lambda_{an} \times 1.8 \right)$$

$$+ \left( \frac{X_{an}RT}{102} \right) \times 18.3 \times (t_e-t_5) + \frac{3.28}{200}$$

$$\left( t_e-t_5 \right) (T_e+T_5) + \frac{1.13}{3 \times 10^6} (T_e^3 - T_5^3) \quad \text{[Eqn No. (3.14)]}$$
where,

te temp. of process stream leaving quench spray (°C)
t4 boiling point of acetic acid (°C)
t5 boiling point of acetic anhydride (°C)
(Sp)ac, (Sp)an mean specific heat of acetic acid and anhydride respectively (cal / gm °C)
RT weight ratio of acetic acid to anhydride in recycle stream
X flow rate of acetic anhydride in recycle stream (lb/hr)
λac, λan latent heat of vapourization of acetic acid and anhydride respectively; (cal/gm)

The quenching started at the quench spray is to be completed in a packed tower by contacting the partly cooled gas with a further quantity of acid and anhydride mixture of the specified composition. The design variable for the quench tower is exit gas temperature of the gas. Some of the acid and anhydride will be condensed, but no chemical reaction takes place in the unit (52). Within the tower, simultaneous heat and mass transfer processes take place. Furthermore, these processes occur at different rates in various parts of the tower. The computations involve simultaneous solutions of the design equations step by Jeffreys (52) has given the procedure of forming mass and heat balance equations. They are not repeated here. The program for calculation of packing height is described in Appendix B.
The gaseous phase leaving the quench unit contains a large quantity of non-condensible gases so, for design purposes a method recommended by Colburn and Hougen(27) has been used. However, in this case, there is also a chemical reaction involved in the liquid phase. The design variables selected for this unit are % ketene to be condensed and cooling water rate. To simplify calculations, the type of the condenser has been specified.

The heat balance equations for the condenser can be expressed as

$$h_o (t_g - t_f) + k M_A \lambda (p_v - p_f) = h_{io} (t_f - t_w)$$

$$= U \Delta t$$

where,

- $h_o$ = shell side dry co-efficient (BTU/lbmole ft°F)
- $h_{io}$ = water side co-efficient based on outside diameter
- $M_A$ = molecular weight of vapour
- $p_f$ = partial pressure of condensables in condensate film (atm)
- $p_v$ = partial pressure of condensables in body of gas (atm)
- $t_f$ = condensate interface temperature (°F)
- $t_w$ = water temperature (°F)
- $\lambda$ = latent heat of condensables (BTU/lb)
The solution of the equation (3.15) requires estimation of values of \( t_f \) and the calculation of partial pressure of condensables in the condensate film; however, since the amount of acetone present in the condensable vapour will be considerably greater than the other components, and also at the condensing temperature the partial pressure of the other components will be negligible compared to that of acetone; it will be assumed that \( p_f \) is the partial pressure of acetone. A number of iterations are required to force agreement to some specified tolerance of the L.H.S. and R.H.S. computed of the equation (3.15). For the calculations at the next point, the temperature of the cooled gas is estimated. Then, assuming that the condensation occurs at constant pressure, the drop in partial pressure of the condensables will be proportional to the moles of the component condensed at that point. The heat balance is carried out. New values of the variables in equation (3.15) are calculated and the equation is solved. This step wise procedure is continued until required quantity of the ketene remains in the gas phase. When this condition is satisfied, the check is made whether exit cooling water temperature agrees with the estimated temperature; if not, the design procedure is repeated with re-estimated water temperature.
d) Absorber

The absorption unit is an example of multicomponent absorption with a chemical reaction.

A large amount of heat is liberated due to chemical absorption of ketene and physical absorption of acetone. Thus, the temperature of the descending liquid can be expected to rise considerably. In order to keep the temperature of the liquid as low as possible, a plate type tower with "interstage" coolers is the most suitable unit to install. The design variables for this unit are, % ketene to be absorbed, and water rate to coolers. In order to determine the absorbent rate, the material balance over the crude product storage is necessary. As one mole of ketene absorbed will form one mole of acetic anhydride, the quantity of acetic anhydride in liquid ex-absorber can be computed. Once the weight ratio of acetic acid to anhydride in the quench column recycle is specified, the material balance over the crude storage can be done without difficulty. Jeffreys (52) has developed a design equation for the number of plates required for ketene absorption.
For acetone absorption, vapour - liquid equilibrium data is taken from Jeffreys and operating line calculations are carried out by material balance for different % of acetone absorbed. The number of plates for acetone absorption can be calculated from solving operating line equation (3.16), equilibrium line equation (3.17) and material balance equation (3.18).

\[ y_i = E \times (y_{i-1} - x_i) \quad \text{[Eqn. No. (3.16)]} \]

where

\[ y_{i-1} = f (x_{i-1}) \quad \text{[Eqn. No. (3.17)]} \]

\[ x_i = f (y_i) \quad \text{[Eqn. No. (3.18)]} \]

where

\[ y_i, x_i = \text{mole fraction of acetone in vapour and liquid resp.} \]

\[ E = \text{plate efficiency of acetone absorption} \]

(assumed to be 50%)

\[ y, x = \text{mole fraction of acetone in vapour in equilibrium with mole fr. of acetone in liquid} \]

The method of interpolation has been used to solve equation (3.18). The calculation is continued until the mole fraction of acetone in liquid stream becomes appreciably small i.e. most of acetone is absorbed. The design of interstage plate heat exchangers is carried out by the conventional method.
The distillate produced by the acetone distillation column must be of satisfactory quality for recycling to the furnace and the bottom product should contain the specified weight ratio of acetic acid-anhydride. The design variables for the acetone column are as follows:

i) reflux ratio

ii) acetone purity in the top product (i.e. top product composition)

iii) acetic acid - anhydride ratio in the bottom product (i.e. bottom product composition)

For the calculation of number of ideal stages for a given separation of a multicomponent mixture, a plate to plate calculation is done by the Lewis - Matheson procedure *, and with a local optimization in one variable to find the optimum reflux ratio. The minimum reflux ratio is determined by Underwood's method(105).

* The Lewis - Matheson stagewise analysis demands an equal molal overflow resulting in linear operating lines, but the three components that are to be separated have widely different molar latent heats. However, the difference in the molar latent heats between acetone and acetic acid is small, and as these substances will be the key components, it is proposed to perform the stagewise analysis by the above method and not to correct for unequal molar overflow(52).
The equilibrium equation for a theoretical plate $i$, is given by the equation (3.19) for each component, $m$,

$$y_{im} = \frac{x_{im} P_m(T)}{\sum_{m} x_{im} P_m(T)} \quad [\text{Eqn No. (3.19)}]$$

where,

- $y_{im}$: mole fr. of component, in the vapour leaving plate $i$
- $P_m(T)$: vapour pressure of component $m$ at temperature $T$
- $x_{im}$: mole fr. of component $m$ in the liquid leaving plate $i$

The plate temperature $T$ is obtained by iterative calculation with the convergence criterion

$$\sum_{m} y_{im} = 1 \quad [\text{Eqn No. (3.20)}]$$

With the assumption of constant molar overflow, the operating equations for the plate $i$ are as follows:

i) below the feed plate:

$$x_{(i+1)m} = y_{im} \frac{V_i}{L_i} + \frac{W}{L_i} x_{wm} \quad [\text{Eqn No. (3.21)}]$$

where,

- $V_i$ and $L_i$ are vapour and liquid flowrates below the feed plate and can be obtained by mass balance of the stripping section.

$\ x_{wm}$: mole fraction of component $m$ in the bottom product
ii) above the feed plate:

\[ x_{(i+1)m} = V_{im} \frac{V_i}{L_i} - x_{dm} \frac{D}{L_i} \]  

\[ \text{Eqn No. (3.22)} \]

where,

- \( V_i, L_i \): vapour and liquid flowrates above the feed plate
- \( x_{dm} \): mole fr. of component \( m \) in the distillate

The above equation in terms of reflux ratio, \( R \), can be written as

\[ x_{(i+1)m} = \frac{R+1}{R} V_{im} - \frac{x_{dm}}{R} \]  

\[ \text{Eqn No. (3.23)} \]

When the difference between ratio of concentration of the key components on a plate and same ratio in the feed becomes minimum, that plate is considered as the feed plate. The plate efficiency is assumed to be 50%.

When the design of this unit is completed, the rate of recycle stream to the reactor becomes known and at this stage, the fresh feed required to the reactor can be determined (see also equation (3.5)).

e) Acetic anhydride column

The bottom product of the acetone column consists of acetone, acetic acid and acetic anhydride. The acetic anhydride column is required to separate this acetone column product into a distillate that is mainly acetic acid and a bottom product that consists of the specified purity of acetic anhydride.
The design variables chosen for the acetic anhydride column are as follows:

i) reflux ratio

ii) acetic anhydride rate (i.e., bottom product rate)

iii) acetic anhydride purity (i.e., bottom product composition)

Unfortunately, the acetic anhydride purity has to be fixed to a value of 98%, because the cost data for other purities is not available.

The feed to the acetic anhydride column consists mainly of acetic acid and acetic anhydride. Therefore, for design purposes the feed can be considered as a binary mixture of acetic acid and anhydride. A computer routine for the McCabe - Thiele method is used for a plate to plate calculation, assuming plate efficiency of 55%. The design equations are mostly the same as those given in acetone column. The equilibrium equation for acetic acid - acetic anhydride is correlated from the data available from Chu(26).
When the objective function has only one optimum, and depends on a single independent variable, the univariable search methods can be used to find the optimum. Although few practical optimization problems involve only one independent or decision variable, many multidimensional optimization procedures involve one dimensional optimizations as subroutines.

The univariable search methods are generally divided into two subclasses, viz. simultaneous methods and sequential methods. In the former methods, all the experiments are run at the same time, while in the latter methods, the locations of the next experiments are based on the results of earlier ones. Naturally, simultaneous methods are much less effective than the sequential methods. The only occasion in process design when the idea might be used is where independent random trials are made, essentially simultaneously, to locate a good starting point for hill climbing, or to explore the region around an apparent optimum. Hence, only sequential methods are discussed here. However, before discussing these methods, some definitions are necessary.

4.1 Terminology

Unimodal function: a function which has one peak, maximum or minimum in the given range. Unimodality requires neither continuity of the function nor the existence of a unique derivative. The univariable search methods assume a unimodal function.
**Interval of uncertainty** the subinterval in which the peak of a unimodal function lies. To start with, the original bounds on the function define the interval of uncertainty. Then it reduces as one proceeds with the search and each time isolates the region in which the maximum or minimum lies.

**Minimax** the maximum value of the final interval of uncertainty obtained by different search procedures using the same number of trials are compared and the 'best' procedure will be that which gives the minimum value of this maximum interval is said to be minimax.

**Constraint** a restriction that exists among the variables, or is imposed by the conditions of the process or due to physical limitations of the equipment. This may be in the form of equality or inequality.

**Feasible region** a region in which all variables are within (or at) bounds, and no constraint has been violated.

**Local optimum** a feasible point such that any small feasible change will cause an increase in the objective function (assuming the objective function is to be minimized).

**Global optimum** the local optimum which has the lowest value of the objective function.

4.2 **Sequential search methods**

The sequential search methods fall into two classes: (17) method which specify an interval in which the optimum lies, and methods which specify the position of the optimum by a point approximating to it.
4. 2. 1. Methods which specify an interval in which the minimum lies

For these methods, it is necessary to assume that an initial interval in which the optimum lies is known, and that the function is unimodal within this interval. These methods reduce this interval in varying ways until the optimum point is located to the required accuracy.

4. 2. 1. 1. Fibonacci search

The general form of a Fibonacci number is

\[ F_n = F_{n-1} + F_{n-2} \]  

\[ n \geq 2 \]

usually with

\[ F_0 = F_1 = 1 \]

A pair of experiments are run equidistant from each end of the interval. This distance \( d_i \) is determined by the repeated use of the following expression.

\[
\begin{align*}
\frac{d_i}{I_{i-1}} &= \frac{F_{n-i-1}}{F_{n-i+1}} \\
I_i &= \frac{F_{n-i}}{F_{n-i+1}} I_{i-1}
\end{align*}
\]

for \( i = 1, 2, 3, \ldots, n; \)

where, \( F_n \) is the \( n \)th Fibonacci number.

After placing \( n \) experiments, the interval of uncertainty reduces to

\[ I_n = \frac{I_0}{F_n} \]
Figure 4.1. The golden section search
Unless the number of experiments to be performed is known in advance, the Fibonacci method cannot be used as it stands. This is because $d_1$, which must be known before the first experiment can be located, depends entirely on $n$, the number of trials.

4.2.1.2. **Golden section search**

The Golden section search procedure developed by Kiefer and Johnson (110) is completely independent of the number of experiments available. In order to obtain a high point in the interval $A-B$ of figure (4.1.a), two experiments are placed in the interval so that $P = \frac{Q}{Q+P}$. Each experiment divides $A-B$ into 'golden sections' so that $Q = [P (\frac{1}{2}+\sqrt{5})]/2 = P \times 1.618\ldots$; Also $R = \frac{P}{Q}$. If the trial point 2 results in a better value of objective function than does trial 1, the third is located symmetrically with respect to trial 2 in the remaining interval of uncertainty (Fig 4.1.b). This procedure is continued until the location of the optimum point is determined with the desired degree of accuracy. After $n$ experiments, the interval $I_n$ remaining is given by

$$I_n = \frac{1}{(1.618\ldots)^{n-1}} [\text{Eqn. No. (4.4.)}]$$

The golden section method requires a relatively large number of experiments for precise location of a vector optimum point.

Harkins (48) has used the golden section method together with the method of parallel tangents to solve many optimization problems.
4.2.2. **Methods which specify the position of the minimum by a point approximating to it**

To use these methods, an initial point approximating to the optimum must be provided. The methods proceed by fitting a low order polynomial through a number of points, and then finding the optimum of the fitted function, the procedure being repeated until the optimum has been found to the required accuracy. The selection of the points through which the fitted polynomial is to pass, and the order of this polynomial, vary from method to method.

4.2.2.1. **The algorithm of Davies, Swann and Campey (17)**

In this method, the function is evaluated at the given initial point. The function is recalculated along the line of search with a given step size. If this point is found better (or equal), then the step size is doubled, and a further move made in the same direction. This process is repeated until a failure point is obtained, indicating that the optimum has been overshot. The step size is then halved and a step again taken from the last successful point. This gives four points equally spaced along the axis of search, at each of which the function has been evaluated. The end point furthest from the point corresponding to the smallest function value is rejected, and the remaining three points used for quadratic interpolation.

If the first step fails, the direction of search is reversed by changing the sign of the step, and the procedure outlined is again followed.
If the first step in the negative direction also fails, then the optimum has been boxed in, and the interpolation may be performed.

4.2.2.2. The algorithm of Powell (77)

In the method of Powell, the function is evaluated at a base point \(X_1\) and at \(X_2 = X_1 + S\), \(S\) being the step size. If the two function values so obtained are \(F_1\) and \(F_2\) respectively. The point \(X_3\) is chosen to be (assuming that function minimization is required).

\[
X_1 + 2S \text{ if } F_1 \geq F_2
\]

but

\[
X_1 - S \text{ if } F_1 < F_2
\]

The function is then evaluated at \(X_3\) to give a value \(F_3\). The optimum \(X_m\) of the quadratic passing through these three points is given by

\[
X_m = \frac{1}{2} \frac{(X_2 - X_3)^2 F_1 + (X_3 - X_1)^2 F_2 + (X_1 - X_2)^2 F_3}{(X_2 - X_3) F_1 + (X_3 - X_1) F_2 + (X_1 - X_2) F_3} \quad \text{[Eqn No. (4.6)]}
\]

If \(X_m\) and whichever of \(X_1, X_2\) and \(X_3\) corresponds to the smallest function value differ by less than required accuracy, the optimum is assumed to have been located. Otherwise the function is evaluated at \(X_m\) and one of the three points \(X_1, X_2\) and \(X_3\) is discarded, whichever has the greatest function value. The process of quadratic interpolation is then continued.
Powell (op. cit.) has pointed out that the turning point predicted by (4.6) will be minimum only if

\[
\frac{(x_2-x_3)F_1 + (x_3-x_1)F_2 + (x_1-x_2)F_3}{(x_1-x_2)(x_2-x_3)(x_3-x_1)} < 0
\]

[Eqn No. (4.7)]

Another undesirable possibility also exists. If too large an extrapolated step is allowed, this can introduce a point distant from the optimum.

If either of these circumstances does arise, a specified maximum permissible step is taken in the direction of decreasing \(F_q\) and the point so obtained is used to replace one of \(X_1\), \(X_2\), and \(X_3\) as before.

Coggins (17) has used the algorithm of Davies, Swann and Campey for the first interpolation and for all subsequent steps Powell's algorithm is used. Box and coworkers (17) have pointed out that by using Coggins' method, the minimum is bracketed and the undesirable possibilities mentioned above cannot arise.
CHAPTER 5

Multivariable Search Methods I

5.1 General considerations

Many problems arise when one passes from univariable to multivariable search problems. One deleterious effect of multidimensionality is that it makes the unimodality assumption less plausible. Moreover it is very difficult to visualize the size of multidimensional space and as the dimensionality increases, the effective region of uncertainty also increases. Wilde (110) has described in details the three phases of a multidimensional strategy, viz. opening phase, middle phase and end phase. In the opening phase, when nothing at all is known about the function, exploration in a small region, chosen at random, is necessary. In the middle of the search, after having left the early regions behind, contour hills should be climbed as fast as possible. Towards the end of the search, when the optimum is near, more local explorations may be needed to attain any increase in the function. This is also necessary to check whether the optimum attained is really a true optimum or not.

Before, any optimization procedure is begun, it is helpful to normalize the independent variables. It may considerably reduce the amount of subsequent work necessary. Chestnut, Duersch and Gaines (24) use the information of the 'best' value of each variable and its allowable range to fix the units to be used for each of the variables. For instance, if a variable $x_2$, say composition $C$, has a near optimum value of 0.06 and a range 0.051 to 0.066, the transformation might be
\[ x_2 = \frac{C - 0.06}{0.066 - 0.051} \quad \text{[Eqn No. (5.1)]} \]

Zellnik, Sondak and Davies (17) prefer the following

\[ x_2 = \frac{C - 0.051}{0.066 - 0.051} \quad \text{[Eqn. No. (5.2)]} \]

The former method tries to shape contours into uniform ones e.g. circular in two dimensional problems with origin at the centre, while in the latter method, all variables will have uniform scaling, from 0. to 1.0.

The determination of the size of the initial step is definitely dependent upon the particular process and any normalization which has taken place. Since the total number of steps which will be taken during the optimization procedure depends upon the initial step size, it is important to select this carefully. The adjustment of step size during the search is very often necessary. Oscillations in the search path may occur due to the presence of ridges or valleys in the response surface. Since such a zig-zag pattern is very inefficient, and an acceleration procedure in such circumstances should be available in the optimization strategy.

It is preferable that the function to be optimized should be continuous, and so the search is always visualized as a smooth continuous path climbing a "hill". But it is important to note that the numbers are held in a digital computer only to eight or ten significant decimal figures. So the hill is composed of a number of steps, like a 'terrace' (83). Any procedure may fail to climb from such a terrace. This is illustrated in fig (5.1). The contours are drawn at intervals of one unit in the last decimal place of \( Y \), the value of objective function.
Figure 5.1. "terrace" on the contours
If two successive search steps occur close together, between such contours, the value of Y are equal and the next steps may wander about on the "terrace", more or less at random.

The actual costs or constraints of many problems are not continuous functions, but contain a step or series of steps. For example, a situation may arise where there is a sharp change in price above a given component size. Weisman, Wood and Rivlin (106) have given a procedure to approximate such steps closely by using two or more functions.

Every optimization method has its own stopping criterion. The method might give the 'false' optimum if:
(i) a saddle point is reached
(ii) a sharp ridge is reached
(iii) the 'current' point is on 'terrace'
(iv) a local optimum is reached.

Generally, a nonlinear exploration might overcome the difficulties (i) and (ii). When the current point is on the terrace, the possible solution would be to multiply the step size by a factor of 2 or 3 and then carry out the local exploration. This will move the current point from one contour to the contour of better response. The optimum point reached from the above 'end game' tactics may be 'local' and it is necessary to explore the solution space to determine whether other optimum exists. The suggested methods in the literature for location of alternate optimum points are at present unsatisfactory. Most methods adopt a procedure of beginning a search at several different random starting points, selected manually or by the computer, and if the same result is obtained from each of the starting points, this confirms that a 'global' optimum is reached.
Constrained optimization problems deserve more attention. In such problems, the constraints are of as much important as the contours and gradient of the function. Transfer of a constrained problem into an unconstrained one by the addition of the penalty function concept does not necessarily become an efficient procedure. In the constrained problems, the global optimum is ensured only when the function is strictly convex in the convex region.

5.2 Transformation techniques

The techniques discussed in the section are methods of transformation by which problems of constrained optimization can be reduced to a form in which no constraint appears explicitly. After such transformation, the problem can be solved by means of the available methods which have been devised to optimize unconstrained functions.

5.2.1. Simple inequality constraints

M. J. Box (16) has adopted an approach of transforming the independent variables and leaving the objective function unaltered. The transformations considered by Box include

\[
\begin{align*}
    x_1 &= y_1^2 \\
    x_1 &= e^{y_1} \\
    x_1 &= |y_1| \\
    x_1 &= \sin^2 y_1 \\
    x_1 &= \frac{e^{y_1}}{e^{y_1} + e^{-y_1}}
\end{align*}
\]

[Eqn No. (5.3)]

[Eqn No. (5.4)]
where, (5.3) forces $x_1$ to be positive and (5.4) forces $x_1$ to be the range $0 \leq x_1 \leq 1$, for any real, unconstrained value of $y^1_i$. If some independent variable $x_i$ is constrained between a lower and upper bound such that
\[ g_i \leq x_i \leq h_i \]  
then the transformation
\[ x_i = g_i + (h_i - g_i) \sin^2 y^1_i \]  
can be applied. After such transformations are done, the unconstrained optimum in the $y$-space is sought. Box has pointed out that such transformations cannot introduce additional local optima. He has used these transformations in conjunction with Powell's method successfully for problems having up to twenty independent variables.

5.2.2. The 'SUMT' method

The Sequential Unconstrained Minimization Technique originated by Carroll (22) and then developed by Fiacco and McCormick (35) form the following function

\[ Y_0(X, r_K) = Y(X) + \sum_{i=1}^{i=m} \frac{1}{g_i(X)} + \sum_{j=1}^{j=p} h_j^2(X) \]

from the original nonlinear programming problem

\[ \text{Min } Y(X) = f(x_1, x_2, \ldots, x_n) = f(X) \]

subject to

\[ g_i(X) \geq 0 \quad i = 1, 2, \ldots, m \]

\[ h_j(X) = 0 \quad j = 1, 2, \ldots, p \]

where, $r_k$ is called a weight factor. For the chosen $r_k$, equation (5.7) is minimised by any unconstrained technique (see later) and this is repeated for $r_2, r_3, \ldots$ until $r_k$ is negligibly small. The argument is that all trials so made satisfy (5.9) and the final ones, converge on the optimum of (5.8) and simultaneously satisfy (5.10).
In a practical problem, $r_1$ is set between 1 and 100 and $r_k$ between 0.1 to 0.01. Fiacco and McCormick have proved that for a well-behaved problem, the optimum obtained is a global one (assuming function to be strictly convex in the convex region). Davies and co-workers have pointed out that, in using this method, the major difficulty is caused whenever the variables are of very different orders of magnitude. They have suggested scaling all variables and then to optimize with respect to the scaled variables.

For the optimization problem with inequality constraints only, Fiacco and McCormick modified 'SUMT' as follows:

Suppose, the objective function to be minimized is given by (5.8), subject to inequality constraint

$$g(X) = AX - b < 0 \quad \text{[Eqn No. (5.11)]}$$

A modified objective function takes the form

$$y_o(X) = Y(X) - \frac{K_2}{g(X)}$$

$$= Y(X) - \frac{K_2}{AX - b} \quad \text{[Eqn No. (5.12)]}$$

As $K_2$ diminishes, the unconstrained minimum of $y_o(X)$ reaches the constrained minimum of $Y(X)$. The value of $K_2$ takes the form accordingly to

$$K_2 = \frac{1}{(\text{number of iterations})\Delta} \quad \text{[Eqn No. (5.13)]}$$

where, $\Delta$ is some predetermined factor.
Schingzinger (91) has pointed out that this method is likely to reach the unconstrained optimum, instead of the constrained optimum. He suggests to multiply the objective function with an infeasibility factor. So, the objective function becomes

\[ Y_0(X) = Y(X) \times \left( \frac{AX}{b} \right)^{K_2} \quad [\text{Eqn No. (5.14)}] \]

for, \( g(X) = AX - b \leq 0 \)
and \( K_2 \) as defined by (5.13)
and,

\[ Y_0(X) = Y(X) \times e^{f_a(X) - a} \quad 2K_1 \quad [\text{Eqn No. (5.15)}] \]

for, \( g_a(X) = f_a(X) - a = 0 \)  \quad [\text{Eqn No. (5.16)}]
and

\[ K_1 = \text{(number of iterations)} \quad \Delta \quad [\text{Eqn No. (5.17)}] \]

If the constraints present are as defined by (5.16), then Kelly (54) has modified the objective function as

\[ Y_0(X) = Y(X) + K_1 \left[ g_a(X) \right]^2 \quad [\text{Eqn No. (5.18)}] \]

Only a large value of \( K_1 \) will bring the unconstrained optimum of \( Y_0(X) \) near the constrained optimum of \( Y(X) \). Yet, a very large \( K_1 \) may render the search very difficult because then the surface of \( Y_0(X) \) becomes a steep and narrow near the optimum. To avoid this difficulty, it is a good strategy to begin with a small \( K_1 \) and let \( K_1 \) grow progressively, say, according to equation (5.17) (91).  

Generally a penalty function of type \( K \left[ g_a(X) \right]^2 \) is added only for those constraints which are actually violated. Here, \( K \) is a positive number whose magnitude depends on the magnitude of the violation of constraint (100). Recently, Powell (78) has developed a transformation procedure for the optimization problem with the equality constraints.
The desired properties of a multivariable search method can be stated as follows (107)

(a) It should exhibit a high degree of stability despite the complexity of the functions involved or the number of variables.

(b) It should readily handle constraints which are both equalities and inequalities.

(c) It should contain provision for exploration of the solution space for alternative optima.

The procedure may be used for any system where:-

(a) The constraints and the objective function can be expressed as continuous functions of the design variables.

(b) The functions can be evaluated with reasonable rapidity.

(c) The objective function has only a limited number of optima.

So many multivariable search methods have been developed recently. Only methods with which the author is conversant have been discussed. It is also difficult to classify these search methods in any logical way. The classification done here is arbitrary.

6.1 Direct search methods

In general, the direct search is the sequential examination of a finite set of trial values of the function under study (110). Each trial is compared with the 'best' previous trial and the new value of the variable accepted or rejected depending on whether an improvement is observed. Different direct search methods have different strategies to find the various trial points.
Direct search methods have been very useful for several reasons. The major ones are as follows (113)
(a) They are well adapted for use in a high speed digital computer.
(b) They provide solutions to some problems where classical methods cannot be applied.
(c) No knowledge of the form of the function being optimized is required. This is rather important in the optimization of engineering designs, where it may be necessary to compute a long sequence of equations to evaluate the function.

The following features are characteristic of problems which are amenable to the use of direct search.
(a) The boundaries of the problem space will usually be such that each variable has definite maximum and minimum limits. There may be auxiliary boundaries which are quite irregular and arbitrary, including isolated, excluded regions entirely within the problem space.
(b) The function to be optimized must have a single, real and finite value at every point $P$ within the problem space.
(c) The value of the function at any point $P$ should be such as to allow the value of $P_1$ to be judged 'better' than that of $P_2$, except that any two points lying on the same contour of the problem space will have equal value.
(d) There should be a single point $P^*$ the optimum which is "better" than all other points $P$ different from $P^*$

If the characteristics (d) and (c) are not entirely fulfilled, with the result that there are local, relative optima, there is probably no generally practical method for finding the true optimum uniquely. If the number of relative optima is not large, direct search will retain a fair degree of utility for studying the problem.
6.1.1. **Pattern search method**

The pattern search method devised by Hooke and Jeeves is based on the hopeful conjecture that any set of moves, that is, adjustments of the independent variables, which have been successful during early experiments will be worth trying again. This strategy is successful if the search is proceeding along the crest of a sharp ridge. Hence further moves in the same direction will be worthwhile if the ridge is straight.

Although the method starts cautiously with short excursions from the starting point, the steps grow with repeated success. Subsequent failure indicates that shorter steps are in order, and if a change in direction is required the method will start again with a new pattern. In the vicinity of the peak the steps become very small to avoid overlooking any promising direction.

The original work by Hooke and Jeeves was concerned with the application of pattern search to mathematical and statistical problems. As they say "In practice, pattern search has proved particularly successful in locating minima on hyper surfaces which contains sharp valleys. On such surfaces classical techniques behave badly and can only be induced to approach the minimum slowly."

6.1.1.1. **Description of pattern search**

Figure (6.1) shows the simplified flow chart for pattern search.

Most of the notation of this section has been taken from Wilde. (110)
Figure 6.1. Simplified flow chart for the Pattern Search
The initial base point $\bar{b}_1$ and a step size $\delta_i$ for each independent variable $x_i$ ($i = 1, 2, \ldots, n$) is chosen arbitrary. Let $\delta_i$ be the vector whose $i$th component is $\delta_i$, all the rest being zero. After measuring the criterion of the initial base $\bar{b}_1$, say $Y(\bar{b}_1)$, the observation at $\bar{b}_1 + \delta_1$ is taken. If this new point is better than the base, the $\bar{b}_1 + \delta_1$ is called the temporary head $\bar{t}_{11}$, where the double subscript shows that the first pattern is being developed and the first variable $x_1$ is already perturbed. If $\bar{b}_1 + \delta_1$ is 'worse' than $\bar{b}_1$, the next point $\bar{b}_1 - \delta_1$ is tried. If this new point is better than $\bar{b}_1$, it is made a temporary head; otherwise $\bar{b}_1$ is designated temporary head. In summary, for minimization,

$$\bar{t}_{11} = \begin{cases} \bar{b}_1 + \delta_1 & \text{if } Y(\bar{b}_1 + \delta_1) < Y(\bar{b}_1) \\ \bar{b}_1 - \delta_1 & \text{if } Y(\bar{b}_1 - \delta_1) < Y(\bar{b}_1) \\ \bar{b}_1 & \text{if } Y(\bar{b}_1) < \min [Y(\bar{b}_1 + \delta_1), Y(\bar{b}_1 - \delta_1)] \end{cases} \quad [\text{Eqn No. (6.1)}]$$

Perturbation of $x_2$, the next independent variable, is now undertaken in the same way, this time about the temporary head $\bar{t}_{11}$ instead of the original base $\bar{b}_1$. In general, the $j$th temporary head $\bar{t}_{1j}$ is obtained from the preceding one $\bar{t}_{1j-1}$ in the following manner.

$$\bar{t}_{1j} = \begin{cases} \bar{t}_{1, j-1} + \delta_j & \text{if } Y(\bar{t}_{1, j-1} + \delta_j) < Y(\bar{t}_{1, j-1}) \\ \bar{t}_{1, j-1} - \delta_j & \text{if } Y(\bar{t}_{1, j-1} - \delta_j) < Y(\bar{t}_{1, j-1}) \\ \bar{t}_{1, j-1} & \text{if } Y(\bar{t}_{1, j-1}) < \min [Y(\bar{t}_{1, j-1} + \delta_j), Y(\bar{t}_{1, j-1} - \delta_j)] \end{cases} \quad [\text{Eqn No. (6.2)}]$$

The above equation covers all $1 < j < n$. If we adopt the convention that

$\bar{t}_{10} \equiv \bar{b}_1$

When all the variables have been perturbed the last temporary head point $\bar{t}_{1n}$ is designated the second base point $\bar{b}_2$. 
This move is termed as 'type 1 - exploratory' or just 'type 1' search. The original base point $b_1$ and the newly determined base point $b_2$ together establish the first pattern, which indicates a probable direction for a successful move. The initial temporary head for pattern based at $b_2$ is given by

$$
t_{20} = b_1 + 2(b_2 - b_1) = b_2 + (b_2 - b_1) = 2b_2 - b_1
$$

The double subscript $t_{20}$ indicates that a second pattern is built up and that perturbation of the variables has not yet begun. A local exploration about $t_{20}$ is carried out to correct the tentative second pattern if necessary. The local equations governing establishment of the new temporary heads $t_{21}, ..., t_{2n}$ will be similar to equation (6.2). The procedure is completed when all the variables have been perturbed and the last temporary head $t_{2n}$ is designated the third base point $b_3$ if its outcome is better than $b_2$.

The exploratory move made after the pattern move is termed as 'type 2 - exploratory' or 'type - 2' search. The pattern move and type - 2 search together form the basic part of pattern search. The type - 1 search is to establish a general direction for the pattern search. The type - 2 search gives continual correction to the direction of the pattern. The pattern loop is maintained until no further improvement can be made.
When a type - 2 search does not produce success, the conditions at the last base point are restored and a type - 1 search is performed to find the new direction for the pattern. When a type - 1 search is unsuccessful, the final closure tests are made. If the step size are greater than minimum, the sizes are reduced and another type - 1 search is performed from the last base point. If the step sizes are less than or equal to the minimum allowable, the optimum is assumed to have been found and the search is stopped.

Figure (6.2) illustrates the progress of Pattern search on a two dimensional figure.

6.1.1.2. Pattern search algorithm

Kaupe Jr., (53) has given the computer algorithm for pattern search. Bell and Pike (10) have pointed out that the algorithm possesses a flaw caused by rounding error. Suppose $X_0$ be a base point and $\Delta$ be a step size. The exploratory search will put new trial point at $X^1 = X_0 + \Delta$. Suppose this move is successful. So the procedure will then do a pattern move. Let the trial point reached by this move, say $X^{11}$, have the same co-ordinates as that of $X^1$. On many machines, however, values of the objective functions at $X^1$ and $X^{11}$ will not be same. So the search begins to move away from $X^1$ in very small steps. This is clearly not desirable. Bell and Pike have experience with many problems which required a large amount of computing owing to this difficulty. The modified algorithm also takes advantage of the knowledge gained by search of the sign of its previous move in each of the $K$ directions, where $K$ is the number of variables.
Figure 6.2. Progress of Pattern search on a two dimensional problem
R. De Vogelaere (32) and recently, Tomlin and Smith (104) and Smith (97) have suggested the minor improvements in the pattern search algorithm.

Computer flowchart of the Pattern Search subroutine is given in the Appendix A.

6.1.1.3. Application of Pattern search to constrained optimization problems

The pattern search devised by Hooke and Jeeves, which is generally termed as LOOK, is not directly applicable when constraints are present. Recently, many modifications have been developed to deal with constrained optimization problems.

The 'optimal search' procedure developed by Weisman, Wood and Rivlin (106) converts the constrained problem to one without constraints by using penalty functions. This approach is particularly useful when both the function and its constraints are nonlinear.

Suppose the objective function

\[ Y = f(x_1, x_2, \ldots, x_n) \]  \hspace{1cm}  \text{[Eqn No. (6.4)]}

is to be minimized subject to the constraints

\[
\begin{cases}
G_1 = g_1 (x_1, x_2, \ldots, x_n) = 0 \\
G_i = g_i (x_1, x_2, \ldots, x_n) = 0 \\
G_m = g_m (x_1, x_2, \ldots, x_n) = 0
\end{cases} \hspace{1cm} \text{[Eqn No. (6.5)]}
\]

Then, a new objective function

\[ Y_N = Y + \sum_{i=1}^{i=m} k_i (G_i) \]  \hspace{1cm}  \text{[Eqn No. (6.6)]}

is formed.
This new objective function is then minimized as a problem without constraints for a succession of increasingly large values of $k$. This procedure is based on the principle that as $k$ goes to infinity, the solution of this problem approaches that of the original problem with constraints (22). The explicit constraints on the variables are handled more simply. The procedure provides that no variable may be assigned a value outside of its allowable range.

Chestnut, Duersch and Gaines (24) define two methods to handle constraints. A 'direct' method consists of computing the excess magnitude of each variable which would violate the constraints. Rather than using the computer magnitude, the limiting value of the variable is used instead. The net effect is that the optimization proceeds up to the constrained boundary, but does not exceed the constraint. An 'indirect' method uses a heavy penalty for an excess magnitude of each of variables violating the constraints. These penalties are used to degrade the value of the objective function so severely that the optimization path will be lead out of the constrained area. The 'direct' method might work well when constraints are linear. In the case of nonlinear constraints and especially with higher dimensional problems, it is very difficult to calculate the limiting value of the variable which violates the constraint. The 'indirect' method will tend to oscillate in moving in and out of constrained region which makes it less desirable.

Figure (6.3) illustrates paths for the 'direct' and 'indirect' methods for two dimensional case.
Figure 6.3. Paths of optimization near a constraint boundary with 'direct' and 'indirect' methods.
When inequality constraints are present, a slack variable is used to form the equalities (107) Thus
\[ g_i(x_1, x_2, \ldots, x_n) \leq K_i \tag{Eqn No. (6.7)} \]
becomes
\[ g_i(x_1, x_2, \ldots, x_n) - K_i + S_i = 0 \tag{Eqn No. (6.8)} \]
\[ 0 \leq S_i \leq K_i \tag{Eqn No. (6.9)} \]
where, \( S_i \) is the additional slack variable. This equation can be satisfied only if the inequality is observed. If a double inequality of the form
\[ k_i \leq g_i(x_1, x_2, \ldots, x_n) \leq K_i \tag{Eqn No. (6.10)} \]
is present, then it can be expressed as
\[ g_i(x_1, x_2, \ldots, x_n) - S_i = 0 \tag{Eqn No. (6.11)} \]
\[ k_i \leq S_i \leq K_i \tag{Eqn No. (6.12)} \]
The new objective function becomes as that given by equation (6.6) and the same procedure is carried out.
Using 'Optimal search' procedure, Weisman, and Wood have succeeded in solving system design problems containing as many as 50 bounded variables and 49 constraint equations.

Spang (100) replaces the value of the objective function by a very large value whenever the constraints are not satisfied. This pseudo value must be proportional to the amount the inequality is violated so that the search routine will force the test points into region where the inequality can be satisfied. Thus, an objective function
\[ Y = f(x_1, x_2, \ldots, x_n) \tag{Eqn No. (6.4)} \]
subject to constraints
\[ g_i(x_1, x_2, \ldots, x_n) = 0 \tag{Eqn No. (6.13)} \]
\[ i = 1, 2, \ldots, p \leq n \]
and
\[ g_i(x_1, x_2, \ldots, x_n) \geq 0 \tag{Eqn No. (6.14)} \]
\[ i = p+1, \ldots, m \]
would become

\[ Y_N = Y \begin{cases} g_i (x_1, x_2, \ldots, x_n) = 0 & i = 1, 2, \ldots, p \\ g_i (x_1, x_2, \ldots, x_n) \geq 0 & i = p+1, \ldots, m \end{cases} \]  

\[ (\text{Eqn No. (6.15)}) \]

\[ Y_N = 1 \times 10^{20} \left( \sum_{i=p+1}^{m} g_i (x_1, x_2, \ldots, x_n) \right) + Y \]  

\[ (\text{Eqn No. (6.16)}) \]

where, \( Y_N \) is the value of objective function used in the search and the sum, \( \sum_{i=p+1}^{m} \), consists of those \( g_i (X) \) which are not satisfied.

Himmelblau (49) proposed a more simple procedure to solve optimization problem with equality constraints. His procedure is particularly useful to optimize a process of which mathematical model is available.

Maximize an objective function

\[ Y = \sum_{j=1}^{j=n} C_j x_j \]  

\[ (\text{Eqn No. (6.17)}) \]

OR

\[ Y = \sum_{k=1}^{k=n} g_k (x_1, x_2, \ldots, x_n) \]  

\[ (\text{Eqn No. (6.18)}) \]

subject to constraints

\[ G_i (x_1, x_2, \ldots, x_n) = 0 \]  

\[ 1 \leq i \leq m \]

\[ m < n \]

and \( L_i \leq x_i \leq U_i \)

\[ (\text{Eqn No. (6.19)}) \]

\[ (\text{Eqn No. (6.20)}) \]

Equation (6.19) may be linear or nonlinear. Equation (6.20) imposes definite limits on the variables, which is generally the case in a real physical situation.
Figure 6.4: Failure of Pattern search in handling constraints
The \((n-m)\) variables can be chosen as independent variables. Himmelblau chooses a few variables as 'specified' variables and the remaining variables are established by search for an optimum. The 'specified' variables in practice will usually be 'fixed' variables, such as feed input rate or feed concentration, and/or controlled variables, such as temperature, pressure. Once the initial trial values of the variables to be searched are selected, the problem then becomes one of solving \(k\) nonlinear and linear equations in \(k\) unknowns so that the values of all the variables can be established. The suggested way to solve these \(k\) sets of nonlinear equations is to use direct search as a subroutine to solve equation (6.21)

\[
\min \varphi \quad i = k \quad \sum_{i=1}^{k} (G_i)^2
\]

(Eqn No. (6.21))

This is equivalent to solve the set of equations (6.19). Once all of the values of the variables are established, the search program checks the constraints (6.20) and the values of the objective function.

Figure (6.4) illustrates how the pattern search cannot cope with a typical constrained problem. Under such conditions, Klingman and Himmelblau (57) proposed a solution by a technique, termed as 'multiple gradient summation technique.' Their technique finds a new successful direction, abbreviated \(\text{NSD}\) below, for further search. The new direction is the vector sum of the normalized gradients of the contacted constraints and the objective function. As shown in Fig. (6.5), this tends to generate feasible moves in the right direction. The vector \(\text{NSD}\) itself is similarly normalized to yield a unit vector.
Figure 6.5: A multiple gradient summation method
The procedure is then to take a step $L_4$, in the calculated direction, that will (a) increase the objective function and (b) not contact a constraint. If the objective function is not increased and no constraint is violated, or if the objective function is increased but the same constraint is contacted, the step $L_4$ is reduced. If this step size becomes smaller than minimum allowable step size, the procedure is stopped. At this point the NSD is considered a failure (the search is in the neighbourhood of a local optimum) and a new exploratory move is made with a reduced step size $\Delta X$. In higher dimensional problems, the initial step $L_4$ taken along the normalized unit vector, will very often contact a new constraint.

In such cases, the suggested direction is

$$\text{NSD} = \frac{\nabla Y}{\nabla Y} + \sum_{m=1}^{M} \frac{\nabla g_m}{\nabla g_m} \quad \text{[Eqn No. (6.22)]}$$

Where $M$ is the number of constraints contacted before a new successful direction can be defined for an initial step size, $L_4$. On several problems tested by Klingman and Himmelblau, the procedure converged rapidly, although not always to the optimum. Difficulties were experienced when the objective function contours were nearly parallel to the constraints. If the constraints are very sharp concave, the procedure converges very slowly. Moreover, the procedure is limited to problems where all constraints are inequalities.

When the pattern search stops long before reaching a local optima, Glass and Cooper (47) use perturbations to estimate the gradient, $\nabla Y$, of the objective function and $\nabla g_m$ of the constraint functions. A direction vector may be computed, $F_1, F_2, \ldots, F_n$ where
for $i = 1, 2, \ldots, n$ and $h$ some small positive increment. 

For, $h \left( \frac{\partial f}{\partial x_i} \right) \approx F_i$, so that

$$h \nabla f (X) \approx (F_1, F_2, \ldots, F_n) \quad \text{[Eqn No. (6.24)]}$$

Supposed that the point $(X^k)$ which is the last successful point, is very near to the constraints $g_j(X) \geq 0$ for $j = 1, \ldots, m^1, m^1 \leq m$ where $m$ is the number of constraints. For each of the constraint function, a vector $(G_{j1}, \ldots, G_{jn})$ can be computed where $G_{ji} = g_j(x_1, \ldots, x_i+h, \ldots, x_n) - g_j(x_1, x_2, \ldots, x_i, \ldots, x_n)$ $[\text{Eqn No. (6.25)}]$ for $i = 1, 2, \ldots, n$, $j = 1, 2, \ldots, m^1$ and for $h$ some small positive increment.

Similarly,

$$h \nabla g_j (X) \approx (G_{j1}, \ldots, G_{jn}) \quad \text{[Eqn No. (6.26)]}$$

Now, using the last successful point $X^k$, as origin of new changes $\Delta X$, Glass and Cooper solve the following linear programming problem.

Minimize $\sum_{i=1}^{n} f_i \Delta x_i \quad \text{[Eqn No. (6.27)]}$

subject to

$$\sum_{i=1}^{n} G_{ji} \Delta x_i \geq \sum_{i=1}^{n} G_{ji} \quad \text{[Eqn No. (6.28)]}$$

for $j = 1, 2, \ldots, m^1$

The $\Delta X$ is a direction vector which may be used to indicate the next successive point in the search. If the steps generated by the procedure move immediately into the infeasible region because of curvature of the constraints, a positive constant vector should be added to the right hand side of the constraint equation (6.28).
Figure 6.6. Alternate routine to find a new direction in a constrained optimization problem.
This will force a move away from the boundaries and permit larger feasible steps. Figure (6, 6) shows the alternate routine suggested by Glass and Cooper.

6.1.1.4. Integer programming problems

Wood (114) has pointed out that pattern search is unable to converge to the optimum when some of the variables are defined only at discrete values. Practical examples of these types of variables can be given as nominal pipe size, number of distillation column plates etc. Figure (6, 7) illustrates the failure of pattern search in such cases. The variable \( x_1 \) assumes any integer value although \( x_2 \) is continuous. A search landing on the ridge at point \( P = (8, 31.2) \) finds it difficult to establish a new pattern by shortening its local exploration steps. In such circumstances, Wood moves to the nearest or most promising discrete value (\( x_1 = 7 \) in this case) and finds the best value of the continuous variable by a search of lower dimensionality. This establishes the new point \( S = (7, 29.7) \). From this point, a pattern can be set along a ridge. Though Wood has had some success with this procedure, it may not work with constrained integer programming problems. One approach to solve such problems is simply round off each nonintegral value in the optimal solution obtained by any of the methods discussed in the previous section. Of course, care must be taken to round off integral values that will satisfy the constraints. Wilde and Beightler (112) has pointed out that such procedure can be misleading, especially in higher dimensions.

Ecols and Cooper (33) have developed a procedure to solve the following integer linear programming problem.
Figure 6.7. A discrete variable problem
Maximize \[ Y = \sum_{i=1}^{n} Z_i X_i \] subject to

\[ \sum_{i=1}^{n} a_{ij} x_i \leq b_j \] for \( j = 1, 2, \ldots, m \)

\[ x_i = 0, 1, 2, \ldots, n \]

The inequality condition defined by equation (6.30) is the necessary restriction for their procedure which consists of four phases. The phase I, is a simple pattern search to move from a lattice point to an adjacent better lattice point by changing one variable at a time. When a feasible lattice point is found on or near a constraint, phase I is terminated. This is when a point \( B_2 \) of figure (6.8) has been reached.

The phase II, begins with the final solution obtained in phase I. The phase II solution tries to get around the 'constrained local optimum' situation encountered. This is done by adding to some variable \( x_i \) in a direction which will increase the objective function regardless of whether or not the new trial point is feasible, unlike phase I in which feasibility is maintained at every move. If the trial point is feasible the move is accepted. If one or more constraints are violated, a second move is determined which will satisfy the constraints by incrementing some other \( x_i \). In figure (6.7) no such move can be determined.
In phase III, each variable in turn is divided by two and truncated to the nearest integer and then uses a phase I procedure to find a better trial point. In fig (6.8) phase III does not find a better solution. The final phase, viz phase IV, is identical to phase II except that two variables are incremented simultaneously in the first part of the incrementing process rather than just one. Phase IV generally reaches near optimum. In fact, in fig (6.8) phase IV has reached point 'm', the optimum lattice point. On many problems, containing as many as 21 variables and 27 constraint equations, the procedure of Ecols and Cooper, converged to the optimal or near optimal solution, although they are not yet satisfied because the procedure is rather approximate and not tested on very large problems.

The situation when one or more of the independent variables assume only integer values, has been treated by Weisman, Wood and Rivlin (107) by replacing the variable under consideration, say $x_j$, in the objective function, which is to be minimized, by $x_j'$ where $x_j'$ is given by:

$$x_j' = x_j + y_j^p$$  [Eqn. No. (6.32)]

and

$$y_j = x_j - \text{(integer part of } x_j\text{)}$$  [Eqn. No. (6.33)]

$p$ is a constant having a value of the order of 0.05. The value of $x_j'$ remains unchanged in the constraint equations. This procedure increases the value of objective function sharply for any departure from an integer value of $x_j$, hence it forces the variable to assume one of the allowable values in the final solution.
Figure 6.8. Path of search by the method of Ecols & Cooper
6.1.1.5. Recent development in 'Pattern Search' method

During the last few years, many modifications to the pattern search have been put forward. In the original procedure, LOOK, the step sizes for all independent variables are changed at the same time and by the same ratio. This causes occasional difficulty when some variables are at the upper ends of their ranges and others are at the lower ends of their ranges. Since the step size for each variable is related to the allowed range for that variable, the ratio of step size to variable size could vary widely. In the code developed by Weisman, Wood and Rivlin, (106) called STEP 50, the initial step sizes are based on the ranges. As the search proceeds, the step sizes are changed depending upon the successes and failures for the moves of each variable during the exploratory move. If the first move for a given variable is a success [i.e., for minimization, \( Y(b_1 + \delta_1) < Y(b_1) \)] the step size is increased by a factor of two in the next exploratory search. If the reverse move is successful [i.e., \( Y(b_1 - \delta_1) < Y(b_1) \)] the same step size but with reverse sign is retained for the next search. If both move fails

\[ \text{i.e., } Y(b_1) < \min \left[ Y(b_1 + \delta_1), \ Y(b_1 - \delta_1) \right] \]

the step size is halved in the next exploratory search.

Flood and Leon (41) have written the program, designated as BEST, in which changes in a particular variable are continued until no further improvement is evident. In short, they do a one at a time search instead of the exploratory search of LOOK.
In one at a time search, a particular variable $x_i$ is increased successively by a step size $\lambda_i \Delta_i$ ($\lambda_i > 1$), $m = 0, 1, 2, \ldots$ until no further improvement is made in the objective function. When this happens, say at step size $\lambda_i^{h+1} \Delta_i$, the last base point is retained, namely the one obtained by step $\lambda_i^h \Delta_i$ and a new sequence is started from this point with initial step size equal to $\Delta_i$ following the same scheme as before. If a step size of $\Delta_i$ in the positive direction does not bring a better point, then a step of length $\Delta_i$ in the negative direction is tried, and the same procedure is followed. If the objective function $Y'$, when all variables have been perturbed, is better than $Y$ at the last base point, then a pattern move is made. The co-ordinates of the $Y'$ point are incremented by the amount proportional to the change experienced for the co-ordinates in going from $Y$ to $Y'$. This rate of change will be greater than one. If this new point, $Y''$, after initial pattern move, happens to be better than $Y'$, a new step length $(\lambda P) (\Delta P)$ is taken in the same direction. The role of $\lambda P$ is identical to that of $\lambda$ in the above described one at a time procedure and the procedure also follows the same scheme. As before, when a point is reached when no improvement is obtained by moving the vector $(\Delta P)$ or $(-\Delta P)$, this point is considered the best of this series of pattern moves. The remaining procedure is same as that of LOOK.

The typical trajectory using the procedure of Flood and Leon is shown in figure (6, 9)
Figure 6.10. Optimum gradient method with pattern move [STRGY 1]
Flood (41) has devised a strategy, named STRGY 1, which uses an optimum gradient method coupled with pattern moves. As shown in fig. (6.10) it determines the direction of gradient at starting point Po and then locates the minimum P₁ on this direction. It again determines the direction of gradient at P₁ and locate the minimum P₂ on this line. A pattern move is made from P₂ to P₃. In the pattern move the modification is carried out according to the equation

\[ \text{new vector } X'' = X' + k \overline{d} \]  

[Equn No. (6.34)]

where, \( k \) is the scalar co-efficient (accelerator), \( \overline{d} \) is the direction vector.

The accelerator \( k \) is varied to permit acceleration when there is evidence of continuing progress and to decelerate the search when the optimum or boundaries are being approached. Mathematically, this can take the form

\[ k = A^n \text{ or } k = A^n n \]  

[Eqn No. (6.35)]

with \( A \) the step size vector, \( n \) = number of successful steps and

\[ k = \frac{1}{A n} \text{ or } k = A^{-n} \]  

[Eqn No. (6.36)]

for \( n \) = number of unsuccessful steps Flood has incorporated a subroutine to locate the minimum along the given direction based on data of steps taken in that direction.

In the pattern search procedure, the pattern move is much more efficient than the exploratory move. With large number of variables, exploratory search takes the most of the machine time without advancing the search very much. Wood (114) has attempted to improve the pattern search strategy to force a relative increase in the number of pattern moves.
Figure 6.9. Univariate search with pattern move
In the procedure which Wood calls 'LOOKr', a random number is chosen for each of the independent variables. These are multiplied by the corresponding step sizes and added to the existing values of the variables. If this new point happens to be better, then the exploratory search is considered complete; otherwise the reverse move is made. If this move yields a better point, the search is complete. If both moves fail, a new set of random numbers is chosen and the procedure is repeated. The rest of the procedure is same as that for LOOK. In the random search procedure, all variables are changed at once. This seems desirable. But if one variable has only a very slight effect on the function, this may be easily be hidden by the effects of changes in other variables. Wood found out that LOOKr do not possess many advantages and fails miserably on some problems.

In another version by Wood, (114) termed as 'exploratory search truncation procedure', the exploratory search is stopped as soon as a move produces an improvement over the last base point. From this point a pattern move is made. The next exploratory search starts with the variable just after the one which produced the last success. Thus, all variables are tested in turn. Wood obtained disappointing results from the exploratory search truncation technique, although there are many functions where this technique was found better than the pattern search method. Figure (6.11) shows the path of truncated search in two dimensions.

**6.1.1.6. Practical applications of pattern search method**

The original work on pattern search was concerned with its application to mathematical and statistical problems.
Figure 6.11. Exploratory search truncation method

Figure 6.12. Oscillation around the minimum of a steepest descent along a tangent

\[ Y(x^P) > Y(x^{P+1}) < Y(x^{P+2}) \]

\[ x^* = \text{True minimum} \]
Hooke and Jeeves (50) themselves have reported success with a curve fitting problem involving neutron flux in a nuclear reactor. Wood (113) uses pattern search successfully for engineering design optimization problems. His applications include the design of a small nuclear power plant for space vehicles, preliminary design of an electro-magnetic pump for liquid metal, design of a thermoelectric generator element. Srygley and Holland (102) have coupled the pattern search with the Θ method of convergence of Thiele and Geddes to achieve the optimum design, in the sense of minimum plates for conventional and complex distillation columns for any set of specifications directly dependent on product purity.

Himmelblau (49) has optimized an n-butane isomerization process, the mathematical model of which contains 10 independent equations and 15 variables. Schinzinger (91) has reported the successful use of the pattern search in the design study of a transformer. Nicholson and Pullen (72) have used the pattern search method to find the optimum design of rubber compounds. Rudd and Watson (87) applied the pattern search method to the optimum design of the three stage refrigeration system. The pattern search procedure is mechanized in the 'opcon' device, developed by the Westinghouse Corporation, U.S.A. and has been applied to the automatic optimization of a DOW Chemical Company's pilot plant for making the styrene by catalytic dehydrogenation of ethylbenzene (110). The same device has been used to optimize operation of a distillation column (108). The similar device called 'optimat' has been developed by Elliot Automation Limited (9).
Himsworth's Sequential Simplex method

Spendley, Hext and Himsworth (101) developed a direct method, called Sequential Simplex method, in which a rapid determination is made of a direction which is steep, though not steepest. This method involves placing trial points on the vertices of a simplex which is the N-dimensional generalization of the equilateral triangle (N=2) and the regular tetrahedron (N=3).

The vertex at which the function has the least value is determined and that vertex is replaced by its reflection in the centroid of the remaining vertices. This procedure is repeated until no progress in the objective function is observed. However, in the end game procedure, it is desired to make a quadratic approximation to determine the character of the apparent stationery point.

In the sequential simplex method, the calculations are trivial, calling for no mathematical knowledge and it is not necessary to have a numerical measure of the response. It is necessary to rank the results and discard the worst. However the method assumes that the relative steps to be made in varying the variables are known and this makes the strategy rather rigid for general use. Nelder and Mead (70) modified the method in which the simplex adopts itself to the local landscape, elongating down long inclined planes, changing direction on encountering a valley at an angle and contracting in the neighbourhood of an optimum. Both methods, the original simplex and the modified, deal with constrained problems merely by the addition of some penalty function concept. M. J. Box (15) pointed out that this approach is rather inefficient and he modified the simplex method for constrained optimization problems.
6.1.3. **Rosenbrock's method**

The method of 'rotating co-ordinates' devised by Rosenbrock (83) has proved to be a powerful optimization technique for various functions, including those having shallow, curving valleys. Instead of perturbing each of the variables independently as in pattern search, Rosenbrock rotates the co-ordinate system so that one axis points along the direction of the ridge as estimated by the previous trial. The other axes are arranged in directions normal to the first. This procedure eliminates most of the interactions between variables and gives very effective ridge following. Moreover, instead of taking a fixed step in each direction, Rosenbrock in effect tries to find the optimum point in each line. This procedure continuously adjusts what would in pattern search the step size. In his paper, Rosenbrock shows a very much simplified analysis of the method. A more comprehensive formulation of the method has been given by Wood (115). Rosenbrock's method is modified to include linear minimization by Davies et al (38).

Rosenbrock has also extended his method to solve the constrained optimization problems. M. J. Box (15) has modified the method to set up a search parallel to the effective constraint(s). In his method, called RAVE, a variable, i, is eliminated whenever the current point is found to have entered a boundary regions of the \(i^{th}\) variable. Thus, the boundaries once entered cannot be left and the final solution lies on the vertex of the N-dimensional feasible region.
It can be seen that Box's procedure is limited for explicit eliminations only.

Storey (103) applied Rosenbrock's direct search method to a number of chemical engineering problems. Andrew (16) used it to find the optimum process design for the manufacture of acrolein by propylene oxidation and found that the method was very reliable and did not give any trouble with constraints.

6.1.4. **Powell's direct search method**

The method proposed by Powell is based on conjugate directions and aiming to find the minimum of a general quadratic form in a finite number of steps. Powell's method possesses as an advantage that it is practically invariant under linear transformations of the co-ordinate space. Moreover, the rate of convergence of the method near the optimum is very efficient; this being a feature of methods with quadratic convergence. In the presence of narrow curving valleys, such methods are successful in generating good directions, in so far as they take account to local curvature of the function in these regions. Fletcher (38) has compared the efficiencies of the methods for minimizing functions without evaluating derivatives, and found out that on the basis of function evaluations the most efficient method is that of Powell. M. J. Box (16) has drawn the same conclusion when testing difference methods for higher dimensional test functions, having as many as twenty variables. However, Powell's method is applicable to unconstrained functions only.
6. 2 Gradient methods

The gradient methods require computation of first or higher order derivatives of the function, in addition to the values of the objective function itself. These methods use measurements of the slope of the function as an indication of the direction towards the minimum. The first trial point is chosen arbitrarily and the remaining test points are determined by the iterative procedure.

\[ x_{p+1} = x_p + \varepsilon_P D^P \]

where, \( x_p \) is an n-dimensional vector whose components are the independent variables \( x_1, x_2, \ldots, x_n \) at the \( p \text{th} \) iteration, \( \varepsilon_P \) is a positive constant and \( D^P \) is an n-dimensional vector evaluated at the \( p \text{th} \) iteration. The vector \( D^P \) determines the direction to be taken from the \( p \text{th} \) point and \( \varepsilon_P D^P \) determines the step size in that direction. The various gradient methods differ in their choice of the scale factor \( \varepsilon_P \) and the direction vector \( D^P \).

6. 2. 1. Relaxation methods

The simplest idea of solving optimization problems is to change each of the variables in turn. In the Southwell relaxation method, \( \frac{dY}{dx_1} \) is evaluated each time and that \( x_i \) which corresponds to the largest \( \frac{2Y}{2x_i} \) is selected for adjustment. In the modified procedure by Southwell and Synge, (99) the variable is chosen for which

\[ \left( \frac{\delta Y}{\delta x_1} \right) \left( 2 \frac{\delta^2 Y}{\delta x_1^2} \right) \] is maximum. In both methods, the step size is chosen by forming a Taylor series about the point \( x^P \).

Thus,
\[
Y(X^{P+1}) = Y(X^P) + \epsilon^P Y_{x_1} \bigg|_{x=x^P} + \frac{(\epsilon^P)^2}{2} \frac{\partial^2 Y}{\partial x_1^2} \bigg|_{x=x^P} + \ldots
\]
[Eqn. No. (6.38)]

For \(Y(X^{P+1})\) to be a minimum

\[
\epsilon^P = \frac{\frac{\partial Y}{\partial x_1} \bigg|_{x=x^P}}{\frac{\partial^2 Y}{\partial x_1^2} \bigg|_{x=x^P}}
\]
[Eqn. No. (6.39)]

In this equation, the second derivative should be positive. If the curve has a point of inflection, the iterative procedure may diverge from the minimum, since the \(\epsilon^P\) will then be infinity. The evaluation of the second derivative can be time consuming. Moreover, if the function has a sharp ridge, the relaxation methods might stop before reaching the optimum.

6.2.2. Steepest descent methods

The methods of steepest descent change all the independent variables at each iteration using the direction vector.

\[
D^P = - B^{-1} \nabla Y
\]
[Eqn. No. (6.40)]

where

\[
\nabla Y = \left[ \frac{\partial Y}{\partial x_1} \bigg|_P, \frac{\partial Y}{\partial x_2} \bigg|_P, \ldots, \frac{\partial Y}{\partial x_n} \bigg|_P \right]
\]
[Eqn. No. (6.41)]

and \(B\) is a positive definite matrix. Cauchy, (100) who is credited with developing the method originally, used

\[
B^{-1} = I = \text{Identity matrix}
\]
[Eqn. No. (6.42)]

Newton's (100) method uses

\[
B = L
\]
[Eqn. No. (6.43)]
where, $L$ is the $n \times n$ matrix of second derivatives having components

$$L_{ij} = \frac{\partial^2 Y}{\partial x_i \partial x_j} \quad \text{[Eqn. No. (6.44)]}$$

If $Y(X)$ is quadratic, the iteration is completed in one step. (19)

From equations $(6.37)$ and $(6.40)$

$$X^{p+1} = X^p - \epsilon^p B^{-1} \nabla_Y^p \quad \text{[Eqn. No. (6.45)]}$$

Currey (29) has shown that the iterative procedure will eventually converge to the minimum if

$$Y(X^{p+1}) < Y(X^p) \quad \text{[Eqn. No. (6.46)]}$$

Thus, $\epsilon^p$ is adjusted in such a way that the above inequality is satisfied. When this is done, $\epsilon^p$ uses its previous value, otherwise $\epsilon^p$ uses half the previous value. Generally, the convergence of this procedure is rather slow. Booth (13) has suggested using the value of $\epsilon^p$ such that $X^{p+1}$ is the intersection of the tangent to the function at the point $X^p$ and the co-ordinate axes. It can be seen from figure (6.12) that close to the minimum this value of $\epsilon^p$ causes $X^p$ to oscillate around the minimum. However, this value of $\epsilon^p$ can be used when the desired minimum has a value of zero.

The Newton-Raphson method (100) uses the following value of $\epsilon^p$

$$\epsilon^p = \frac{Y(X^p)}{(\nabla_Y^p)^T (\nabla_Y^p)} \quad \text{[Eqn. No. (6.47)]}$$

To obtain the approximate optimum along the line $B^{-1} \nabla_Y^p$, Booth uses a small value of $\epsilon^p$ so that three points are obtained along $B^{-1} \nabla_Y^p$. A quadratic polynomial is passed through these points and the location of its minimum is selected as $X^{p+1}$. 
The 'accelerated optimum gradient' method proposed by Forsythe and Motzkin (43) uses the direction vector as

\[ D^p = D^{p-1} \epsilon^{p-1} + D^{p-2} \epsilon^{p-2} \quad [\text{Eqn. No. (6.48)}] \]

For a quadratic surface, the direction \( D^p \) passes through the absolute minimum. For nonquadratic surfaces, further iterations are necessary. The theorem upon which the method is based, is valid for two independent dimensions. A related procedure, in a sense more general, is proposed by Finkel (37). The minima on any parallel lines lying in a solution space are determined and then the minimum on the line joining these two minima is found. Applying the theorem of parallel chords it can be shown that for \( n = 2 \), this procedure reaches the optimum, although Finkel reports that the procedure is fairly successful for more than two independent variables.

In the methods of steepest descent, it is not necessary to know the first and second derivatives analytically. Brown (20) has given the necessary formulae for finite difference approximations. Zellnik, et al., have developed a subroutine to avoid saddle points. They have tested the procedure successfully on some practical problems such as optimization of distillation column-condenser system etc.

The steepest descent method has been used by many workers for optimization problems. Schrage (92) used it for optimizing a catalytic cracking operations. Moser, et al. (69) used it to optimize naphtha reforming process. When used on the problem of optimization of an isopentane recovery unit, R. M. Wood (116) found that different 'optima' have been obtained.
The contour tangent method of Wilde (109) uses each locally measured tangent to the contour as a boundary eliminating part of the solution space from further consideration. In this way, it resembles the unvariable sequential search methods which involve successively reducing the size of an interval of uncertainty. The decision as to which area is eliminated is determined by the partial derivatives. One fundamental requirement in this method is that the dependent variable be strongly unimodal. The computations of the method become cumbersome as the number of variables increase.

Based on two dimensional acceleration technique, Shah, Buehler and Kempthorne (93) have developed a steepest descent 'Partan' method. They have proved that if the function being optimized is a monotonic function of a quadratic function and if the vectors and vector 'best' points are determined without error, then the solution to an n-dimensional optimization problem will be reached at point $P_{2n}$ or sooner. Obviously, in the practical case, both conditions will seldom, if ever, be met. Powell (76) has developed the variant of this method independently. Shah, et al. (94) have also proposed the variations of partan which do not use steepest descents. Harkins (48) has found Partan to give a performance comparable even to Rosenbrock's method, at least on Rosenbrock's test function.

Although the tangent methods have been extended to the multivariable problems, with more than three variables, we enter the realm of hyperplanes and hyperspace which makes the solution more complex.
6.2.4. **Use of Lagrange Multipliers**

The method of use of Lagrange Multipliers is applied when equality constraints are present. The number of Lagrange Multipliers introduced are equal to the number of constraining equations. The Lagrange Expression is then developed which is equal to the objective function plus* the product of the Lagrange Multipliers and constraints. Suppose, the objective function to be minimized is given by

\[ Y = f(x_1, x_2, \ldots, x_n) \]  

subject to

\[ g_i(x_1, x_2, \ldots, x_n) = 0 \]  

\[ i = 1, 2, \ldots, p \leq n \]  

Then, the Lagrange Expression becomes

\[
W(x_1, x_2, \ldots, x_n) = Y + \lambda_1 g_1(x_1, x_2, \ldots, x_n) + \lambda_2 g_2(x_1, x_2, \ldots, x_n) + \ldots + \lambda_p g_p(x_1, x_2, \ldots, x_n)
\]

It has been shown that the partial derivatives of the Lagrange Expression with respect to each independent variables (including the Lagrange Multipliers) must be equal to zero for an extremum to exist. (112) So, there are \((n + p)\) equations in the \(p\) unknowns, \(\lambda_p\) and \(n\) unknowns \(x_n\), which can be solved for \(x^*\), optimum and \(\lambda\).

Although, the above discussion applies only to equality constraints, Kuhn and Tucker (60) have generalized the concept of Lagrange Multipliers to include inequality constraints.

* sometimes, a minus sign is used here.
Methods of conjugate directions

The methods of conjugate directions calculate each new direction of search as part of the iteration cycle. Consider, the quadratic function \( Y(X) \).

\[
Y(X) = Y(h) + \frac{1}{2} (X - h)^T A (X - h)
\]  
(\text{Eqn. No. (6, 50)})

which possesses its minimum value at \( X = h \), where \( A \) is a positive definite matrix \((n \times n)\), generally taken as the matrix of second order partial derivatives. The minimization methods of conjugate directions utilize the theorem, (77) which states that, if \( S_1, S_2, \ldots, S_m \) \((m \leq n)\) are mutually conjugate directions, then the minimum of the quadratic function \( Y(X) \) may be found by searching along each of the directions once only.

This minimum point is given by

\[
X^* = X^0 + \sum_{i=1}^{m} \alpha_i S_i
\]  
(\text{Eqn. No. (6, 51)})

where, \( X^0 \) is an arbitrary starting point. The parameters \( \alpha_i \) \((i = 1, 2, \ldots, m)\) may be found by means of a unidimensional minimization

\[
\text{Min } Y = (X^i + \alpha_i S_i)
\]  
(\text{Eqn. No. (6, 52)})

The relationship (6.52) is equivalent to (58)

\[
\frac{d}{d \alpha_i} Y(X^i + \alpha_i S_i) = (\nabla_Y i+1) S_i = 0
\]  
(\text{Eqn. No. (6, 53)})

where,

\[
\nabla_Y i+1 = \text{grad } Y (X^i + \alpha_i S_i)
\]  
(\text{Eqn. No. (6, 54)})

so, the procedure finds \( X^{i+1} = X^i + \alpha_i S_i \) and then, the next direction \( S^{i+1} \), which satisfies

\[
(S^{i+1})^T A S^j = 0
\]  
(\text{Eqn. No. (6, 55)})

\[ j = 0, 1, 2, \ldots, i \]

is determined.
For the quadratic function, this procedure yields a solution within \( n \) steps. For the nonquadratic function, the process is iterative. The direction \( S \) can, however, still be generated in such a way that they correspond to a local quadratic approximation to the function in the neighbourhood of the current point. Fletcher and Reeves (40) have experienced that the convergence rate of the method of conjugate directions is very slow for shallow curving valley functions. They modified the procedure by adopting the steepest descent direction instead of conjugate direction after every \((n + 1)\) iterations.

The conjugate directions may be generated by different techniques. The most powerful technique so far reported, is the variable metric method proposed by Davidon (14) and reformulated by Fletcher and Powell (39).

In the variable metric methods, the conjugate directions, \( S \), are given by
\[
S^{i+1} = -H^{i+1} \nabla Y^{i+1}
\]
where, \( H^0 \) is an arbitrary, positive definite matrix \((nxn)\). It is convenient to take the unit matrix initially for \( H \), so that the first direction is down the line of steepest descent. Then, \( \lambda^i \) is determined in such a way that \( Y(X^i + \lambda^i S^i) \) is a minimum with respect to \( \lambda \) along \( (X^i + \lambda S^i) \) and \( \lambda^i > 0 \). Fletcher and Powell have proved that \( \lambda^i \) can always be chosen to be positive. The procedure for obtaining a minimum along a line uses a cubic interpolation method and is given in detail by Davidon.
Thus,
\[ X^{i+1} = X^i + \alpha^i S^i \]

\[ Y(X^{i+1}) \] and \( \nabla_Y^{i+1} \) are evaluated, noting that \( \nabla_Y^{i+1} \) is conjugate (orthogonal) to \( S^i \) i.e.
\[ (S^i)^T (\nabla_Y^{i+1}) = 0 \]

The new \( H^{i+1} \) can be given as
\[ H^{i+1} = H^i + A^i + B^i \]

where,
\[ A^i = \frac{(\alpha^i S^i)^T (\alpha^i S^i)}{(p^i)^T (\alpha^i S^i)} \]

\[ B^i = -\frac{H^i (p^i)^T H^i}{(p^i)^T H^i (p^i)} \]

and,
\[ p^i = \nabla_Y^{i+1} - \nabla_Y^i \]

The procedure is then repeated setting \( i = i+1 \)

The variable metric method has the following properties (39).

(i) The matrices \( H^i \) are symmetric, positive definite.

(ii) The minimization process is stable i.e.
\[ Y(X^{i+1}) < Y(X^i) \]

(iii) If \( Y(X) \) is quadratic, the method finds the minimum in \( n \) iterations.

(iv) It has been shown by Davidon that as the procedure converges to the minimum, \( H \) tends to \( A^{-1} \), where \( A \) is defined by equation (6.50). Thus, the method yields the full information on the curvature of the function near the minimum. This information, however, is obtained at the price of providing storage space for the matrix \( H \) and time for its manipulation.
The conjugate gradient method has also been successfully applied to minimization of unconstrained quadratic functions as a means of solving large sets of linear algebraic equations (58). Kropholler and Spikins (59) have given the simplified analysis of the variable metric method for the two variable problem. Fletcher and Powell have tested Davidon’s method on a variety of numeric tests and remarked that the method is probably the most powerful general procedure for finding a local minimum. This remark is confirmed by M. J. Box (16) and Leon (64).
7.1 Linear programming

A linear programming problem arises when the objective function and all the constraints are linear functions of nonnegative variables.

Maximize

$$Y(X) = \sum_{i=1}^{n} c_i x_i$$  \hspace{1cm} \text{(Eqn. No. 7.1)}

subject to

$$f_j(X) = \sum_{i=1}^{n} a_{ji} x_i \leq g_j$$  \hspace{1cm} \text{(Eqn. No. 7.2)}

where the $c_i$, $a_{ji}$, and $g_j$ are constants. The optimal solution corresponds to an extreme point of the convex set defined by the linear constraints.

Linear programming algorithms provide methods (basically solving linear equations) for moving from one extreme point to another adjacent one, always increasing the value of the objective function.

The importance and power of linear programming is partly due to the large size problem that it can solve. The best linear programming codes at present can handle problems with as many as 5000 variables and 1000 constraints(111).
Because of the requirement of linearity in both objective function and constraints, linear programming is not generally applicable to process designs. Linear programming methods have been extended to the more general area of mathematical programming to handle certain nonlinear functions. However, the restrictions on the types of functions which can be handled are too severe to make these procedures any use for our purpose.

7.2 Geometric programming

The geometric programming developed by Zener, Duffin and Peterson applies to the minimization of any algebraic equation called a generalized polynomial.

Consider the objective function which is a sum of \( T \) terms \( c_j p_j(X) \), where the \( c_j \) are positive constants and the \( p_j(X) \) are products of powers of the \( x_i \)

\[
Y = \sum_{j=1}^{T} c_j p_j(X) \quad \text{[Eqn. No. (7.3)]}
\]

The product function \( p_j \) is defined by

\[
p_j(X) = \prod_{i=1}^{n} x_i^{a_{ij}} \quad \text{[Eqn. No. (7.4)]}
\]

where \( a_{ij} \) are arbitrary real positive or negative exponents.
Interesting methods have been developed for minimizing equation (7.3) but the techniques seem inapplicable to process design because of the special form, equation (7.4), in which the variables $x_i$ are required to be introduced.

7.3 Dynamic programming

Dynamic programming is an optimization technique which simplifies the problem of optimizing $N$ stages simultaneously to a problem of solving $N$ on stage problems, one such stage being shown in figure (7.1).

In the above figure, $X_n$, $D_n$ and $Y_n$ may all be vectors i.e., input and output may consist of several components or streams and there may be several designs or operating conditions to be specified. The stage return, $R_n$, is a scalar which measures the net contribution of the stage to the process objective and is usually expressed in terms of net profit, cost or yield etc. The output, $Y_n$, is generally dependent on $X_n$, and $D_n$ i.e.

$$Y_n = t_n (X_n, D_n) \quad \text{[Eqn. No. (7.5)]}$$

The stage return, $R_n$, which may depend on $X_n$, $D_n$, and $Y_n$ is

$$R_n = g_n (X_n, D_n, Y_n) \quad \text{[Eqn. No. (7.6)]}$$

From (7.5) and (7.6), we may write

$$R_n = g_n (X_n, D_n) \quad \text{[Eqn. No. (7.7)]}$$
Figure 7.1. Typical stage(n) of a multistage process

Figure 7.2. Simple multistage process (N stages)
A simple serial multistage process consists of a sequence of single stage in which the output from any stage becomes the input to the next stage. Figure (7.2) illustrates a simple N stage process. It will be noted that

\[ Y_n = X_{n-1} \]  
[Eqn. No. (7.8)]

The input \( X_n \) and the final output \( X_0 \) may be either fixed by external conditions or may be design variables subject to some degree of choice. The dynamic programming analysis of a simple process, as shown in figure (7.2) is based on the recursive applications of the relations,

\[ Q_n (X_n, D_n) = g_n (X_n, D_n) + f_{n-1} (X_{n-1}) \]

with \( X_{n-1} = t_n (X_n, D_n) \)

and \( f_0 (X_0) = 0 \)  
[Eqn. No. (7.9)]

and \( f_n (X_n) = \max_{D_n} (Q_n (X_n, D_n)) \)  
[Eqn. No. (7.10)]

for \( n = 1, 2, \ldots, N \) over all feasible values of the inputs \( X_n \). The above equations (7.9) and (7.10), \( f_n (X_n) \) is the maximum (optimal) return from the \( n \) - stage process consisting of stages 1 through \( n \); and \( f_n (X_n) \) indicates that the optimal return from a process depends on the input \( (X_n) \) to the process. The quantity \( Q_n (X_n, D_n) \) is the combined return from stages 1 through \( n \) and consists of the stage \( n \) return \( g_n (X_n, D_n) \) plus the maximum return, \( f_{n-1} (X_{n-1}) \), from stages through \( (n - 1) \).
Equation (7.9) is a formal statement of the dynamic programming "principle of Optimality". No matter what the input \((X_n)\) and decision \((D_n)\) and the resulting output \((X_{n-1})\) at stage \(n\) may be, the decisions \((D_1, D_2, \ldots, D_{n-1})\) must be made in such a way as to yield the maximum return from the \((n-1)\) stage process (comprising stages 1 through \(n-1\)) with input \(X_{n-1}\).

The above procedure is applicable to the process with specified input. When the output is specified, the procedure is started in the reverse order and \(f_n(X_0)\) is to be found. The dynamic programming procedure has been extended to non serial processes by Aris et al. (4), Mitten and Nemhauser (67), and by Beightler and Meier (8). In general, a non serial structure exists whenever at least one state in the system receives input from more than one stage or provides input to more than one stage. Use of the modified methods involves introduction of an additional variable, called a cut variable, at the junction between the branch and serial chain. The introduction of the cut state allows the separation of the problem into \(P\) serial problems where \(P\) is the number of junctions. For recycle problems, optimization over some of these cut variables usually becomes necessary. For illustration, the recycle problem shown in figure (7.3) can be solved by the following recursive procedure (71).
Figure 7.3. A multistage process with a recycle
a) Optimize stages 1 through n, to obtain \( f_n(X_n) \).

b) Optimize the branch consisting of stages \((n+1)^1\) through \((N^1)\) to obtain \( f_{n+1}^1(Y_{N^1}, X_{n+1}^1) \).

c) Now, at the stage \((n+1)\) we cannot choose \( D_{n+1} \) since,

\[
X_{n+1} = t_{(n+1)^1}(X_{n+1}, D_{n+1}) \quad \text{[Eqn. No. (7.11)]}
\]

and, \( X_{n+1} \) cannot be specified as a function of \( X_{n+1} \) until the branch has been absorbed *.

Assuming at stage \((n+1)\) that we can express \( D_{n+1} \) as a function of \( X_{n+1} \) and \( X_{n+1}^1 \), then \( X_n \)
can be expressed as a function of \( X_{n+1} \), that is

\[
D_{n+1} = \hat{t}_{(n+1)^1}(X_{n+1}, X_{n+1}^1) \quad \text{[Eqn. No. (7.12)]}
\]

* \( t_{n+1} \) and \( t_{n+1}^1 \) are the transformations at stages \((n+1)\) and \((n+1)^1\) respectively, and \( t_{(n+1)^1} \) is the additional transformations at stage \((n+1)^1\) which joins the diverging branch to the main serial system.

\[
X_n = t_{n+1} \left[ X_{n+1}, \hat{t}_{(n+1)^1}(X_{n+1}, X_{n+1}^1) \right] = t_{n+1} \left[ X_{n+1}^1, X_{n+1} \right] \quad \text{[Eqn. No. (7.13)]}
\]
If the "reverse" transformation, \( \hat{f}_{n+1} \),
does not exist, (which is the general case) a
maximization over \( D_{n+1} \) for all feasible values
of \( X_{n+1} \) is necessary, subject to equation (7.11)
and
\[
f_{n+1} (X_{n+1}) = \max_{D_{n+1}} \left[ Q_{n+1} (X_{n+1}, D_{n+1}) + \right.
\]
\[
\left. f_n (t_{n+1} (X_{n+1}, D_{n+1})) \right]
\]
[Eqn. No. (7.14)]

\( d) \) Stages \((n+2)\) through \((N-1)\) are optimized
in the standard dynamic programming procedure
to obtain \( f_{N-1} (X_{N-1}, X_{n+1}) \)

\( e) \) At stage \( N \), the optimal branch return is absorbed,
and there is an optimization over three variables

\[
f_{N+t(n+1)} (X_N) = \max_{Y_{N1}, X_{n+1}, D_N} \left[ g_n (Y_{N1}, X_{n+1}, D_N) \right]
\]
\[
+ f_{N-1} (t_N (X_N, D_N), X_{n+1}) + \]
\[
+ f_{n+1} (Y_{N1}, X_{n+1+1}) \right] \]
[Eqn. No. (7.15)]

\( f) \) Stages \((N+1)\) through \( M \) are optimized to
find \( f_{M+(n+1)} (X_M) \).
When more than one recycle is present, the dynamic programming analysis becomes more complex. However, dynamic programming has many advantages when applied to the process industry. By the use of the principle of optimality, a chemical process can be separated into different segments and each segment can be optimized by different optimization methods. Dynamic programming can handle conventionally available technical and economical data, whether it may be in tabular, graphical or analytical form. The constraints are actually helpful in this technique, because they limit the range to be investigated. Another advantage of dynamic programming is that it always finds the global optimum.

The primary limitation of dynamic programming is in the number of components in the input vectors \( (X_n) \). For most practical purposes, vectors with at most two or under some circumstances, three, components are the largest that are computationally feasible. In order to be able to investigate one stage at a time, all possible combinations of the state variables for the previously calculated stage must be stored in the memory of the computer. This storage requirement increases very rapidly with the increase in the number of state variables.
For $N$ stages with $p$ state variables per stage, each having $K$ feasible values and $s$ decision variables per stage, the total storage requirement would be $N \cdot (s + 2) K^p (71)$. The factor that has the most significant influence on the total storage requirement is the number of state variables per stage, $p$. Continued research is being done to lessen this difficulty (112), and various ways have been proposed. The obvious one would be to reduce the number of values calculated for each state variable, which is known as coarsening the grid. It is based on the notion of solving a series of problems, beginning with only a few widely spaced values for each state variable. The solution to the first problem yields an approximation to the true solution. Based on this approximation some previously feasible values of state and decision variables can be eliminated. In the new and smaller feasible region, finer spacing is used on the state and decision variables to obtain a better approximation to the true solution. This procedure continues until the desired accuracy is obtained. The danger of the coarse grid approach is that the optimum may be missed because of a narrow ridge. Moreover, additional computations are always required to carry out the interpolation of the grid points (assuming the state variables to be continuous).
Another proposal would be to correlate the values into polynomials, and then store the co-efficients of the polynomials instead of the original table\(^8\).

The dynamic programming analysis requires to find the optimum \(D_n\) for given \(X_n\). When the decision vector, \(D_n\), contains a single element, the computation is rather straightforward. However, for a higher dimension vector, the computations become more difficult. The effect of the number of decision variables per stage on the storage requirement is insignificant when compared with effect of the number of state variables. The number of entries in the lists of optimal functions increases linearly with the number of decision variables\(^7\). Incorporation of optimum seeking methods\(^{10}\), can profitably lessen the computation difficulty. The work of Lee\(^6\), Beightler and Meier\(^8\), and of Bryson and Denham\(^{21}\) is on the same lines.

Despite some of its limitations, dynamic programming is a serious contender for solving process design problems. Several application of dynamic programming to chemical engineering problems appear in the literature. Aris\(^3\), solved problems concerning the design of adiabetic tubular reactors. Westbrook\(^{12}\) applied the technique in solving multistage heat exchanger cases in petrochemical and refinery operations.
Aris(5) and Rudd(86) used it in solving the problems of cross current extraction. Mitten and Nemhauser(67) dealt with the application of the technique in solving multistage liquid-liquid extraction, multicomponent solid separation and other plant design problems. Itahara and Stiel(51) discussed the use of dynamic programming for the optimal design of multiple effect evaporators. Rafal and Dranoff(79) studied the optimization of a multibed, adiabatic catalytic reactor for the water-gas shift reaction. Aris, et.al(4) showed how to make the best use of the dynamic programming approach for systems containing branches.
There are numerous optimization methods available and it is extremely difficult to say boldly that a particular method is the best. Some are more useful than others for a particular class of problems. In most process design problems, the functions involved are not well behaved and quite often are tabulated, discontinuous and consist for a long sequence of equations. Moreover, quite often both dependent and independent variables are constrained. The chosen optimization method should also deal effectively with constraints.

When the objective function and all constraints are linear, the problem may be handled by the widely used techniques of linear programming. However, linear programming is not generally applicable to process design, since normally neither the objective function nor constraints are linear. The linear model method developed by Nishimura et al. (73), in which a mathematical model of process is constructed which is linear in terms of inputs and outputs, does not seem to be suitable for complicated process designs.

The classical treatment of constrained optimization problems where the functions are nonlinear, is by means of Lagrangian multipliers. In its classical form, this technique is applicable only when constraints are equalities. Klein (56) has shown that this difficulty can be avoided by converting each such inequality to an equality.
This procedure however is adopted to handle calculations where there are only a few variables. Carroll's technique (22) for maximization problem when all the constraints are inequalities has the disadvantage that a feasible starting point must be used. These can be extremely difficult to predict in a complicated problem. In addition, the procedure is obviously limited in application since it is not directly applicable when the constraints are equalities. The efficiency of the method of Fiacco and McCormick (35) which can handle the equality constraints depends upon the selection of weights (17). The gradient projection technique of Rosen (82) involves appreciable computing time of nonlinear systems with several inequalities.

The steepest ascent (or descent) method is basically a gradient method, which requires the first derivatives of the function to be computed as well as the function itself. When the problem space is characterized by concentric circular, spherical or hyperspherical contours, the gradient methods work well. In any case, the progress is likely to be rather slow. This problem has been recognized for sometime. The methods of parallel tangents by Shah et al (93), and contour tangents by Wilde (109) were designed to combat this difficulty. These methods appear very effective for relatively small numbers of dimensions. However, their usefulness appears rather questionable for systems having many (say, twenty or more) variables.
M. J. Box (16) has pointed out that Davidon's method (39) presents the most consistent behavior among the group of methods based on conventional mathematical techniques. In cases involving complex functions or having no algebraic expressions for the objective functions, the application of Davidon's method or similar procedures would be rather difficult.

The merit of the Geometric Programming technique developed by Zener et. al. (118) lies in the facility it gives in making quick evaluations of the minimum cost of a particular design. This is of special interest during the study of a family of designs. Once the cost function has been generated, the effects of different parameters can be found with minimal effort. The difficulty with this method is that the cost function in process designs is seldom a generalized polynomial.

Dynamic Programming has an apparent place in design optimization, since a chemical process usually consists of a large number of interconnected steps. However, it has at least two serious limitations. First, as usually applied, it is limited to handling no more than one or two variables at each stage. Second, the method becomes more complex when applied to processes with complex recycles.
The primary attraction of search methods is their generality. They can handle all the problems which can be solved by any one of the methods discussed above and moreover they will handle many other problems too. The search methods can be divided into two subclasses: first, the 'direct search' methods which require a subroutine to compute function values only and second, the other search methods which do require the first derivatives of the function to be computed as well as the function itself. Principally, the gradient methods fall into the latter subclass. The direct search methods do not require any particular form of the function to be optimized. Generally, process designs involve the solutions of a long sequence of design equations. Thus, direct search methods are the most suitable for these problems.

The simplex method of Himsworth, Spendley and Hext (101) (and later on modified by M. J. Box (15) for constrained problems), Powell's method, (77) the method due to Rosenbrock (84) and the 'pattern search' method of Hooke and Jeeves (50) are the available direct search methods. The Simplex method performs well for a problem with two variables, but for complicated problems, it is progressively less successful. Powell's method becomes efficient in the region of the optimum where the function can be well approximated by a quadratic. However the work at I.C.I. has proved that the method is inefficient on a number of problems which are badly scaled, with the function exhibiting a steep valley skew to the co-ordinate directions.
The 'pattern search' method has been successfully used by many workers for problems ranging from curve fitting to the design of space power plant. This method possesses the following characteristics:

i) A large number of variables can be handled even when various restrictions are placed on them.

ii) Hooke and Jeeves have found empirically that the computation time for pattern search increased only as the first power of the number of variables. This is important because with classical minimization techniques the computations grow with the cube of the dimensionality.

iii) It appears that pattern search strategy can efficiently locate and follow ridges of the objective function, and that this is the reason for its efficiency in process design in which ridges appear to be common.

The direct search method of Rosenbrock generally shows a performance superior to any other direct search methods. The primary merit of it is that of rotating the orthogonal search directions such that one of them lines with a ridge if one is present.

This procedure eliminates most of the interactions between design parameters and gives very effective ridge following. However, it appears that the method is attractive on a high speed computer only if the number of variables is less than some number such as ten. Wood(115) has pointed out that the number of computations required at the end of each stage of the search varies as the fourth power of the number of variables and the storage space as the square.
Therefore, the method does not appear so useful for problems involving large number of variables.

From the above discussion, it appears that the direct search methods are the most suitable for process design purposes and that the pattern search method is the most general and the most easily adaptable for use on a computer. It has therefore been chosen in this study.

8.2 Need for Improvement

The pattern search strategy described in (6.1.1) operates satisfactory for a considerable number of problems. However, it possesses certain weakpoints. The major ones are:

a) It requires rather more trials per successful attempt. The maximum number of trials per variable between two base points is five and the minimum is three.

b) If the test function has a sharp valley or ridge, the pattern search fails to reach the optimum. Figure (8.1) illustrates this dilemma. A pattern search hits the ridge at point A and will stop there, whatever reduced step size is taken, whereas the true optimum is far away at point B.

c) The pattern search seems not to use as much of past information as it could. It even does not take the advantage of its knowledge of the sign of its previous move in each of the K directions, where K is total number of variables.
Figure 8.1. Failure of Pattern Search in following a sharp ridge

Figure 8.2. The modified Pattern Search method I
The above indicates that as we have decided to use the pattern search method, it is desirable to look for possible improvements in it.

Since this project was started, there has been a continuing effort to develop better search techniques. The work to improve the pattern search has produced a number of disappointments. However some improved strategies have been found. These are described below.

Modified method I (MSP - 1)

In this modified procedure, an attempt is made to increase the number of pattern moves, because the pattern move is basically more rewarding than the exploratory moves. Instead of doing an exploratory search after each pattern move, a second pattern move is made, providing the first pattern move is successful. Moreover the second pattern will have a length double its previous move. Thus, the pattern moves grow until they fail to find a better point. The computer will store this failure and a pattern move with the original step length is repeated from the last successful point. When the pattern move exceeds the stores failure point, the exploratory move is made.

This modified method works well on the test function having a shallow, curving valley as shown in figure (8.2)
In the original pattern search, the step sizes are reduced when the exploratory type-I search fails. Before reducing the step sizes, the present code checks the corner of a square formed (assuming each variable having same step size) by step size increments in the case of two variables. (For three variables, there will be eight points each at the corner of a cube). These are points a, b, c and d for figure (8.3).

These points are tested and if any point is a success, the pattern move is made and the search is continued. If all four points are unsuccessful, then the step sizes are reduced. From figure (8.1) it can be seen that the pattern search fails when it reaches the point A on the sharp ridge. But the present code successfully avoids the ridge and reaches the better point, as point c of figure (8.1).

Though the modified procedure is faster than the original pattern search, it is efficient only for two dimensional functions. For higher dimensions, the programming becomes more difficult, and the number of trials also become much larger.

8.4 Modified method II (MSP - II)

For a function having contours as shown in figure (8.4), the pattern search with the starting point B0, will move to B1 and then to the next base point B2 and so on. The direction of search will be towards Bn. Although this represents an improvement in the objective function, the optimum point C lies away from this direction.
Figure 8.3. The corner of a square formed by step size increments

Figure 8.4. The desired direction of a search
Moreover, the need of a search strategy which would use the absolute value of the change in objective function observed due to change in each variable has appeared on several problems. The basic idea of this modified procedure is to increase the step size of each 'successful' variable during the exploratory search in proportion to the step size of the 'least' successful variable. The most efficient proportional factor was found to be the ratio

\[
\frac{(Y_p - Y_0)}{(Y_i - Y_0)} \tag{Eqn. No. (8.1)}
\]

where
- \( Y_p \) = Value of objective function of the 'successful' point.
- \( Y_0 \) = Value of objective function at the last base point.
- \( Y_i \) = Value of objective function at the 'least' successful point.

Suppose, the function

\[
Y = f(x_1, x_2, \ldots, x_n) \tag{Eqn. No. (8.2)}
\]

is to be maximized, and for this function, the exploratory search for the \( x_k \)th variables is successful and for \( x_m \)th variables is unsuccessful. Moreover, amongst \( x_k \) variables, \( x_i \)th variable is having the 'least' successful value.
Then (not allowing for scale effects), the new trial point would be

\[ x'_p = x_p + \left[ \frac{(Y_p - Y_0)}{(Y_i - Y_0)} \right] \Delta x_i \]

for \( p = k \) and \( p \neq i \) \hspace{1cm} \text{[Eqn. No. (8.3)]}

and

\[ x'_p = x_p \text{ for } p = m \] \hspace{1cm} \text{[Eqn. No. (8.4)]}

and for \( i \)th variable

\[ x'_i = x_i + \Delta x_i \] \hspace{1cm} \text{[Eqn. No. (8.5)]}

where,

\[ \Delta x_i = \text{step size for } i \text{th variable} \]

It can be seen that the value of the squared bracket will be always greater than unity and thus, the step size for each 'successful' variable will be greater than \( \Delta x_i \) in proportion to the improvement in the objective function at \( p \)th and \( i \)th variable, and consequently the search direction will tend to proceed in more desired direction e.g. in the direction \( B'n \) of figure (8.4)

To clarify the concept, suppose \( Y = f(x_1, x_2, x_3, x_4, x_5, x_6) \) is to be maximized. Let, for this function, exploratory search for \( x_1, x_3, x_5 \) and \( x_6 \) is successful and for \( x_2, x_4 \) is not successful. Also, \( x_6 \) is having the 'least' successful value. Then according to above notations, \( k = 1, 3, 5, 6; m = 2, 4 \) and \( i = 6 \); and the new trial point \( X' = (x'_1, x'_2, x'_3, x'_4, x'_5, x'_6) \)
becomes
\[ x_1' = x_1 + \left( \frac{Y_1 - Y_0}{Y_6 - Y_0} \right) \times \Delta x_6 \]
\[ x_2' = x_2 \]
\[ x_3' = x_3 + \left( \frac{Y_3 - Y_0}{Y_6 - Y_0} \right) \times \Delta x_6 \]
\[ x_4' = x_4 \]
\[ x_5' = x_5 + \left( \frac{Y_5 - Y_0}{Y_6 - Y_0} \right) \times \Delta x_6 \]
\[ x_6' = x_6 + \Delta x_6 \quad [\text{Eqn. No. (8.6)}] \]

On a theoretical basis, the procedure seems to be very attractive. However, when tested on the Rosenbrock's function (83), the results obtained were not very encouraging. The major drawback of this procedure is that if
\[ \frac{\Delta x_p}{\Delta x_i} > \frac{(Y_p - Y_0)}{(Y_1 - Y_0)} \]
for \( p = k \)
and \( p \neq i \) \quad [\text{Eqn. No. (8.7)}]

then the efficiency of the procedure diminishes and the search direction still tends to direct towards \( B_n \) of figure (8.4). Also, the procedure is only applicable when all variables are scaled.
Modified method III (MSP - III)

In the original pattern search method, the step sizes of all variables are changed at the same time and by same ratio. This procedure occasionally causes difficulty when some variables are at upper ends of their ranges and some at the lower ends. Since the step size for each variable is related to the allowed range for that variable, the ratio of step size to variable size can vary widely. Therefore, a more efficient procedure is to base the initial step sizes according to the ranges and adjust them during the search so that the magnitude of each step size is proportional to the change in the objective function due to the corresponding independent variable.

In the present modified method, the initial step sizes are based on the ranges and as the search proceeds step sizes are changed depending on the success and failure. If the first move of a variable is a success (i.e. if \( x_i + \Delta x_i \) is a success for \( i \)th variable), then the step size for that variable is increased by a factor which is a ratio of the functional value at the present point to the value at the last base point, for a function to be maximized. (For a minimization problem, the inverse ratio is used). If the reverse move is a success (i.e. if \( x_i - \Delta x_i \) is a success for \( i \)th variable), the step size is increased by the same factor but with the reverse sign. If both moves are failed, the step size is halved in the next exploratory search. Figure (8.5) shows the path of a search by MSP - III procedure.
Figure 8.5. Search path of "MOSP" method
The dotted line path shown is the progress of a search by the original pattern search method.

The major advantages of the present code are as follows:

a) The procedure increases the efficiency of the exploratory search, simultaneously the pattern steps grow with repeated success.

b) The individual control of the step size for each variable is completely dependent upon the improvement of the objective function.

c) The pattern search takes care of the sign of its previous move in each direction.

d) The search will always proceed in the most desired direction.

e) Although the resulting code is somewhat faster than the earlier versions, the primary gain is in generality. The new method seems to be useful with a much broader class of problems.

f) With a cautious start, the steps grow rapidly with repeated success. However, in the vicinity of the optimum, the steps are efficiently shortened to avoid overlooking any promising direction.
8.6 **Location of alternate optima**

If the original problem contains a number of relative optimum points, the pattern search may not seek out the 'global' or true one. The workers in this area do not seem to explore for multiple optima. If it is to be done, their method seems to require many starting points for higher probability. This difficulty has been recognised since the work to improve the pattern search method has been undertaken. The following strategy is the result of the efforts on the same lines.

Instead of beginning the search at several different starting points, say n, the functional values at these 'n' points are compared and the starting point is chosen at which the functional value is the 'best'. The search is then started from this 'best' starting point. This method requires fewer functional evaluations and intuitively might be as good as any other method. The uniform spreading of the starting points over the search space might avoid the saddle points, local optimum points, and the high probability of obtaining a true optimum can be given.

The proposed 'opening gambit' strategy has been included as a subroutine in the modified method III (hence forward, termed as MOSP).

8.7 **Comparison with other search methods**

To test the modified methods, the function given by Rosenbrock(83), is taken.

This is \[ Y = f(x_1, x_2) \]

\[ = 100(x_2 - x_1^2)^2 + (1 - x_1)^2 \]  \[\text{[Eqn. No. (8, 8)]}\]
with starting point,

\[ x_{10} = -1.20, \ x_{20} = 1.00 \]

and

\[ y_0 = 24.20 \]

This function is difficult to minimize on account of its having a steep sided valley following the curve \[ x_1^2 = x_2 \]

The results obtained are compared with other search methods and the performance of various methods after 200 trials is shown in Table 8A.

The results for the sectioning method and the step ascent method have been taken from Wilde(110) and the results for the pattern search method and the Rosenbrock's method are recorded by Wood(114).

It can be seen that all three modified methods are faster than the original pattern search procedure. The modified method III (MOSP) is quite comparable with the method of Rosenbrock. The only direct search procedure that appears to be superior to the modified method III is that of Powell(77). Powell's method reaches the optimum point of the Rosenbrock function in less than 200 trials(38). However, the Powell's method for complex design problem is not very suitable.
Table 8. A

Performance of various search methods after 200 trials on

\[ Y = 100(x_2 - x_1)^2 + (1 - x_1)^2 \]

<table>
<thead>
<tr>
<th>Method</th>
<th>( x_1 )</th>
<th>( x_2 )</th>
<th>( Y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sectioning</td>
<td>-0.970</td>
<td>0.945</td>
<td>3.882</td>
</tr>
<tr>
<td>Steep Ascent</td>
<td>-0.605</td>
<td>0.371</td>
<td>2.578</td>
</tr>
<tr>
<td>Ordinary Pattern</td>
<td></td>
<td></td>
<td>0.803</td>
</tr>
<tr>
<td>Modified Pattern (Bell and Pike)</td>
<td>0.813</td>
<td>0.650</td>
<td>4.547 ( 10^{-2} )</td>
</tr>
<tr>
<td>Wood's Step 50</td>
<td></td>
<td></td>
<td>1.03 ( 10^{-2} )</td>
</tr>
<tr>
<td>Rosenbrock's method</td>
<td>0.995</td>
<td>0.991</td>
<td>2.20 ( 10^{-5} )</td>
</tr>
<tr>
<td>Proposed Modified Methods</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSP - I</td>
<td>0.869</td>
<td>0.762</td>
<td>2.09 ( 10^{-2} )</td>
</tr>
<tr>
<td>MSP - II</td>
<td>0.373</td>
<td>0.132</td>
<td>0.397</td>
</tr>
<tr>
<td>MSP - III (MOSP)</td>
<td>1.0004</td>
<td>1.0006</td>
<td>1.00 ( 10^{-6} )</td>
</tr>
<tr>
<td>OPTIMUM</td>
<td>1.0000</td>
<td>1.0000</td>
<td>0.000</td>
</tr>
</tbody>
</table>
The different pattern search procedures have been developed with the idea of producing a general purpose tool that will handle a wide range of functions. Out of three modified methods, the procedure MSP - III (called, MOSP) appears to be very efficient. This method is not just an extension of the clever logical procedure of Hooke and Jeeves, but at every step, a move is based on the careful study of the previous moves in all directions. It has been also tested on functions with more than two variables and the results obtained are very encouraging. Furthermore, it appears to be very general and useful for a much broader class of problems. Incorporation of the 'opening gambit' subroutine makes it even more useful. When tested on functions with saddle points, given by Zellnik et al, it successfully avoids the saddle points and reaches the 'global' optimum point.

The proposed modified method (MSP - III) is not directly applicable when more complicated constraints are present. However, the procedure of Weisman, Wood and Rivlin (106), or that of Fiacco and McCormick (36), to convert the constrained optimization problem to one without constraints can be readily adopted to this method. Other than this, no more modifications are necessary to handle most detailed design calculations.
CHAPTER 9

Optimization Calculations

After analysis of the process flowsheet and selection of the optimization method, it is now necessary to formulate the objective function for the optimization. It involves the incorporation of costs of the various items and the optimization method subroutine into the main process model program. In this chapter, these steps are discussed, with the help of computer flow diagrams, and the optimization results are outlined.

9.1 Incorporation of costs

The cost function for the particular design gives an overall cost or the value of that design, and is made up of an appropriate combination of the capital and annual (including operating and raw materials) costs. The annual charges are worked out from the flow rates of services and raw materials, generated by the mass balance and detailed process model, using known unit costs. Capital costs of the main process items are worked out from formulae giving costs as functions of the main equipment parameters. These formulae are based on available cost information, which have to be kept continuously up to date. In the design cost estimation, charges for labour and supervision are generally excluded, since the costs of these items are not greatly affected by the size of a unit in the large plant. For the same reason, general factory costs such as office services are excluded. The cost of instrumentation is also not considered in this optimization study.
9.1.1 Capital costs

a) Furnace
   The capital cost of the furnace is evaluated from its heat loads. The co-relation for the cost of furnace is developed from the graphical data given by Galagher (45). This includes the costs of furnace materials, foundation materials, external piping and also a factor for conversion of data in U.S. dollars to £ stated by Baumann (7).

b) Quench unit
   As already stated before, the cost of the quench spray is neglected. The cost of the quench tower is taken from the British Chemical Engineering cost file (18). Hydronyl Limited supplied the price of the packings. The cost for the continuous pressure filter is not available, instead, cost data for stainless steel filter press has been used.

c) Condenser
   The cost co-relation for shell and tube heat exchanger in terms of heat transfer area is taken from British Chemical Engineering (18). The cost of the separator (which is required to separate gaseous and liquid product of the condenser), is not included, because the cost data is not available and in any case is likely to be unchanged for successive trial designs.
d) Absorber
The costs of the column and the bubble caps are taken from British Chemical Engineering (18). The cost equation for the plate heat exchangers is co-related from the data supplied by A. P. V. Company.

e) Acetone and Acetic anhydride columns
The costs of the columns and their accessories are taken from British Chemical Engineering (18).

The costs of pumps, blower and flowmeters are not considered. Generally, the total installed cost of the plant is taken to be 2.8 times the cost of major equipment. Annual maintenance and depreciation costs are then expressed as 15 - 20% of the total installed cost (98). Taking mean value viz 17.5%, this makes the annual charges $17.5 \times 2.8 = 50\%$ of the capital cost of the major equipment.

9.1.2 Operating costs
It has been given in the original reference (52) that the following services are available.

a) cooling water:
   $100 \text{ lb/in}^2$ at a maximum summer temperature of $23^\circ\text{C}$.

b) dry saturated steam at 400 and 150 lb/inch$^2$.

c) electrical power at 400V, 3 phase 50 c/s.

d) town gas, 500 BTU/ft$^3$ at $32^\circ\text{F}$ and 1.0 atmosphere.
Charlesworth (23) gives the price of cooling water as 3 d/1000 Imp. Gallon, and price of power as 1 d/KWhr. Smith and Sawistoski (98) have given the price of 150 psig steam as 0.55 £/1000lb. North Thames Gas Board have supplied the price of the town gas. However, the cost of the town gas is not included, because this town gas is required only for 'starting up'.

9.1.3 Costs of raw materials

The prices of the acetone and acetic acid, with required specification are readily available. In the original design project, the required product purity has been stated as 95% acetic anhydride in acetic acid. However, the cost data for acetic anhydride purity other than 98% was not available.

British Drug House have supplied the following prices of the raw materials:

a) acetone:
   B.S.S. 509 (1957) 2/- per lb
b) acetic acid:
   glacial, B.S.S. 576 (1950) 3/4d per lb
c) acetic anhydride:
   98% w/w in ac. acid 5/- per lb

The above mentioned costs (annual and capital) are combined to give a single criterion which can be used as a basis for optimization. The optimization criterion used for the present study is to maximise the annual profit. To keep the information up to date, the average of cost indices for first two quarters of 1968, supplied by the Association of Cost Engineers, has been used.
The cost model, i.e., the detailed process model with costs added, enables a cost to be ascribed to any set of values of the parameters which corresponds to an operable flowsheet. Thus this forms a valuable tool for exploring the effect of various factors on the economics of the process. It is also a starting point for automatic optimization, as discussed below.

9.2 Optimization procedure

The process model, with incorporation of costs, produces a profit corresponding to any set of values of the decision variables, and the optimum process design will correspond to that set of the decision variables which makes the profit maximum, subject to the constraints which ensure that the process flowsheet satisfies all practical requirements.

The modified pattern search method (MOSP) is used to find the 'best' set of decision variables. Figure (9.1) shows the computer flow diagram for the method. The computer code consists of three portions: a 'opening gambit (designated as 'OPBIT') subroutine, the optimization procedure and a subroutine which computes the values of the cost equations and the objective function (designated as 'DESIGN'). By placing the specified constraints and cost equations in a separate subroutine, only that subroutine need be changed when a new problem is considered.
Figure 9.1. (A). Computer flow diagram for the optimization procedure
(Subroutine 'OPBIT')
Figure 9.1.(B). Computer flow diagram for the optimization procedure.
The 'OPBIT' subroutine reads the starting points, and the DESIGN subroutine is called. The subroutine finds out the 'best' starting point for the search. The optimization procedure subroutine conducts the search. Note that the code shown in Figure (9.1) is for maximization of the objective function; the same code can be used for minimization problem, but with some minor modifications. Since the subroutine does not contain the equations necessary to evaluate the objective function (S, S1 or S2), after each change in variable, the 'DESIGN' subroutine is called.

9.3 Computations

Computer flow diagram of each process unit are shown in Figure (9.2(B) to 9.2(F)). The procedure for calculation of the objective function is shown in Figure (9.2(A)). This procedure forms the subroutine 'DESIGN' of the computer flow diagram shown in Figure (9.1).

The Fortran listing of the program for process design optimization is given in the Appendix D.

9.4 Optimization results

The detail output of the computer program for the optimization of acetic anhydride process design using 'MOSP' method is given in Appendix (D.4)

Seven out of initially selected 14 design variables are chosen as the decision (or independent) variables for the optimization study. Their values, as well as the values of the dependent variables at starting and optimum conditions are shown in Table (9.4.A(i)). The remaining design variables are taken as specified variables and their values are kept fixed during optimization. The different optimum conditions for the acetic anhydride process design can be found out by using their other values, if desired. Table (9.4.A(ii)) gives the values of the specified variables used in the program.
OBJECTIVE FUNCTION

Decision variables for process optimization

Determine dependent variables e.g. anhydride yield in terms of acetone conversion

Mass flow rate calculation of process output and raw materials Eqn. (refer e.g., 3.6.)

FURNACE DESIGN

QUENCH UNIT DESIGN

CONDENSER DESIGN

ABSORBER DESIGN

ACETONE COLUMN DESIGN

ANHYDRIDE COLUMN DESIGN

Calculate capacities of storage units

Calculate total capital and running cost

Calculate process profit

RETURN

Figure 9.2.(A). Flow diagram for calculation of objective function
Figure 9.2.(B). Flow diagram of Furnace

Figure 9.2.(C). Flow diagram of Quench unit
Figure 9.2.(D). Flow diagram of CONDENSER

Figure 9.2.(E). Flow diagram of ABSORBER
DISTILLATION COLUMN DESIGN

Decision variables and process flow rates

Calculate heat transfer area of feed boiler and heating steam capacity

Estimate cost of feed boiler

Calculate min. reflux ratio, R_m

Determine range of search

n=1

Give value of R

n' -> n+1

Calculate number of plates

Calculate diameter of column

Calculate h/t area of condenser & dist. cooler

Calculate h/t area of reboiler

Calculate fixed and running cost of tower, C[n]

Have all values in range studied?

Yes

Store minimum cost of tower C[n] & R[n]

RETURN

No

Is n > 1?

Yes

Is C[n] < C[n-1]?

Store C[n] & R[n]

C[n] -> C[n-1]

R[n] -> R[n-1]
# Table 9.1

**Process variables at starting and optimum points for acetic anhydride plant**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Lower limit</th>
<th>Upper limit</th>
<th>Starting value</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a) Independent Variables</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Acetone conversion, (%)</td>
<td>10.0</td>
<td>30.0</td>
<td>25.0</td>
<td>10.0</td>
</tr>
<tr>
<td>2. Quench-unit inlet gas temp, (°F)</td>
<td>800</td>
<td>1000</td>
<td>950</td>
<td>1000</td>
</tr>
<tr>
<td>3. Quench-unit exit gas temp, (°F)</td>
<td>290</td>
<td>310</td>
<td>300</td>
<td>290</td>
</tr>
<tr>
<td>4. Weight ratio of ac. acid to ac. anhydride in recycle, (lb/lb)</td>
<td>0.70</td>
<td>1.50</td>
<td>1.0</td>
<td>0.70</td>
</tr>
<tr>
<td>5. Reflux ratio for acetone column</td>
<td>0.33</td>
<td>0.91</td>
<td>0.72</td>
<td>0.33</td>
</tr>
<tr>
<td>6. Reflux ratio for anhydride column</td>
<td>1.38</td>
<td>3.74</td>
<td>2.57</td>
<td>1.77</td>
</tr>
<tr>
<td>7. Cooling water rate to cooler condenser, (lb/hr)</td>
<td>600,000</td>
<td>900,000</td>
<td>778,000</td>
<td>600,000</td>
</tr>
<tr>
<td><strong>b) Dependent variables</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Yield of ketene, (%)</td>
<td>65.0</td>
<td>85.0</td>
<td>70.0</td>
<td>85.0</td>
</tr>
<tr>
<td>2. Total liq. rate to quench spray, (lb/hr)</td>
<td>-</td>
<td>-</td>
<td>9040</td>
<td>8108</td>
</tr>
<tr>
<td>3. Irrigation rate to quench tower, (lb/hr ft²)</td>
<td>-</td>
<td>-</td>
<td>10000</td>
<td>9500</td>
</tr>
<tr>
<td>4. Height of packing for quench tower (ft)</td>
<td>4.0</td>
<td>15.0</td>
<td>6.7</td>
<td>11.37</td>
</tr>
<tr>
<td>5. Exit liquor temperature from quench-unit, (°F)</td>
<td>200</td>
<td>230</td>
<td>213</td>
<td>229</td>
</tr>
<tr>
<td>6. Condenser-cooler exit gas temperature, (°F)</td>
<td>-</td>
<td>-</td>
<td>160</td>
<td>166</td>
</tr>
</tbody>
</table>
Table 9. A (i) continued

<table>
<thead>
<tr>
<th></th>
<th>Lower limit</th>
<th>Upper limit</th>
<th>Starting value</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>b) Dependent variables (cond).</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Number of plates reqd. for absorption unit.</td>
<td>-</td>
<td>-</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>8. Number of &quot;HT&quot; plates required for absorber</td>
<td>-</td>
<td>-</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>9. Number of plates for acetone column</td>
<td>-</td>
<td>-</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>10. Number of plates for anhydride column</td>
<td>-</td>
<td>-</td>
<td>26</td>
<td>33</td>
</tr>
<tr>
<td>11. Fresh acetic acid required, (lb/hr)</td>
<td>-</td>
<td>-</td>
<td>4062</td>
<td>3969</td>
</tr>
<tr>
<td>12. Fresh acetone required, (lb/hr)</td>
<td>-</td>
<td>-</td>
<td>4949</td>
<td>4087</td>
</tr>
<tr>
<td><strong>c) Output variables</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Operating cost, (£/year)</td>
<td>-</td>
<td>-</td>
<td>178,534</td>
<td>224,948</td>
</tr>
<tr>
<td>2. Annual profit, (£/year)</td>
<td>-</td>
<td>-</td>
<td>1,083,227</td>
<td>1,231,353</td>
</tr>
</tbody>
</table>
It is interesting to note that computer program with 15 starting points spread uniformly over the feasible region gave the same optimum point (Appendix D, 4). Therefore, it can be said that there is a high probability that a global optima has been obtained. The detailed unitwise process design at optimum conditions is discussed below. Most of the results are tabulated in a similar way to Jeffreys (52), for comparison purpose.

### Table 9.4A. (ii)

Values of the specified variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Reaction temperature in furnace (°F)</td>
<td>1400</td>
</tr>
<tr>
<td>(2) % Ketene to be condensed in condenser - cooler</td>
<td>90.0</td>
</tr>
<tr>
<td>(3) Cooling water rate to heat exchangers of absorption unit, (lb/hr)</td>
<td>12,500</td>
</tr>
<tr>
<td>(4) Acetone composition in top product of acetone column (% wt.)</td>
<td>99.98</td>
</tr>
<tr>
<td>(5) Acetone composition in bottom product of acetone composition (% wt.)</td>
<td>0.25</td>
</tr>
<tr>
<td>(6) Process product composition, (% w/w anhydride in acid)</td>
<td>98.0</td>
</tr>
<tr>
<td>(7) Process product rate, (lb/hr)</td>
<td>6,000</td>
</tr>
</tbody>
</table>
9.4.1 Optimum process design

9.4.1.1 Furnace

Table (9.4.B) gives the material balance over the furnace.

**TABLE 9.4.B**

Material balance over furnace

<table>
<thead>
<tr>
<th>Component</th>
<th>Input</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight (lb/hr)</td>
<td>Wt. %</td>
</tr>
<tr>
<td>Acetone</td>
<td>40138.13</td>
<td>100.00</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ketene</td>
<td>2470.59</td>
<td>6.16</td>
</tr>
<tr>
<td>Methane</td>
<td>1144.29</td>
<td>2.85</td>
</tr>
<tr>
<td>Unsaturated</td>
<td>116.03</td>
<td>0.29</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>266.38</td>
<td>0.66</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>14.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.57</td>
<td>0.01</td>
</tr>
<tr>
<td>Total</td>
<td>40138.13</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Total heat duty of furnace = 43,660 BTU/hr. The temperature of vapours leaving furnace = 1400°F.
9.4.1.2 Quench units

a) Quench spray design
   Temperature of process stream leaving quench spray = 1000 °F
   Total liquor rate for quench spray = 8108 lb/hr

b) Quench tower design
   The irrigation rate = 9500 lb/hr ft²
   Minimum wetting rate = 1420 lb/hr ft²
   Tower loading = 80%

Calculation of packing height
The summary of the incremental calculations to calculate the height of packing for the outlet liquor temperature of 225 °F is given in Table (9.4.C).

<table>
<thead>
<tr>
<th>Increment No. &amp; packed height (ft)</th>
<th>Gas temperature (°F)</th>
<th>Liquid temperature (°F)</th>
<th>Acetic acid in gas (lb/lb dry gas)</th>
<th>Acetic anhydride in gas (lb/lb dry gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1000.0</td>
<td>225.0</td>
<td>0.202</td>
<td>0.202</td>
</tr>
<tr>
<td>1</td>
<td>898.98</td>
<td>218.0</td>
<td>0.400</td>
<td>0.268</td>
</tr>
<tr>
<td>2</td>
<td>809.72</td>
<td>204.0</td>
<td>0.490</td>
<td>0.299</td>
</tr>
<tr>
<td>3</td>
<td>729.77</td>
<td>183.7</td>
<td>0.486</td>
<td>0.289</td>
</tr>
<tr>
<td>4</td>
<td>657.18</td>
<td>159.2</td>
<td>0.418</td>
<td>0.271</td>
</tr>
<tr>
<td>5</td>
<td>590.66</td>
<td>134.0</td>
<td>0.324</td>
<td>0.226</td>
</tr>
<tr>
<td>6</td>
<td>529.56</td>
<td>111.0</td>
<td>0.241</td>
<td>0.171</td>
</tr>
<tr>
<td>7</td>
<td>473.67</td>
<td>91.6</td>
<td>0.178</td>
<td>0.124</td>
</tr>
<tr>
<td>8</td>
<td>422.74</td>
<td>76.0</td>
<td>0.139</td>
<td>0.089</td>
</tr>
<tr>
<td>9</td>
<td>376.49</td>
<td>62.0</td>
<td>0.102</td>
<td>0.065</td>
</tr>
<tr>
<td>10</td>
<td>334.57</td>
<td>-49.0</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>11</td>
<td>296.64</td>
<td>-40.0</td>
<td>0.065</td>
<td>0.04</td>
</tr>
</tbody>
</table>
The above calculations were repeated twice. In each the inlet gas temperature of 1000°F was kept constant, but the outlet liquor temperature was taken as 200°F and later 215°F. The results of these calculations are shown in Table (9.4.D), and plotted in Figure (9.4.1). The material balance indicates that gas leaving the quench unit will contain 0.09 lb of acetic acid per lb of dry gas.

**TABLE 9.4.D**

Calculation of packed height of quench tower

<table>
<thead>
<tr>
<th>Exit liquor temperature (°F)</th>
<th>Height of packing required to cool gas to 290°F (ft)</th>
<th>Height of packing required to give exit gas 0.09 lb acid/lb dry gas (ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>10.31</td>
<td>6.44</td>
</tr>
<tr>
<td>215</td>
<td>10.82</td>
<td>8.11</td>
</tr>
<tr>
<td>225</td>
<td>11.19</td>
<td>9.99</td>
</tr>
</tbody>
</table>

From figure (9.4.1.), it can be seen that the height of packing to cool the gas to 290°F and at the same time discharge the gas with 0.09 lb acetic acid is 11.32 ft. The height calculated by the program using interpolation method is 11.37.

The total height of column will be 15.0 ft.

**Make up for quenching system**

Acetic acid discharged from the tower = 3529.41 lb/hr
Anhydride discharge from the tower = 864.7 lb/hr
Therefore, total make up = 4394.3 lb

Hence, make up acetic acid required = 2923.98 lb/hr

Table (9.4.E) gives the overall material balance over the quench tower.
Figure 9.4.1. Graph to calculate height of packing
### TABLE 9.4.E

Material balance over the quench tower

<table>
<thead>
<tr>
<th>Component</th>
<th>INPUT</th>
<th></th>
<th>OUTPUT</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gaseous reaction products</td>
<td>Liquid recycle acid</td>
<td>Liquid make up acid</td>
<td>Vapour to condenser</td>
</tr>
<tr>
<td></td>
<td>Weight (lb/hr)</td>
<td>% Wt</td>
<td>Weight (lb/hr)</td>
<td>% Wt</td>
</tr>
<tr>
<td>Acetone</td>
<td>36124.26</td>
<td>90.00</td>
<td>605.43</td>
<td>41.18</td>
</tr>
<tr>
<td>Acetic acid</td>
<td></td>
<td></td>
<td>864.90</td>
<td>58.82</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ketene</td>
<td>2470.59</td>
<td>6.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>1144.29</td>
<td>2.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unsaturates</td>
<td>116.03</td>
<td>0.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>266.38</td>
<td>0.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>14.01</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.57</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>40138.13</td>
<td>100.00</td>
<td>1470.33</td>
<td>100.00</td>
</tr>
</tbody>
</table>
9.4.1.3 Condenser - cooler

Table (9.4.F) gives the analysis of gas leaving the quench tower.

**TABLE 9.4F**

Analysis of gas leaving quench tower

<table>
<thead>
<tr>
<th>Component</th>
<th>(lb/hr)</th>
<th>Weight %</th>
<th>(lb - mole/hr)</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>36124.26</td>
<td>81.12</td>
<td>621.97</td>
<td>74.62</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>3529.41</td>
<td>7.92</td>
<td>58.77</td>
<td>7.05</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>864.90</td>
<td>1.94</td>
<td>8.47</td>
<td>1.02</td>
</tr>
<tr>
<td>Ketene</td>
<td>2470.59</td>
<td>5.55</td>
<td>58.82</td>
<td>7.06</td>
</tr>
<tr>
<td>Methane</td>
<td>1144.29</td>
<td>2.57</td>
<td>71.34</td>
<td>8.56</td>
</tr>
<tr>
<td>Unsaturates</td>
<td>116.03</td>
<td>0.26</td>
<td>2.98</td>
<td>0.36</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>266.38</td>
<td>0.60</td>
<td>9.51</td>
<td>1.14</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>14.01</td>
<td>0.03</td>
<td>0.32</td>
<td>0.04</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.57</td>
<td>0.01</td>
<td>1.28</td>
<td>0.15</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>44532.44</strong></td>
<td><strong>100.00</strong></td>
<td><strong>833.46</strong></td>
<td><strong>100.00</strong></td>
</tr>
</tbody>
</table>

Temperature of exit gas = 166°F

Area of condenser - cooler required = 1894 ft²

Table (9.4.G) gives the material balance over the condenser - cooler.
<table>
<thead>
<tr>
<th>Component</th>
<th>WT (lb/hr)</th>
<th>%</th>
<th>WT (lb/hr)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>36124.26</td>
<td>81.12</td>
<td>5938.14</td>
<td>14</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>3529.41</td>
<td>7.92</td>
<td>1279.41</td>
<td>2.57</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>350.0</td>
<td>0.74</td>
<td>796.98</td>
<td>1.94</td>
</tr>
<tr>
<td>Ketene</td>
<td>2470.59</td>
<td>5.55</td>
<td>45403.69</td>
<td>104.98</td>
</tr>
<tr>
<td>Methane</td>
<td>1144.29</td>
<td>2.57</td>
<td>2224.53</td>
<td>5.11</td>
</tr>
<tr>
<td>Unsatrates</td>
<td>146.03</td>
<td>0.30</td>
<td>3.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>266.38</td>
<td>0.03</td>
<td>17.041</td>
<td>0.001</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>14.01</td>
<td>0.01</td>
<td>100.00</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>44532.44</td>
<td>100.00</td>
<td>36387.04</td>
<td>-</td>
</tr>
</tbody>
</table>

**Material Balance over Cooler - Condenser**

**Input**
- Gaseous mixture to absorption tower
- Weight (lb/hr)
- Component
  - Acetone
  - Acetic acid
  - Acetic anhydride
  - Ketene
  - Methane
  - Unsatrates
  - Carbon monoxide
  - Carbon dioxide
  - Total

**Output**
- Liquid products leaving condenser
- Weight (lb/hr)
- Component
  - Acetone
  - Acetic acid
  - Acetic anhydride
  - Ketene
  - Methane
  - Unsatrates
  - Carbon monoxide
  - Carbon dioxide
  - Total
9.4.1.4 Absorption Unit

Column dimensions

Diameter of the column = 4.0 ft.
Number of plates = 11.0
Plate spacing = 20.0 inches
Total height of the column = 23.5 ft.

Table (9.4.4) gives the summary of plate heat exchanges of the absorption unit.

TABLE 9.4.4
Summary of plate heat exchangers

<table>
<thead>
<tr>
<th>Heat exchanger number</th>
<th>Position in relation to column plate nos. i.e. between</th>
<th>Heat load (B.t.u/hr)</th>
<th>Number of &quot;HT&quot; plates required</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 and 2</td>
<td>174,480</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>2 and 3</td>
<td>101,950</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>3 and 4</td>
<td>59,820</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>4 and 5</td>
<td>35,500</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>5 and 6</td>
<td>20,950</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>negligible</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (9.4.1) gives the overall material balance over absorption unit.
<table>
<thead>
<tr>
<th>Component</th>
<th>Input Gas feed</th>
<th>Input Absorbent Liquor</th>
<th>Output Unabsorbed Gaseous Effluent</th>
<th>Output Liquid Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight (lb/hr)</td>
<td>Wt. (%)</td>
<td>Weight (lb/hr)</td>
<td>Wt. (%)</td>
</tr>
<tr>
<td>Acetone</td>
<td>5938.14</td>
<td>72.89</td>
<td>51.28</td>
<td>2.55</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>350.00</td>
<td>4.30</td>
<td>350.00</td>
<td>17.37</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>67.92</td>
<td>0.83</td>
<td>67.92</td>
<td>3.37</td>
</tr>
<tr>
<td>Ketene</td>
<td>247.06</td>
<td>3.03</td>
<td>2.00</td>
<td>0.10</td>
</tr>
<tr>
<td>Methane</td>
<td>1144.29</td>
<td>14.05</td>
<td>1144.29</td>
<td>56.80</td>
</tr>
<tr>
<td>Unsaturates</td>
<td>116.03</td>
<td>1.43</td>
<td>116.03</td>
<td>5.76</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>266.38</td>
<td>3.27</td>
<td>266.38</td>
<td>13.22</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>14.01</td>
<td>0.17</td>
<td>14.01</td>
<td>0.70</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.57</td>
<td>0.03</td>
<td>2.57</td>
<td>0.13</td>
</tr>
<tr>
<td>Total</td>
<td>8146.40</td>
<td>100.00</td>
<td>5103.77</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2014.48</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11235.69</td>
<td>100.00</td>
</tr>
</tbody>
</table>
9.4.1.5 Combined crude storage

Material balance over combined crude storage is given in the following table.

<table>
<thead>
<tr>
<th>Steam A</th>
<th>Acetone (lb/hr)</th>
<th>Acetone (lb mole/hr)</th>
<th>Acetic acid (lb/hr)</th>
<th>Acetic acid (lb mole/hr)</th>
<th>Acetic anhydride (lb/hr)</th>
<th>Acetic anhydride (lb mole/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid ex-condenser</td>
<td>30186.12</td>
<td>519.73</td>
<td>0.29</td>
<td>0.005</td>
<td>6200.67</td>
<td>60.74</td>
</tr>
<tr>
<td>Liquid ex-ketene absorber</td>
<td>5886.86</td>
<td>101.36</td>
<td>4755.53</td>
<td>79.193</td>
<td>593.30</td>
<td>5.81</td>
</tr>
<tr>
<td>Total liquid in crude storage</td>
<td>36072.98</td>
<td>621.09</td>
<td>4755.82</td>
<td>79.198</td>
<td>6793.97</td>
<td>66.55</td>
</tr>
</tbody>
</table>

9.5.1.6 Acetone distillation column

With the given products' specifications (page 176), the material balance for the acetone column can be prepared as shown in the table (9.4.K).

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed Weight (lb/hr)</th>
<th>Feed Wt. (%)</th>
<th>Distillate Weight (lb/hr)</th>
<th>Distillate Wt. (%)</th>
<th>Bottom Product Weight (lb/hr)</th>
<th>Bottom Product Wt. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>36072.98</td>
<td>75.75</td>
<td>36044.05</td>
<td>99.98</td>
<td>28.94</td>
<td>0.25</td>
</tr>
<tr>
<td>Ac. acid</td>
<td>4755.82</td>
<td>9.99</td>
<td>7.21</td>
<td>0.02</td>
<td>4748.61</td>
<td>41.04</td>
</tr>
<tr>
<td>Ac. anhydride</td>
<td>6793.97</td>
<td>14.26</td>
<td></td>
<td></td>
<td>6793.96</td>
<td>58.71</td>
</tr>
<tr>
<td>Total</td>
<td>47622.77</td>
<td>100.00</td>
<td>36051.26</td>
<td>100.00</td>
<td>11571.51</td>
<td>100.00</td>
</tr>
</tbody>
</table>
The minimum reflux ratio for the column is computed to be 0.235. The figure (9.4.2) gives the relationship between the number of plates and reflux ratio. Influence of reflux ratio on capital and operating cost of column is shown in figure (9.4.3). It can be seen that the optimum reflux ratio for acetone column is 0.33. The summary for the plate to plate calculations for optimum reflux ratio for the acetone column is given in the table (9.4.1).
Figure 9.4.2. Relationship between no. of plates & reflux ratio for acetone column

Figure 9.4.3. Influence of reflux ratio on capital and running costs of acetone column
<table>
<thead>
<tr>
<th>Plate now and its temp. (°C) (in bracket)</th>
<th>Component</th>
<th>Mol. fr. in vapour</th>
<th>Vapour pressure (atm)</th>
<th>Partial pressure (atm)</th>
<th>mol. fr. in vapour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Still (125.5°C)</td>
<td>Acetone</td>
<td>0.0034</td>
<td>7.236</td>
<td>0.0245</td>
<td>0.0248</td>
</tr>
<tr>
<td></td>
<td>Ac. acid</td>
<td>0.5412</td>
<td>1.245</td>
<td>0.6738</td>
<td>0.6768</td>
</tr>
<tr>
<td></td>
<td>Ac. anhydride</td>
<td>0.4554</td>
<td>0.652</td>
<td>0.2970</td>
<td>0.2984</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>1.0000</td>
<td></td>
<td>0.9973</td>
<td>1.0000</td>
</tr>
<tr>
<td>Plate 1 (119.98°C)</td>
<td>Acetone</td>
<td>0.0216</td>
<td>6.329</td>
<td>0.1366</td>
<td>0.1367 (683)</td>
</tr>
<tr>
<td></td>
<td>Ac. acid</td>
<td>0.6565</td>
<td>1.049</td>
<td>0.6886</td>
<td>0.6893</td>
</tr>
<tr>
<td></td>
<td>Ac. anhydride</td>
<td>0.3219</td>
<td>0.540</td>
<td>0.1739</td>
<td>0.1740</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>1.0000</td>
<td></td>
<td>0.9991</td>
<td>1.0000</td>
</tr>
<tr>
<td>Plate 2 (105.04°C)</td>
<td>Acetone</td>
<td>0.1167</td>
<td>4.319</td>
<td>0.5041</td>
<td>0.5035</td>
</tr>
<tr>
<td></td>
<td>Ac. acid</td>
<td>0.6671</td>
<td>0.6430</td>
<td>0.4289</td>
<td>0.4284</td>
</tr>
<tr>
<td></td>
<td>Ac. anhydride</td>
<td>0.2162</td>
<td>0.3151</td>
<td>0.0681</td>
<td>0.0681</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>1.0000</td>
<td></td>
<td>1.0011</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

(continued)
<table>
<thead>
<tr>
<th>Plate nos. and its temp. ($^\circ$C) (in bracket)</th>
<th>Component</th>
<th>Mol. fr. in vapour</th>
<th>Vapour pressure (atm)</th>
<th>Partial pressure (atm)</th>
<th>mol. fr. in vapour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate 3 ($78.89^\circ$C)</td>
<td>Acetone</td>
<td>0.4285</td>
<td>2.046</td>
<td>0.8771</td>
<td>0.8762</td>
</tr>
<tr>
<td></td>
<td>Ac. acid</td>
<td>0.4453</td>
<td>0.247</td>
<td>0.1101</td>
<td>0.1099</td>
</tr>
<tr>
<td></td>
<td>Ac. anhydride</td>
<td>0.1262</td>
<td>0.110</td>
<td>0.0139</td>
<td>0.0139</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>1.0000</td>
<td></td>
<td>1.0011</td>
<td>1.0000</td>
</tr>
<tr>
<td>Plate 4 ($64.79^\circ$C)</td>
<td>Acetone</td>
<td>0.7452</td>
<td>1.304</td>
<td>0.9720</td>
<td>0.9711</td>
</tr>
<tr>
<td></td>
<td>Ac. acid</td>
<td>0.1747</td>
<td>0.139</td>
<td>0.0242</td>
<td>0.0242</td>
</tr>
<tr>
<td></td>
<td>Ac. anhydride</td>
<td>0.0801</td>
<td>0.058</td>
<td>0.0047</td>
<td>0.0047</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>1.0000</td>
<td></td>
<td>1.0009</td>
<td>1.0000</td>
</tr>
<tr>
<td>Feed Plate plate 5 ($62.34^\circ$C)</td>
<td>Acetone</td>
<td>0.8259</td>
<td>1.201</td>
<td>0.9921</td>
<td>0.9837</td>
</tr>
<tr>
<td></td>
<td>Ac. acid</td>
<td>0.1018</td>
<td>0.125</td>
<td>0.0127</td>
<td>0.0126</td>
</tr>
<tr>
<td></td>
<td>Ac. anhydride</td>
<td>0.0723</td>
<td>0.052</td>
<td>0.0038</td>
<td>0.0037</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>1.0000</td>
<td></td>
<td>1.0086</td>
<td>1.0000</td>
</tr>
<tr>
<td>Plate 6 ($58.91^\circ$C)</td>
<td>Acetone</td>
<td>0.9353</td>
<td>1.069</td>
<td>0.9995</td>
<td>0.9947</td>
</tr>
<tr>
<td></td>
<td>Ac. acid</td>
<td>0.0498</td>
<td>0.107</td>
<td>0.0054</td>
<td>0.0053</td>
</tr>
<tr>
<td></td>
<td>Ac. anhydride</td>
<td>0.0149</td>
<td>0.044</td>
<td>0.0007</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>1.0000</td>
<td></td>
<td>1.0056</td>
<td>1.0010</td>
</tr>
</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>Component</th>
<th>Plate 7 (57.47°C)</th>
<th>Plate 8 (57.09°C)</th>
<th>Plate 9 (56.94°C)</th>
<th>Plate 10 (56.88°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetone</td>
<td>Ac. acid</td>
<td>Ac. anhydride</td>
<td>Total</td>
</tr>
<tr>
<td>Mol. fr. in vapo</td>
<td>0.9793</td>
<td>0.0207</td>
<td>-</td>
<td>1.0000</td>
</tr>
<tr>
<td>Partial pressure</td>
<td>1.017</td>
<td>0.101</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vapour pressure</td>
<td>0.9979</td>
<td>0.0021</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(atm)</td>
<td>0.9978</td>
<td>0.008</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.9982</td>
<td>0.0078</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.9962</td>
<td>0.003</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.9975</td>
<td>0.0025</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.9976</td>
<td>0.004</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.9958</td>
<td>0.0003</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.9955</td>
<td>0.0004</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.9955</td>
<td>0.0001</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.9956</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Column dimensions

- Diameter of the column = 7.0 ft.
- Number of plates, theoretical = 10.0
  actual = 20.0
- Tray spacing = 200 inches
- Height of the column = 39.0 ft.

9.1.4.7 Acetic anhydride column

Table (9.4.M) shows the material balance for acetic anhydride column.

**TABLE 9.4.M**

Material balance over acetic anhydride column

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed</th>
<th>Distillate</th>
<th>Bottom product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight (lb/hr)</td>
<td>Wt. (%)</td>
<td>Weight (lb/hr)</td>
</tr>
<tr>
<td>Acetone</td>
<td>25.26</td>
<td>0.25</td>
<td>25.26</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>4145.23</td>
<td>41.04</td>
<td>4024.46</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>5930.69</td>
<td>58.71</td>
<td>12.93</td>
</tr>
<tr>
<td>Total</td>
<td>10101.18</td>
<td>100.00</td>
<td>4062.65</td>
</tr>
</tbody>
</table>

The minimum reflux for the column is computed to be 0.9851. The relation between numbers of plates and reflux ratio is shown in figure (9.4.4). Influence of the reflux ratio on total cost of column is shown in figure (9.4.5.). It can be seen that the optimum reflux for anhydride column is 1.77. The table (9.4.N) summarizes the plate-to-plate analysis, for the optimum reflux ratio.
Figure 9.4.4. Relationship between number of plates & reflux ratio for anhydride column

Figure 9.4.5. Influence of reflux ratio on capital and running costs of anhydride column
<table>
<thead>
<tr>
<th>Plate number</th>
<th>Mol. fr. in liquid</th>
<th>Mol. fr. in vapour</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9846</td>
<td>0.9917</td>
</tr>
<tr>
<td>2</td>
<td>0.9762</td>
<td>0.9872</td>
</tr>
<tr>
<td>3</td>
<td>0.9717</td>
<td>0.9818</td>
</tr>
<tr>
<td>4</td>
<td>0.9646</td>
<td>0.9789</td>
</tr>
<tr>
<td>5</td>
<td>0.9538</td>
<td>0.9744</td>
</tr>
<tr>
<td>6</td>
<td>0.9373</td>
<td>0.9675</td>
</tr>
<tr>
<td>7</td>
<td>0.9129</td>
<td>0.9570</td>
</tr>
<tr>
<td>8</td>
<td>0.8772</td>
<td>0.9413</td>
</tr>
<tr>
<td>9</td>
<td>0.8275</td>
<td>0.9185</td>
</tr>
<tr>
<td>10</td>
<td>0.7618</td>
<td>0.8867</td>
</tr>
<tr>
<td>11</td>
<td>0.6816</td>
<td>0.8447</td>
</tr>
<tr>
<td>12</td>
<td>0.5933</td>
<td>0.7934</td>
</tr>
<tr>
<td>13</td>
<td>0.5073</td>
<td>0.7370</td>
</tr>
<tr>
<td>14</td>
<td>0.4061</td>
<td>0.6590</td>
</tr>
<tr>
<td>15</td>
<td>0.2731</td>
<td>0.5254</td>
</tr>
<tr>
<td>16</td>
<td>0.1557</td>
<td>0.3498</td>
</tr>
<tr>
<td>17</td>
<td>0.0854</td>
<td>0.1948</td>
</tr>
<tr>
<td>18</td>
<td>0.0448</td>
<td>0.1021</td>
</tr>
</tbody>
</table>

Column dimensions

- Diameter of the column = 3.5ft
- Number of plates theoretical = 18
  actual = 33
- Tray spacing = 18 inches
- Height of the column = 55 ft
### 9.4.2 Cost analysis

The equipment and running costs of the acetic anhydride plant for computed optimum conditions are shown in the following tables.

#### TABLE 9.4.2

**Capital investment for equipment**

**A** Major equipment (including accessories)

<table>
<thead>
<tr>
<th>Item</th>
<th>Purchased cost, £</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace</td>
<td>65,600</td>
</tr>
<tr>
<td>Quench unit</td>
<td>22,200</td>
</tr>
<tr>
<td>Condenser-cooler</td>
<td>22,200</td>
</tr>
<tr>
<td>Absorption unit</td>
<td>8,500</td>
</tr>
<tr>
<td>Acetone column</td>
<td>59,300</td>
</tr>
<tr>
<td>Anhydride column</td>
<td>36,300</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>214,100</strong></td>
</tr>
</tbody>
</table>

**B** Storage units

<table>
<thead>
<tr>
<th>Item</th>
<th>Purchased cost, £</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude product storage</td>
<td>9,800</td>
</tr>
<tr>
<td>Acetic acid storage</td>
<td>28,200</td>
</tr>
<tr>
<td>Acetone storage</td>
<td>5,600</td>
</tr>
<tr>
<td>Anhydride storage</td>
<td>24,500</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>68,100</strong></td>
</tr>
</tbody>
</table>
Therefore,
Total capital investment = £282,200.

### TABLE 9.4.R
- Running expenses

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity (lb/hr)</th>
<th>Annual cost (£ / hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling water</td>
<td>1,368,110</td>
<td>13,700</td>
</tr>
<tr>
<td>Steam</td>
<td>15,630</td>
<td>68,800</td>
</tr>
<tr>
<td>*Electricity</td>
<td>-</td>
<td>1,400</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>-</td>
<td><strong>83,900</strong></td>
</tr>
</tbody>
</table>

*The cost of electricity is estimated as 10% of cost of cooling water.

Total operating expenses
= 0.5 * Capital expenses + Running expenses
= £225,000

### TABLE 9.4.S
- Costs of the raw materials

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Quantity (lb/hr)</th>
<th>Annual cost (£ / year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>4086.84</td>
<td>1,050,300</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>3968.66</td>
<td>1,374,300</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>-</td>
<td><strong>2,424,600</strong></td>
</tr>
</tbody>
</table>
TABLE 9.4.1
Summary of the economic analysis

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity (lb/hr)</th>
<th>Annual value (£ / year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic anhydride</td>
<td>6038.54</td>
<td>3,881,000</td>
</tr>
<tr>
<td>product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total yearly operating</td>
<td>-</td>
<td>225,000</td>
</tr>
<tr>
<td>cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total yearly cost</td>
<td>-</td>
<td>2,424,600</td>
</tr>
<tr>
<td>of raw materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total yearly profit</td>
<td>-</td>
<td>1,231,400</td>
</tr>
</tbody>
</table>

Total profit calculated by the program is 1,231,353.37 £/year.

9.4.3 Computer time

The program was run on IBM 360/65 machine. The total execution time taken was 9.37 minutes including C. P. U. time and time spent on input and output.
Sensitivity analysis

The optimal solution of the process design problem using a mathematical method is seldom used in practice without modification, because values of the process and plant parameters may change in time. To compensate for the effects of such changes, design margins or so-called safety factors are often taken into account for practical design. These values are usually estimated from experience, but this estimation becomes more difficult as process systems become more complex. However, if the computerized model of the process is available, it becomes possible to determine quantitatively the kind and amount of design variables where margins should be taken into account. In view of these facts, once the optimum solution is obtained, it becomes necessary to estimate the impact of the input data upon the obtained optimum. Determining the rate of change of the optimum value with respect to perturbations in the independent variables is called sensitivity analysis.

The optimum values of the design variables are given in the previous section. Now, it is interesting to investigate the effect on optimum values due to changes in design variables near the optimum region.

Figure (9.5.1.) shows that though an increase in % acetone conversion causes the operating cost to decrease the quantity of fresh acetone requirement increases rapidly and thus the annual profit drops down. It is interesting to note that the make up acetic acid required is nearly constant for all acetone conversions.
**Figure 9.5.1. Sensitivity analysis**

(Parameter: % Acetone conversion)
Figure 9.5.2. **Sensitivity analysis**  
(Parameter: Quench unit inlet gas temp.)

Figure 9.5.3. **Sensitivity analysis**  
(Parameter: Quench unit exit gas temp.)
Figure 9.5.4. Sensitivity analysis
(Parameter: Acid to anhydride ratio in recycle)

Figure 9.5.5. Sensitivity analysis
(Parameter: Water rate to condenser-cooler)
The profit decreases sharply for first two degree temperature rise of quench unit exit gas and then it decreases linearly (Figure 9.5.2). The annual profit increases linearly with the rise in quench unit inlet gas temperature (Figure 9.5.3).

From figure (9.5.4), it can be seen that profit decrease linearly with acid to anhydride ratio in recycle. The operating cost almost increases linearly with this ratio. This is an expected result.

At first, the annual profit decreases sharply with the cooling water rate to condenser cooler and then this decrease becomes linear with the cooling water rate (Fig. 9.5.5).

The above briefly discussed sensitivity analysis takes into consideration the effect of one single design variable at a time upon the optimum value. In practice, sometimes it becomes necessary to consider the impact of several variables during the same period. However, such study has not been done in the present project.

9.6 Remarks
The optimization results present sufficient information to the process designer to carry out the detailed process design of the acetic anhydride process.

The optimization study of the acetic anhydride process design shows that the optimum point lies at the corner of constrained region. All of the design variables, except quench unit exit gas temperature, are at their lowest constrained values. The value of quench unit exit gas temperature, is at its upper constrained limit.
The value of the profit given is rather higher than expected in practice. This is mainly due to the cost of raw materials and the value of the product. Their values supplied by the manufacturer are based on retail prices. The values for the tonnage chemicals are varied from one manufacturer to another. Also, the price of the product material has been reduced recently. Therefore, it was found very difficult to specify the correct prices for the chemicals. Finally, it was decided to use retail prices. It is interesting to carry out the economic analysis at the optimum conditions using the tonnage prices. This analysis is shown below.

**TABLE 9, 6. A.**

Economic analysis of the acetic anhydride process
(based on price of the chemical/long ton)

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value of the product, £</td>
<td>2,674,000</td>
</tr>
<tr>
<td>(price £ 124/long ton)</td>
<td></td>
</tr>
<tr>
<td>Total yearly operating cost, £</td>
<td>225,000</td>
</tr>
<tr>
<td>Cost of the raw materials, £</td>
<td></td>
</tr>
<tr>
<td>Acetone (price £72/long ton)</td>
<td>1,021,000</td>
</tr>
<tr>
<td>Acetic acid (price £95/long ton)</td>
<td>1,387,000</td>
</tr>
<tr>
<td>Total yearly profit, £</td>
<td>41,000</td>
</tr>
<tr>
<td>* Percentage return on investment on installed cost</td>
<td>5.2%</td>
</tr>
</tbody>
</table>

* Taking total installed cost to be 2.8 times the total capital cost.
In the present projects, it has been shown how a fairly complex design problem can be optimized using a mathematical technique. The value of treating design studies in this way is very difficult to assess, but it is definitely invaluable to have a computer program which provides instant evaluation of variations in the flowsheet, and also the potentialities of automatic multivariate optimization.

10.1 Generality and usefulness of the proposed direct search method "MOSP"

In the present work, emphasis was placed on writing the computer program as general as possible. Recently, many scientific methods are proposed for writing the programs. The work of Roberts (81) has been taken here as a central tool. The details of the program is given in Appendix D. The main program, containing the input data and the optimization method, MOSP, can be used for any other process design project without many changes. The written program can optimise a problem having 50 independent variables and from one to 20 starting points. However, these numbers are arbitrary and can be changed to any higher values, if desired. The subroutine, DESIGN, which evaluates the acetic anhydride process design is also general in the sense that it designs the process for any specified composition and rate of the product.

The proposed direct search method, MOSP, is found to be very efficient and useful for process design problems. The comparison of MOSP with other methods is already given in Table (8. A). The acetic anhydride process design was also optimized using Look, the original direct search method of Hooke and Jeeves. Both methods gave the same optimum point. However, "MOSP" required 289 function evaluations to reach the optimum point compared with 1011 function
evaluations required by "LOOK." "MOSP" is an unconstrained optimization method. A suitable transformation technique could be incorporated into it, if required. In the present work, all constraints are linear, simple and easy to deal with in other ways, e.g. methods available for 'riding' constraints. Therefore, no transformations were used.

The computer program prints out, if any of the implicit constraints is violated. In such a situation, the program takes the maximum or minimum specified value of the constraint, depending upon the nature of the constraint, and the optimization path proceeds along the boundary. Briefly, the procedure uses the 'direct' method of dealing with the constraints. However, such situations did not arise in the present work.

10.2 Discussion on optimum process-design results

The optimum values of the design variables are given in Table (9. A). It can be seen that the optimum point lies on the boundaries of constraints. All design variables except quench - unit inlet gas temperature are at their lower limits.

From the study of the pilot plant data, Jeffreys (52) has pointed out that the operation of the reactor at lower conversion would result in an increased yield of anhydride, but the separation problem would be greater and therefore, chemical efficiency has to be sacrificed for overall economy. However, during optimization study at lower conversion, the separation difficulty was not encountered.

The optimum value of the acetone conversion confirms the remark made by Rietema (80) who estimated that the optimum design would be at 10-12% conversion. The present work shows that the annual profit can be increased by about 14% by decreasing the conversion from 25% to 10% (and also by changing other variables to their optimum values).
**TABLE 10. A**

Influence of reflux ratio on capital and operating costs of acetone column

<table>
<thead>
<tr>
<th>Reflux ratio</th>
<th>Column diameter (ft.)</th>
<th>Capital cost (cc) (£)</th>
<th>Running cost (cr) (£/year)</th>
<th>Operating cost (0.5 x cc + cr) (£/year)</th>
<th>Total cost (cc + cr) (£)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>7.0</td>
<td>59,328</td>
<td>57,542</td>
<td>87,206</td>
<td>116,870</td>
</tr>
<tr>
<td>0.43</td>
<td>7.0</td>
<td>57,234</td>
<td>62,122</td>
<td>90,739</td>
<td>119,356</td>
</tr>
<tr>
<td>0.52</td>
<td>7.5</td>
<td>60,486</td>
<td>66,476</td>
<td>96,719</td>
<td>126,962</td>
</tr>
<tr>
<td>0.62</td>
<td>7.5</td>
<td>58,076</td>
<td>70,824</td>
<td>99,862</td>
<td>128,900</td>
</tr>
<tr>
<td>0.72</td>
<td>8.0</td>
<td>61,192</td>
<td>75,164</td>
<td>105,760</td>
<td>136,356</td>
</tr>
<tr>
<td>0.81</td>
<td>8.0</td>
<td>61,730</td>
<td>78,950</td>
<td>109,815</td>
<td>140,680</td>
</tr>
<tr>
<td>0.91</td>
<td>8.5</td>
<td>65,000</td>
<td>83,292</td>
<td>115,792</td>
<td>148,292</td>
</tr>
</tbody>
</table>
For the quench unit, the optimum inlet gas temperature is found to be 1000°F. This means that the process stream in the quench spray is to be cooled from 1400°F by the recycle stream which consists of 3338.42 lbs of acetic acid and 4769.17 lbs of acetic anhydride. The optimum exit temperature of the quench unit is 290°F. The liquid rate to the unit is 9500 lb/hr ft^2. At this liquor rate the tower would be 80% loaded. The height of packing calculated in the program and graphically calculated from Fig. (9.4.1.) is the same. In the situation when both lines of Fig. (9.4.1.) become parallel, the linear interpolation subroutine fails to find the height of packing. In such a case, the program prints out an error message and the value for the height of packing for the subsequent calculation is taken as 15.0 ft., which is a value specified for the maximum height. However, such a situation also did not arise in this work.

For the design of condenser - cooler, the exit water temperature is taken as a specified variable, having a value of 81°F. The rise in temperature of water is estimated to be 8°F. The optimum water rate to the cooler - condenser is 600,000 lb/hr. This corresponds to a water velocity of 2.32 ft/sec. through the tubes, considering the size of the exchanger to be same as that proposed by Jeffreys. The total heat transfer area of the exchanger is calculated to be 1894 ft^2, which is about 12% lower than required for the design at 25% acetone conversion.

The absorption unit contributes only 3% of the total capital cost of the plant. The major design variable for the absorption unit is the absorbent rate which itself depends on the overall material balance of the crude product storage unit. The absorbent rate first increases slowly with the acetone conversion, then it drops down suddenly and finally it again begins to rise slowly. (Fig. 10.1.) However, the overall effect of acetone conversion on the absorbent rate is not very significant.
Figure 10.1. % Acetone conversion Vs. Absorbent rate

Figure 10.2. Relation between number of plates and reflux ratio for acetone column
The absorption unit requires 20 plate heat exchangers compared with 16 required at 25% acetone conversion design.

For the acetone column, the following variables are specified.

<table>
<thead>
<tr>
<th>Specified Variables</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) acetone composition in the top product</td>
<td>99.98%</td>
</tr>
<tr>
<td>b) acetone composition in the bottom product</td>
<td>0.25%</td>
</tr>
</tbody>
</table>

The program gives lower number of ideal plates than calculated by Gilliland's correlation (52), for the lower reflux ratio. However, the difference becomes smaller as the reflux ratio increases (Fig. 10.2). Figure (10.2) is drawn for the design at 25% acetone conversion.

The cost of a distillation unit is considered to be made up of a capital cost of the column, determined largely by the number and diameter of the plates, and the operating costs, determined by the steam and cooling water requirements. It is already shown in Fig. (9.4.2) that the number of plates decrease very slowly with reflux ratio. The table (10.A.) illustrates the influence of reflux ratio on capital and operating costs of the column. The fig. (9.4.2) was based on this table.

It can be seen from Table (10.A.) that the capital cost fluctuates slightly initially and then increases continuously. The running cost of the column obviously rises with reflux ratio. The total cost is the lowest at the 0.33 reflux ratio.

For the acetic anhydride column, the number of plates drops sharply with the reflux ratio compared with the acetone column (Fig. 9.4.4).
### TABLE 10. B

**Influence of reflux ratio on capital and running costs of anhydride column**

<table>
<thead>
<tr>
<th>Reflux ratio</th>
<th>Column diameter (ft)</th>
<th>Capital cost (cc) (£)</th>
<th>Running cost (cr) (£ / year)</th>
<th>Operating cost (0.5 x cc + cr) (£ / year)</th>
<th>Total cost (cc + cr) (£)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.38</td>
<td>3.5</td>
<td>41,794</td>
<td>12,895</td>
<td>33,792</td>
<td>54,679</td>
</tr>
<tr>
<td>1.77</td>
<td>3.5</td>
<td>36,276</td>
<td>14,389</td>
<td>32,527</td>
<td>50,665</td>
</tr>
<tr>
<td>2.17</td>
<td>4.0</td>
<td>35,582</td>
<td>15,987</td>
<td>33,778</td>
<td>51,569</td>
</tr>
<tr>
<td>2.57</td>
<td>4.0</td>
<td>34,856</td>
<td>17,533</td>
<td>34,961</td>
<td>52,389</td>
</tr>
<tr>
<td>2.96</td>
<td>4.0</td>
<td>34,114</td>
<td>19,079</td>
<td>36,136</td>
<td>53,183</td>
</tr>
<tr>
<td>3.35</td>
<td>4.5</td>
<td>36,252</td>
<td>20,624</td>
<td>38,750</td>
<td>56,876</td>
</tr>
<tr>
<td>3.74</td>
<td>4.5</td>
<td>36,346</td>
<td>22,170</td>
<td>39,843</td>
<td>58,516</td>
</tr>
</tbody>
</table>
For the design of the acetic anhydride column, only bottom product specifications (i.e. product composition and rate) are necessary.

Table (10.B.) illustrates the influence of reflux ratio on capital and running costs of the anhydride column. The results are also shown in Fig. (9.4.5.).

Similar to the acetone column, the diameter of the plates for the anhydride column increases very slowly with the reflux ratio. The optimum reflux ratio of the anhydride column is 1.77.

Comparing the costs of the individual equipments from Table (9.4.P.), it can be seen that the furnace is the most expensive equipment contributing about 24% of the total capital cost, next comes the acetone column having 21% of the total capital cost. The steam costs are about 82% of the total running costs.

Taking the prices of the raw materials based on tonnage quantity, the annual profit at optimum point is 5.5% of the total installed equipment cost, and about 19% of the annual operating cost. This is an attractive saving.

10.3 Influence of the design variables
It is of interest to study the influence of the design variables on the profit as well on the cost of the different units of the acetic anhydride process. Firstly, we will concentrate the discussion on the effect of one design variable at a time, and later on, we will study the effect of two variables at a time, mainly on the profit. It is rather difficult to plot the contours, showing the variation in objective function due to change in the variables, for multidimensional cases (e.g. for more than two variables) and such a presentation is not attempted in this project.
For the study of the effect of one design variable at a time, it is assumed that all other design variables are at the optimum conditions. A note is necessary here. This study should not be confused with the sensitivity analysis. In both cases, the effect on the optimum value due to variation in a variable is determined. However, in the sensitivity analysis, only the region near the optimum point is of interest, on the other hand, in the present study the whole feasible region is to be investigated.

Sensitivity analysis has shown that "% acetone conversion" is the key design variable of the acetic anhydride process. From fig. (10.3.), it can be seen that the annual profit drops quickly with rise in the acetone conversion. As the acetone conversion increases, the operating cost of the process decreases, but at the same time the quantity of fresh acetone required increases (Figs. 10.4 and 10.5.). This tends to favour the lower acetone conversion for overall economy. The acetone conversion has also an important effect on the cost of the furnace. By increasing the conversion from 10% to 25%, the cost of the furnace decreases by 40% (Fig. 10.6). The cost of the acetone column also decreases sharply with the increase in conversion (Fig. 10.7).

The annual profit increases steadily with the rise in quench unit inlet gas temperature (Fig. 10.8). The effect of quench unit exit gas temperature on the annual profit is very small (Fig. 10.9). The cost of the quench unit decreases sharply with the increase in both its inlet and exit gas temperatures (Fig. 10.10 and 10.11.). As the weight ratio of acetic acid to anhydride in recycle increases, the annual profit drops steadily (Fig. 10.12). However, the absorbent rate to the absorption unit increases very sharply (Fig. 10.13.). From (Fig. 10.14.), it can be seen that the cost of the anhydride column increases slowly first with this ratio, the increase becomes linear and finally, the cost shows a tendency to remain steady. The weight ratio of acid to anhydride does not seem to have much effect on the cost of the acetone column (Fig. 10.15).
Figure 10.3. Acetone conversion Vs. Profit

Figure 10.4. Acetone conversion Vs. Operating cost
Figure 10.5. Acetone conversion Vs Fresh acetone required

Figure 10.6. Acetone conversion Vs. Furnace cost
Figure 10.7. Acetone conversion Vs. Acetone column cost

Figure 10.8. Quench unit inlet gas temp. Vs. Profit
Figure 10.9. Quench unit exit gas temp. Vs. Profit

Figure 10.10. Quench unit exit gas temp. Vs. Quench unit cost
Figure 10.11. Quench unit inlet gas temp. Vs. Quench unit cost

Figure 10.12. Acid to anhydride ratio in recycle Vs. Profit
Figure 10.13. Acid to anhydride ratio in recycle Vs. Absorbent rate

Figure 10.14. Acid to anhydride ratio in recycle Vs. Anhydride column cost
Figure 10.15. Acid to anhydride ratio in recycle Vs. Cost of acetone column.

Figure 10.16. Cooling water rate to condenser-cooler Vs. Profit.
Figure 10.17. Water velocity Vs. Condenser-cooler cost
Figure 10.18. Variation of profit with acetone conversion and quench-unit inlet gas temp.
Figure 10.19. Variation of profit with acetone conversion and quench-unit exit gas temperature
Figure 10.20. Variation of profit with acetone conversion and acid to anhydride ratio in recycle.
Figure 10.21. Variation of profit with acetone conversion and water rate to condenser-cooler
The water rate to the condenser cooler also does not have significant effect on the annual profit (Fig. 10.16). However, it has a great influence on the cost of condenser unit. The condenser-cooler cost increases sharply with the water velocity up to 3.5 ft/sec. and then it becomes nearly steady (Fig. 10.17).

In the figures (10.18 to 10.21) the contours showing the effect of two variables at a time on the profit, are drawn. There are five design variables chosen for the optimization study. Therefore, there will be ten combinations for such study. However, in the present case, the design variable "% acetone conversion" is is kept as a fixed variable for all combinations. This reduces the number of combinations to four. The contours for all combinations are uniform, without any saddle point and shallow, curving valley. Generally, most of the process design problems have similar contours. This favours the use of the pattern search method, Look, which is a practical compromise between the methods which are extremely easy to implement and slow to converge and the methods which are quick to converge but troublesome to implement. The proposed method, MOSP, has definitely improved the efficiency of Look, at the same time, keeping its simplicity for implementation.

From the program output (Appendix D.4), it can be seen that the point vary near to the optimum is reached with the first 100 iterations. The remaining iterations which number 2/3 of the total, are done merely to reach and test the true optimum, i.e. for the manoeuvre termed "End Game".

10.4 Suggestions for future research

The result of the optimization of acetic anhydride process design give sufficient information to the process designer to carry out the detailed design at optimal conditions. It will be extremely useful if the detailed equipment designs can be done in the program itself. Such calculations can be done unitwise in the subroutines, which are called after the optimum point has been reached.
There is an advantage in writing the detailed design procedure of each unit in a separate subroutine. This gives the flexibility of removing any subroutine when new design methods are developed.

This is, of course, a tremendous task and a great deal of effort is required by a team consisting of designers and programmers. Once such programs become available, it will reduce the heavy burden of a process engineer doing the conventional design calculations.

b) In the sensitivity analysis of the process, the effect of one variable at a time on the performance of the process is studied. In practice it becomes necessary to study the effects of two or more variables at a time. As the number of variables increases, the sensitivity analysis study can not be presented in graphical form. The system equations have to be formed to estimate reasonable safety factors in a complex design problem. At present, no mathematical algorithm is available which can give a systematic procedure to form the system equations. Such work is really needed to make the obtained optimization results, more useful in practice.

c) In the process design optimization, it is a general practice to build a preliminary mass balance program. This program is run a few times to have an idea of the effect of the chosen design parameters. It is rather easier to form the explicit constraints. However, it is very difficult to guess the feasible limits for the implicit constraints. Moreover, these limits also have an effect on the chosen limits for the explicit constraints. Although, mass balance program can give some idea of the limits for the implicit constraints, it is very time consuming to explore the process design in order to determine these limits. Again, a systematic procedure is necessary to overcome this difficulty.
An optimization study of the acetic anhydride process design using a Modified Search Procedure, MOSP, has been performed. The following conclusions are drawn from this study.

1. The optimum design of the acetic anhydride process is at acetone conversion of 10%. The values of other design variables at optimum conditions are as follows.

<table>
<thead>
<tr>
<th>Design variable</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quench unit inlet gas temp., (°F)</td>
<td>1000</td>
</tr>
<tr>
<td>Quench unit exit gas temp., (°F)</td>
<td>290</td>
</tr>
<tr>
<td>Weight ratio of acetic acid to acetic anhydride in the recycle, (lb/lb)</td>
<td>0.70</td>
</tr>
<tr>
<td>Cooling water rate to condenser-cooler, (lb/hr)</td>
<td>600,000</td>
</tr>
</tbody>
</table>

2. The optimum point lies on the constraint boundaries. All design variables except quench unit inlet gas temperature are at their lower limits.

3. The cost of the computing time and programming effort required for such a one-off full optimization study amounts to a few thousands of pounds, and against this should be set the savings which the optimum design promises. The results of the optimization study show an estimate return on capital investment for installed equipment, (based on prices of the raw materials per long ton) of 5.2% and also a cash improvement of £148,000 over a non-optimized design done by Jeffreys (52). The profit figures shown by the program are rather high, mainly due to the values of the raw materials, which were based on prices per lb. of chemicals. Furthermore, such an optimization study pays off especially if the optimizing program is useable for future problems. Potential savings therefore, are reckoned to be very large.
4. The proposed method, MOSP, is found to be very efficient and easy to implement for process design problems. It is seen from Table (II.A) that, against the very tough test function generated by Rosenbrock (83), the proposed method shows performance extremely good. It is proved that there is a high probability of having only one optimum set of conditions for all sets of design variables, i.e. there is only one peak on the response surface. The 'MOSP' method climbs the peak without any difficulty from given $\frac{1}{2}$ starting points.

5. The number of objective function evaluations required to reach the optimum, or computing time is directly proportional to the values of the step size control parameters for all decision variables (i.e. parameters STEP and DELTTA of Appendix D.1), and the minimum allowable value for STEP (i.e. parameter RHO of Appendix D.1). In the present work, their best values are found to be 0.01, 0.05 and $\frac{1}{20}$ respectively. The value of the parameter RHO can be increased if the process design is required for preliminary evaluation purpose, where the computing efficiency is less important and an assessment of many alternative configurations may be required in a minimum time.

**TABLE II.A**

Performance of 'MOSP' against various search methods after 200 trials on

$Y = 100 \left( X_2 - X_1^2 \right)^2 + (1 - X_1)^2$

Starting point $X_1 = -1.20, X_2 = 1.00, Y = 24.20$

<table>
<thead>
<tr>
<th>Method</th>
<th>$X_1$</th>
<th>$X_2$</th>
<th>$Y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sectioning</td>
<td>-0.970</td>
<td>0.945</td>
<td>3.882</td>
</tr>
<tr>
<td>Steep Ascent</td>
<td>-0.605</td>
<td>0.371</td>
<td>2.578</td>
</tr>
<tr>
<td>Ordinary Pattern (LOOK)</td>
<td>......</td>
<td>......</td>
<td>0.803</td>
</tr>
<tr>
<td>Modified Pattern (Bell and Pike)</td>
<td>0.813</td>
<td>0.650</td>
<td>4.547$_{10}^{-2}$</td>
</tr>
<tr>
<td>Wood's Step 50</td>
<td>......</td>
<td>......</td>
<td>1.03$_{10}^{-2}$</td>
</tr>
<tr>
<td>Rosenbrock's method</td>
<td>0.995</td>
<td>0.991</td>
<td>2.20$_{10}^{-5}$</td>
</tr>
<tr>
<td>'MOSP'</td>
<td>1.0004</td>
<td>1.0006</td>
<td>1.00$_{10}^{-6}$</td>
</tr>
<tr>
<td><strong>OPTIMUM</strong></td>
<td>1.0000</td>
<td>1.0000</td>
<td>0.000</td>
</tr>
</tbody>
</table>
6. One of the major benefits of an optimization study is the ability to study the topography of the response surface by obtaining intermediate printouts as a 'search' progresses. The adjustment of step size, sudden decrease in the profit or objective function, encounters with constraints - all provide information regarding design in various regions as defined by different sets of levels of the design variables.

One must be sure that the optimum set of design variables is not on so sharp a peak of the multidimensional hill that a slight change will plunge the design into a highly uneconomic abyss. Once an optimum condition is obtained, therefore, the region around this summit must be explored. The response surface near the optimum is very sensitive to the design variable acetone conversion. The operating cost of the process drops down with the acetone conversion. However, the fresh acetone requirement increases sharply and thus, it favours the lower acetone conversion in point of view of overall economy. The acetone conversion also has an important influence on the cost of the furnace and of the acetone column, two major units of the process. Therefore it can be said that the acetone conversion is the key design variable of the acetic anhydride process. The next important design variable is the weight ratio of acid to anhydride in the recycle. This ratio controls the fresh acetic acid required to the process and also cost of the anhydride column.

The response surface is fairly flat with respect to the remaining design variables.

7. The development of a preliminary mass balance program is an essential part of an optimization study. It gives insight to the process model, which is very helpful in building the limits on both explicit and implicit constraints. It also avoids the elements of state variables (e.g. composition of a component in the stream) becoming negative in the final run of the optimization program.
The algorithms used in the present work for the selection of design variables and also to reduce the recycle computations seem to be very useful tools and in future might become integrated parts of the optimization calculations.

Using the algorithms, 5 out of the initial chosen 14 process variables are selected as the design variables. The application of the algorithms to solve the recycle problem suggested that the minimum no. of recycle parameters are 2 i.e. it is necessary to assume the values of at least 2 parameters to render recycle calculations acyclic. It is shown that if the two recycle parameters are chosen from the already selected design variables, the iterative calculations for the recycle streams can be successfully avoided.

The computer program developed for the optimization study is very general. The main program containing input data and the optimization method, MOSP, can be used for any other design problem having upto 50 decision variables. The program also contains a subroutine which chooses the best starting point from given sets of starting decision variables (maximum number of sets can be 20). It is up to programmer's choise whether to use this subroutine or not. However, it is experienced that this procedure reduces the computing time at the sametime giving the same probability of obtaining a 'global' optimum compared to conventional methods of starting from the different sets of decision variables and climb hills until the "highest peak" is found.

The computer program can also be used for the same process, but with different production rate and product composition.
Bibliography


This appendix presents a description of the operation of pattern search. The generalized flow charts, figures A(a-d), are intended to show the operation of the pattern search. Before entering the program, the calling program must contain the following quantities: total number of independent variables, subroutine to calculate value of the function to be optimized, step size, minimum allowable value of the step size, and ratio by which step size is to be changed.

In the generalized flow chart, the program is broken into four sections, initialization, exploratory search, pattern move and final closure tests. The notations used are essentially those used in the original paper on pattern search by Hooke and Jeeves(50).

Table of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DELTA</td>
<td>current step size for all independent variables.</td>
</tr>
<tr>
<td>delta</td>
<td>minimum allowable value of DELTA</td>
</tr>
<tr>
<td>rho</td>
<td>ratio by which DELTA is to be changed</td>
</tr>
<tr>
<td>k</td>
<td>variable number</td>
</tr>
<tr>
<td>K</td>
<td>total number of independent variables</td>
</tr>
<tr>
<td>Spsi</td>
<td>the value of function at the base point</td>
</tr>
<tr>
<td>Sphi</td>
<td>instantaneous value of the function</td>
</tr>
<tr>
<td>SS</td>
<td>minimum value of Sphi during a set of search moves of either type.</td>
</tr>
<tr>
<td>theta</td>
<td>previous base point</td>
</tr>
<tr>
<td>phi(k)</td>
<td>instantaneous value of k-th variable</td>
</tr>
<tr>
<td>psi(k)</td>
<td>value of phi (k) at last base point</td>
</tr>
<tr>
<td>S(ψi)</td>
<td>indicates that the value of the function is to be calculated by an independent program or subroutine.</td>
</tr>
</tbody>
</table>
Figure A. (a). *Initialization of Pattern search*

START

Input

for $k=1,K$

initial value of $\psi[k]$

Calculate $S(\psi)$

$S(\psi) \rightarrow S_{\psi}$

1

$S_{\psi} \rightarrow SS$

for $k=1,K$

$\psi[k] \rightarrow \phi[k]$
Figure A. (b). Exploratory search

\[ \phi[k] + \Delta \rightarrow \phi[k] \]
Calculate \( S(\phi) \)
\[ S(\phi) \rightarrow S\phi \]

Is \( S\phi \leq SS \) ?

\[ \phi[k] = 2\Delta \rightarrow \phi[k] \]
Calculate \( S(\phi) \)
\[ S(\phi) \rightarrow S\phi \]

Is \( S\phi \leq SS \) ?

\[ \phi[k] + \Delta \rightarrow \phi[k] \]

Is \( k < K \) ?

\[ k+1 \rightarrow k \]
Figure A. (c). Pattern move

Figure A. (d). Final closure test
To analyse the problem in detail and to develop the process model, is
the most difficult phase of the optimization study. Jeffreys(52)
has done the detailed chemical engineering design of this process
and his design is used as a major source of reference for the present
work.

The process model contains (a) mass balance program, (b) physical
properties program, and (c) heat balance and the design of process
equipment, each of which though not entirely independent, is
conveniently treated separately in the following paragraphs.

(a) The Mass balance program

This is the basic design work on which the rest of the calculations
are developed. The mass balance program must be able to generate
the flowsheets from values of a set of design variables and should
include the solution of all recycle loops. The choice of the design
variables is a crucial stage and this is already discussed in
chapter (3, 5). It is also often useful to specify information about
streams within the recycle loops, as these can cut down the number
of equations and iterations to be solved. It has already shown
that selecting the top product composition of the distillation unit as
a fixed design variable simplifies the major recycle problem. Also,
the choice of acetic acid - acetic anhydride weight ratio simplifies
the quench unit - distillation column cycle calculations. Both
loops in fact, do not require any iteration. In the condenser and
quench unit design however, the iteration calculations are less
simple as the mass and heat balances cannot be separated and it is
necessary to carry out step-wise procedures. The composition of
output streams in both cases will not be known until the design
analysis is completed.
In the quench unit, the controlling variable is the temperature of exit gases and in the condenser, it is the exit water temperature.

The main purpose of the mass balance program is to provide the foundation of the complete process design model. This program may be used to explore the effect on the flowsheet of variations in the process layout (e.g., the inclusion or omission of a recycle).

It is the general practice, to have a few runs with the mass balance program to give an idea of the effect of the parameters selected. What matters at this stage is that the parameters should be sufficient to specify the flowsheet completely, and that the basic flowsheet should be rapidly soluble. However, the comparisons are best made at a later stage after costs have been added, so that the effect of changes may be evaluated directly in economic terms.

(b) Physical properties programs

The programs for the co-relation and prediction of thermodynamic and physical properties are probably the most widely needed of all, for they provide essential data for many calculations. Most of the co-relations for calculation of physical and thermodynamic properties for the present study are taken from the work of Sherwood (95), Perrey (75), Davies (31), and Gambill (46). In the original project work by Jeffreys, the following data is available in graphical and/or tabulated form:

(i) % ketene yield - % acetone conversion.
(ii) composition of the reaction mixture - % conversion
(iii) quench unit effluent temperature - mass of acetic acid - anhydride injected
(iv) liquid temperature - saturation of film in equilibrium with liquid for quench unit design.

(v) acetone - acetic. Acid equilibrium data

The above data is programmed into computer routine form. The acetic acid - acetic anhydride equilibrium data is taken from Chu (26). For quench tower loading calculations, the co-relation presented by Leva (65) has been programmed. The graphs given by Kern (55) to calculate heat transfer co-efficients have been co-related.

(c) The Heat balance and the design of the process equipments

The mass balance program discussed above calculates the flow rates around the flowsheet with as little reference as possible to the actual equipment parameters. It is now necessary to add procedures to calculate these parameters, and also quantities as heat loads and utility consumptions. To do this, chemical engineering design methods for the various items of equipment must be added to the program. Most of the design procedures are the same as those used by Jeffreys (52). These procedures involve various classical chemical engineering and mathematical methods. Thus each item of equipment is discussed in the following paragraphs, with its purpose in the process and its design procedure.

(i) Furnace (Reactor)

This is one of the most important items of equipment in the flowsheet. It covers about \( \frac{1}{3} \) of the total capital cost of the plant. The cracking of acetone has two special features (30). Firstly, the feed stock is an extremely high priced one and hot acetone is the most searching material in finding leaks through jointed tubes.
Secondly, the plant is to be geared to the needs of a very costly works, where an interruption of anhydride supply would be extremely expensive, so that immediate replacement of split or faulty cracking tubes is imperative. Thus, special material of construction for the furnace tubes is necessary. Jeffreys has recommended 25/20 nickel chromium steel for the furnace tubes.

The furnace is represented in the flowsheet model by its heat duty. The total heat requirement is considered to be made up of six contributing parts as follows:

1. heating reaction products to exit temperature of furnace
2. preheating feed to acetone column.
3. supply the heat of cracking
4. superheating the acetone.
5. vapourization of the acetone.
6. preheating the liquid acetone to its boiling point.

The heat duty of the furnace depends upon the chosen conversion, feed rate, feed composition, and reaction temperature. In the present work, to simplify calculations, it has been assumed that:
(a) the datum temperature of the liquid acetone feed is at 86°F.
(b) the furnace tubes operate at a pressure of 5 atm.
(c) the temperature of the liquid mixture in the crude storage tank to the acetone unit is 104°F.
(d) the thermal efficiency of the furnace is 75%.

If the total heat available from the process gas is not sufficient to provide the heat duty of the furnace, town gas will be required, the quantity of which will depend on the additional heat required.
Once the above stated parameters are specified, the furnace model can be calculated without much difficulty. For design purposes, Jeffreys has recommended a conventional type of tube-still furnace, although for optimization studies the detailed design is not necessary.

(ii) Quench spray

The hot vapour leaving the cracking furnace at specified temperature must be rapidly cooled to prevent decomposition of the ketene. This quenching is most conveniently carried out by injecting a fine spray of acetic acid - acetic anhydride of selected weight ratio, which is obtained as bottom product from acetone distillation column. The temperature of the process stream leaving the quench spray is also a decision parameter, besides recycle composition. The simple four jet unit has been employed for this.

Once the exit gas temperature has been specified, the material balance over the quench spray can be done.

(iii) Quench tower

The quenching started at the quench spray is to be completed in a packed quench tower by contacting the partly cooled gas with a further quantity of acid anhydride mixture of specified composition. For packing, 3" stacked stoneware rings have been chosen and Morris and Jackson (68) state that for 3" rings the gas rate should be 19800 ft³/ft² hr of air. The quench liquor rate has to satisfy the constraints already stated in chapter (3.4.)
The exit gas temperature is the major decision parameter for quench unit design. It is necessary to know the acetic acid concentration in the exit gas, for the height of packing calculation. The former quantity can be easily computed once the inlet gas composition is determined, because the exit gas phase must contain 1.0 mole of acetic acid per mole of ketene.

The rise in liquor temperature is assumed to be 100°F. The quench tower is a classic example of process design involving solution of simultaneous heat and mass transfer equations by finite difference method. The detailed method of solution has been given by Jeffreys. However, Jeffreys has calculated the height of packing to cool the gas to a specified temperature and with required acetic acid concentration by plotting the results for different exit liquor temperature. The point at which these two curves meet gives the required height of packing and the corresponding exit liquor temperature. For the automatic calculations, this method cannot be used. To avoid the difficulty, linear co-relations for the above mentioned two curves have been developed. On solving these two linear equations simultaneously, the height of packing and exit liquor temperature are obtained. This subroubneis built into the main program. Difficulty has been experienced when these curves are not linear or when they have nearly the same slopes. The latter situation is the worst because in such case, the results obtained are impractical. The obvious remedy is to impose constraints on dependent parameters.

The material balance over the quench spray and tower can be done after completion of unit design. This design has an important influence on acetone column - quench unit recycle and this is already discussed in chapter (3.7). The liquid leaving the base of the quench tower will be passed to a filter which will remove any coke carried out of the reaction furnace. Perry (75) recommends continuous pressure precoat filter for such operation.
(iv) Condenser - cooler

The gases leaving the quench unit contains a large quantity of non-condensable gases. These non-condensable gases will lower the heat transfer co-efficient that would otherwise be the case. Moreover, the values of the co-efficients will vary considerably throughout the unit as the amount of condensable vapour in the gas phase is diminished. Hence the use of the logarithm mean temperature etc. is impossible and because of these difficulties, the design procedure recommended by Colburn and Hougen (27) for cooler - condensers for cooling mixtures of vapours and non-condensable gas has been used.

In the condenser design, there is a liquid phase reaction between acetic acid and ketene in addition to simultaneous heat and mass transfer. The percentage ketene condensed from the gas phase is the major design parameter. It is assumed that all the ketene that is condensed will react with the condensed acetic acid before it leaves the condenser and condensation occurs at constant pressure. The rate of reaction between acetic acid and ketene is rapid and according to the equation

\[ CH_2:CO + CH_3COOH \rightarrow (CH_3CO)_2O \]  

Eqn No. (B.1)

and the heat of solution is

\[ \Delta H = -11500 \text{ Cal / mole of anhydride formed} \]  

(Eqn No. B.2)

The cooling water rate through the tubes is also selected as a parameter. For design purposes, it has been estimated that a suitable exchanger would be 14' in length containing 300 tubes each 1.0 in. O.D. and tubes would be arranged on a square pitch with 0.25" spacing.

The design of the condenser involves the following iterations.
The rise in temperature of cooling water is estimated and iterated until convergence is achieved. This iteration procedure is necessary because it is not possible to make an overall heat balance in order to evaluate the exit water temperature. Also, the procedure of Colburn and Hougen involves a series of step wise calculations and thus it is not possible to know in advance the total amount of vapour condensed.

The step wise procedure of Colburn and Hougen also involves the assumption of condensate interface temperature at each step and then carries out the heat balance and this iteration is continued until the heat balance is satisfactory.

The heat transfer surface is calculated by numerical integration of the results obtained by stepwise calculations.

Both the quench unit and condenser occupies an important position in the process flowsheet and it has been found that the major proportion of computing time taken for flowsheet calculations is consumed by these units.

(v) Absorption unit

The uncondensed vapour leaving the condenser is to be passed into an absorption column in which the ascending gas is to be contacted with acetic acid to remove 99% of the ketene. At the same time acetone will be absorbed in acetic acid. Moreover, immediately the ketene is absorbed it reacts with the acetic acid to form acetic anhydride and a large amount of heat is liberated.
The heat of solution and reaction of ketene and acetic acid are given according to equation (B.1) and (B.2) respectively. The chemical reaction is of pseudo first order with reaction rate co-efficient \( k = 0.075 \text{ second}^{-1} \) (52). The equilibrium relation between the ketene in the gas and the interface and ketene in the liquid phase can be expressed by relation (B.3)

\[
y^* = 2.0X
\]

(Eqn No. B.3)

where,

\[
y^* = \frac{\text{lb mole ketene}}{\text{lb mole of gas}}.
\]

\[
X = \frac{\text{lb mole ketene}}{\text{lb mole liquid}}.
\]

Thus, the expected plate efficiency is 40\%. (52)

Thus, the absorption unit is an example of multicomponent absorption with a chemical reaction. The solubility of the acetone in acetic acid is high; and as a large quantity of acetone is present in the gas phase, the heat of absorption of acetone will be high. So to keep the temperature of the descending liquid as low as possible, it is recommended to use plate type tower with interstage cooling. (52)

The major function of the absorption unit is to recover the ketene from the gas. When the number of stages necessary to absorb the ketene has been established the amount of acetone that would be absorbed by this contacting will then be evaluated. If the absorption of the acetone is near completion some adjustment in number of stage will be made to make recovery of acetone also complete. This design approach is due to Jeffreys.

The absorption unit occupies a central position in the process, and its design has an important influence on the flowsheet calculations.
Its design is not only based on its own design parameters (i.e., decision variables), but also on certain key parameters which have major influence on whole flowsheet e.g. until the acetic acid-anhydride weight ratio for quench unit - acetone column recycle is specified, the absorbent rate to the absorber cannot be determined. In fact, it is necessary to carry out the material balance over crude product storage tank to decide the absorbent rate.

The number of plates are calculated using the method of finite difference equations (52). Jeffreys used the graphical plate analysis to calculate the quantity of acetone that will be absorbed on each plate. To convert this procedure into computer routine form, the following procedure is used. The material balance for different preselected percentage of acetone absorbed is done and stored in the machine. Using this stored information, it is easy to find the co-ordinates of any point on the operating line for acetone absorption, by the method of linear interpolation. Similarly, from the co-relation developed for the vapour-liquid equilibrium data, heat balance calculations are done using previous stored information. The water rate to an external plate exchanges is recommended to be 12,500 lb/hr (52). However, this rate is considered as a design parameter in the present study. The remaining design procedure for plate exchangers is the same as that of Jeffreys.

(vi) Crude product storage tank

The liquid product from the cooler-condenser is passed to the crude product storage tank, where it is mixed with the liquid product from the absorber.
The material balance for the storage tank has already been done in the absorber design. The mixture from this storage tank will constitute the feed to the acetone distillation column. The composition of top product of the column is specified to simplify reactor-acetone column recycle calculations and the part of the bottom product is recycled to the quench unit. Thus the weight ratio of acid-anhydride in the latter recycle influences the material balance over the crude storage. Jeffreys has shown that the temperature of the mixture in the storage tank would be 104°F. In the present work, this value is kept constant, so that a heat balance over the storage unit for every flowsheet calculation is unnecessary. The tank capacity is calculated on the basis of a three hour holding time.

(vii) Acetone distillation column

Acetone distillate produced by the acetone distillation unit must be of satisfactory quality for recycling to the reactor and the bottom product should have specified acetic acid-ac. anhydride weight ratio for recycle to the quench unit. The material balance over the acetone distillation column can be done once these parameters and the acetone composition in the bottom product are specified.

The design of the acetone column is done by conventional plate to plate calculation with heat balance and with a local optimization in one variable to find the optimum value of the reflux ratio. As this is the separation of a multicomponent mixture, a trial and error procedure of Lewis-Matheson (28) has been used. The plate efficiency is taken to be 50%. The column diameter is calculated by the method given by Smith and Sawistoski (98). There are few iteration loops in the distillation column design.
For the calculation of the plate temperature, a value of the temperature is assumed and from the partial pressure - temperature co-relations for three components, the sum of the partial pressures of the three components is made equal to the column pressure of 760 mm Hg. For convergence an accuracy of 1% is considered adequate.

The detail design of plates such as plate spacing, bubble cap design etc. is not necessary for an optimization study. The designs of accessory heat exchangers are carried out using conventional methods.

The quench unit - acetone column recycle rate is already determined in the quench unit design, (and its composition is a specified parameter). Therefore the bottom product rate to the acetic anhydride column can be determined without any difficulty.

(viii) Acetic anhydride column

The acetic anhydride column is required to separate the part of the bottom product of the acetone column into a distillate which is principally a pure acetic acid and a bottom product that consists of acetic anhydride with required purity and production rate. The design of this column is carried out by means of a plate to plate calculation with heat balance and the local optimization in one variable to find the optimum reflux ratio. The design procedure is very similar to previous column, except that the treatment here is much simplified by the fact that it is possible to treat the mixture as a binary.
This is justifiable because the acetone in the feed amounts to very small percentage. The overall material balance for the column is very straightforward. The computer routine form of McCabe - Thiele method is used for a plate to plate calculation assuming plate efficiency of 55%. The column diameter calculations are done in the same way referred to previously.

**General design considerations**

It is necessary to point out that in the present work, the designs of certain accessories such as pumps, blower, separators are not considered.

The design capacities of storage tanks for acetone, acetic acid and acetic anhydride are calculated on the basis of three weeks supply. The capacity of reflux accumulator for distillation column is calculated on the basis of volumetric reflux flow.

As the detailed chemical engineering design of the process done by Jeffreys (52) is available, it was decided to keep the same type of equipment for the particular operation as that designed by Jeffreys. For instance, Daroux (30) pointed out that the use of Rosenblad spiral plate exchangers are more economic than shell and tube heat exchangers because of their lower cost per equivalent square foot of steel surface. Such alternative equipment design is not considered in the present work. The same is true for the material of construction used for the equipments. Fortunately, the cost data for the equipments with the material of construction stated by Jeffreys are readily available in the literature.
The purity and the production rate of acetic anhydride product are chosen as the specified parameters. The advantage of this is that the generalized computer program can be used for any desired specification of product rate and purity. Unfortunately as for the reason given before, it was necessary to choose the purity of product as a fixed parameter for optimization study.
APPENDIX C

Application of Dynamic Programming to Acetic Anhydride Process Flowsheet

The serial structure of the process flowsheet creates a perfect environment for dynamic programming application. This is the major reason why dynamic programming has been widely used in process designs. In this Appendix the application of dynamic programming to the acetic anhydride process is discussed briefly. The exact numerical values for any state or decision variable is not considerable, because the basic idea is to discuss the procedure of dynamic programming and its limitations.

C.1 Recursive equations

Generally, dynamic programming analysis is carried out backwards, i.e. starting from the last stage of the flowchart and ending at the first stage (and thus the numbering of stages is chosen backwards, see figure C.1). This is because, for most process stages there exists a transformation given by the equation:

\[ X_{n-1} = t_n(X_n, D_n) \]  

[Eqn No. (C.1)]

The approach is very suitable for a process with fixed input. However, in the acetic anhydride process, output has been fixed. This is a 'final' state problem. The recommended solution (71) for such problem is to treat it as "initial - final" state problem i.e. to find \( f_n(X_n, X_0) \), the optional N stage return as a function of the input state of stage N and the output state from stage one. The recursive equations are rather different from those given in Chapter 7. At stage one, a two state problem is solved.

\[ f_1(X_1, X_0) = \max_{D_1} \left[ g_1(X_1, D_1, X_0) \right] \]

subject to

\[ X_0 = t_1(X_1, D_1) \]  

[Eqn No. (C.2)]
After determining \( f_1(X_1, X_0) \), the remainder of the recursive analysis proceeds exactly the same as described in Chapter 7, except that at each stage of the analysis, \( X_0 \) is carried as an additional state. Thus, the recursive equations are:

\[
    f_n(X_n, X_0) = \max_{D_n} \left[ g_n(X_n, D_n) + f_{n-1}(X_n, D_n, X_0) \right]
\]

for \( n = 2, 3, \ldots, N \)  \hspace{1cm} \text{[Eqn No. (C.3)]}

Finally, the optimization over the initial state is done

\[
    f_n(X_0) = \max_{X_n} (X_n, X_0)
\]

\hspace{1cm} \text{[Eqn No. (C.4)]}

When the above recursive equations are applied to the acetic anhydride process, the stagewise procedure will as discussed in the next section.

Dynamic programming procedure

Figure (G, 1) shows the simplified flowsheet of the acetic anhydride process, with each stage represented in numerical order.

In the following discussion, the subscript denotes the stage number and superscript denotes the element of that vector, e.g. \( X_1^{12} \) represents the second feasible value of the state variable 1 of stage 1.

Tables (C.1) to (C.11) shows the stagewise dynamic programming analysis. Under the stage decision column, only the optimal decision (shown by starred value) for the corresponding input is shown.

1) One stage returns

The procedure begins with Stage 1, For \( n = 1 \), equation (7.9), with some modification, becomes

\[
    Q_1(X_1, D_1, X_1) = g_1(X_1, D_1, X_1), \text{ since } f_0(x_0) \text{ is taken to be zero, which is simply the net stage 1 return. The computation is carried out for every stage 1 input - decision combination, with results as shown in Table (C.1).}
Figure C.1. Simplified acetic anhydride stagewise flowsheet
Table C.1

One stage returns, $Q_1(X_1, D_1, X_0)$

<table>
<thead>
<tr>
<th>Stage 1 input, $X_1$</th>
<th>Stage 1 decision $D_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed rate</td>
<td>Feed composition</td>
</tr>
<tr>
<td>( x_1 )</td>
<td>( x_1 )</td>
</tr>
<tr>
<td>( 11 )</td>
<td>( 21 )</td>
</tr>
<tr>
<td>( 22 )</td>
<td>( x_1 )</td>
</tr>
<tr>
<td>( 23 )</td>
<td>( x_1 )</td>
</tr>
<tr>
<td>( 24 )</td>
<td>( x_1 )</td>
</tr>
<tr>
<td>( 25 )</td>
<td>( x_1 )</td>
</tr>
<tr>
<td>( 12 )</td>
<td>( x_1 )</td>
</tr>
<tr>
<td>( 12^{**} )</td>
<td>( 24^{**} )</td>
</tr>
<tr>
<td>( 15 )</td>
<td>( 2\frac{3}{4} )</td>
</tr>
<tr>
<td>( x_1 )</td>
<td>( x_1 )</td>
</tr>
<tr>
<td>( x_{25} )</td>
<td>( x_1 )</td>
</tr>
</tbody>
</table>
The final step in the analysis of stage 1 is the
designation of the optimal decision – calling it
$D_1^* = (X_1^*)$ and the maximum return, $f_1(X_1, X_0)$,
for each of the feasible values for the input $(X_1)$.
The starred values in Table (C.1) provides this
designation, e.g. $D_1^* (x_{11}, x_{12}) = d_{115}$. This
corresponding value for the stage return will be
the optimal return, $f_1(X_1, X_0)$, which is the revenue
from the sale of the product plus the price of the
acetic acid made available as the top product minus
the operating cost (capital + running cost) of the
column. The feasible values of the feed composition
(i.e. $x_{12}$ etc.) are dependent upon the acetic acid/
anhydride weight ratio in quench unit – acetone column
recycle, which is a major decision variable in the
process.

ii) Two stage returns

Turning now to two stage process, consisting of
stage 1 and 2, the combined two stage return is
calculated from equation (7.9) i.e.

$$Q_2(X_2, D_2) = g_2(X_2, D_2) + f_1(X_1, X_0)$$

Therefore, for every feasible value of the input
and decision at stage 2, there will be a value of
stage 2 return and the output (i.e. stage 1 input).
Table (C.1) gives the optimal stage 1 return for
the particular output. Thus the value of
$Q_2(X_2, D_2)$ for every stage 2 input - decision
combination can be found. This computation
is shown in Table (C.II).
The optimal stage 2 decision (giving optimal return, $f_2(X_2, X_0)$) is again indicated by the starred value for each possible input ($X_2$).

One of the outputs of stage 2, acetone column, is divided into two parts. One part becomes feed to the stage 1 and the second part is recycled to the quench unit. The stage 2 return consists of the price of acetone made available for recycle minus the operating cost of the tower.

iii) Three stage returns
No process design is involved in stage 3 analysis. The stage 3 return is negative since it is the capital cost of the storage unit.

iv) Four stage returns
Unlike the previous stages, stage 4, absorber, has two decision variables. Thus, for each input, $X_4$, there is an optimal value for each decision, $d_4^m$ and $d_4^{2n}$, where $m$ and $n$ are positive integers, whose values represent the grid points. For the four stage process consisting of stage 4 plus the three stage process just considered above, the return is computed from equation (7.9) with $n = 4$, carrying out the computations for all input decision combinations yield Table (C. III) where the starred values again designate the optimal decisions $D_4^*(X_4)$, and the maximum four stage return, $f_4(X_4, X_0)$, for each possible input value ($X_4$).
As above, stage 4 return is negative. It consists of operating cost of the tower plus the price of absorbent and cooling water required. However, it can be noted that the four stage process return is positive.

v) Five stage process

Here again two decision variables are present, viz, cooling water rate and % ketene to be condensed. The stage 5 has two output states, the gaseous product becoming stage 4 input and the liquid product is to pass to the crude storage. The computation for all input - decision combinations is as shown in Table (C. IV).

Stage 5 return is also a negative quantity, it consists of operating cost of the condenser plus the price of the cooling water.
Table C. II

Two stage returns, \( Q_2(X_2, D_2, X_0) \)

<table>
<thead>
<tr>
<th>Stage 2 input, ( X_1 )</th>
<th>Stage 2 decision, ( D_2 )</th>
<th>Reflux ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed rate</td>
<td>Feed composition</td>
<td>Reflux ratio</td>
</tr>
<tr>
<td>( x_{11} )</td>
<td>( x_{21} )</td>
<td>( d_{21}^1 )</td>
</tr>
<tr>
<td>( x_{2} )</td>
<td>( x_{22} )</td>
<td>( . )</td>
</tr>
<tr>
<td>( x_{2} )</td>
<td>( . )</td>
<td>.</td>
</tr>
<tr>
<td>( x_{2} )</td>
<td>( . )</td>
<td>( d_{2}^2 )</td>
</tr>
<tr>
<td>( x_{2} )</td>
<td>( 11^{**} )</td>
<td>( 25^{**} )</td>
</tr>
<tr>
<td>( x_{2} )</td>
<td>( . )</td>
<td>.</td>
</tr>
<tr>
<td>( x_{2} )</td>
<td>( . )</td>
<td>.</td>
</tr>
<tr>
<td>( x_{2} )</td>
<td>( 15 )</td>
<td>( 25 )</td>
</tr>
</tbody>
</table>
Table C. III

Four stage returns, $Q_4(X_4, D_4, X_0)$

<table>
<thead>
<tr>
<th>Stage 4 input, $X_4$</th>
<th>Stage 4 decisions, $D_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed rate</td>
<td>Feed composition</td>
</tr>
<tr>
<td>$x_4^{11}$</td>
<td>$x_4^{21}$</td>
</tr>
<tr>
<td>$x_4^{13}$</td>
<td>$x_4^{25}$</td>
</tr>
<tr>
<td>$x_4^{15**}$</td>
<td>$x_4^{23**}$</td>
</tr>
<tr>
<td>$x_4^{15}$</td>
<td>$x_4^{24}$</td>
</tr>
<tr>
<td>$x_4^{25}$</td>
<td>$d_4^{11*}$</td>
</tr>
</tbody>
</table>
Table C. IV

Five stage returns, \( Q_5(X_5, D_5, X_0) \)

<table>
<thead>
<tr>
<th>Stage 5 input, ( X_5 )</th>
<th>5 stage decisions, ( D_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed rate ( x_5 )</td>
<td>Feed comp. ( x_5 )</td>
</tr>
<tr>
<td>( x_5^{11} )</td>
<td>( x_5^{21} )</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>( x_5^{13**} )</td>
<td>( x_5^{23**} )</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>( x_5^{25} )</td>
<td>...</td>
</tr>
<tr>
<td>( x_5^{15} )</td>
<td>...</td>
</tr>
<tr>
<td>( x_5^{25} )</td>
<td>...</td>
</tr>
</tbody>
</table>
vi) Six stage returns

The partly cooled gas leaving the quench spray (stage 7) is completely quenched in a packed tower by contacting the gas with a acetic-acid/ acetic anhydride mixture. The temperature of the cooled gas leaving the tower is a decision variable. The computation for six stage process is shown in Table (C. V)

Table (C. V)

Six stage returns, \( Q_6(x_6, D_6, X_0) \).

<table>
<thead>
<tr>
<th>Stage 6 input, ( X_6 )</th>
<th>Stage 6 decision, ( D_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed rate</td>
<td>Feed composition</td>
</tr>
<tr>
<td>( x_6^{11} )</td>
<td>( x_6^{21} )</td>
</tr>
<tr>
<td>( x_6^{22} )</td>
<td>( x_6^{1*} )</td>
</tr>
<tr>
<td>( x_6^{14} )</td>
<td>( x_6^{21} )</td>
</tr>
<tr>
<td>( x_6^{14**} )</td>
<td>( x_6^{24**} )</td>
</tr>
<tr>
<td>( x_6^{15} )</td>
<td>( x_6^{25} )</td>
</tr>
</tbody>
</table>
The stage 6 return consists of operating cost of the tower plus the cost of make up acetic acid required, of course, the stage return is a negative quantity as before.

vii) Seven stage returns

The hot vapour leaving the cracking furnace (stage 8) are quenched by injecting a fine spray of a mixture of acetic acid and acetic anhydride.

The temperature of the process leaving the quench spray is a decision variable for this stage. Table (C. VI) shows the computation for seven stage process.

Table C. VI

<table>
<thead>
<tr>
<th>Seven stage returns, ( Q_{7,1}(X_7, D_7, X_0) )</th>
<th>Stage 7 input, ( X_7 )</th>
<th>Stage 7 decision, ( D_7 )</th>
<th>Exit gas temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed rate</td>
<td>Feed comp.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>( x_7 )</td>
<td>21</td>
<td>( x_7 )</td>
</tr>
<tr>
<td>22</td>
<td>( x_7 )</td>
<td>( d_7 )</td>
<td>( d_7 )</td>
</tr>
<tr>
<td>11</td>
<td>( x_7 )</td>
<td>23</td>
<td>( x_7 )</td>
</tr>
<tr>
<td>13</td>
<td>( x_7 )</td>
<td>24</td>
<td>( x_7 )</td>
</tr>
<tr>
<td>15</td>
<td>( x_7 )</td>
<td>25</td>
<td>( x_7 )</td>
</tr>
</tbody>
</table>
viii) Eight stage returns

In stage 8, the pyrolysis of acetone to ketene is carried out. The decision variables for this stage are, % acetone conversion and temperature of the thermal cracking. The stage input consists of pure acetone. Therefore, the input state, \( X_8 \), has only one element viz. feed rate. The computation for eight stage process is shown in Table (C. VII).

### Table C. VII

Eight stage returns, \( Q_8(X_8, D_8, X_0) \)

<table>
<thead>
<tr>
<th>Stage 8 input, ( X_8 )</th>
<th>Stage 8 decision, ( D_8 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed rate ( x_8 )</td>
<td>%Acetone conversion</td>
</tr>
<tr>
<td>1</td>
<td>( d_{15} * )</td>
</tr>
<tr>
<td>2</td>
<td>( d_{14} * )</td>
</tr>
<tr>
<td>3**</td>
<td>( d_{13} * )</td>
</tr>
<tr>
<td>4</td>
<td>( d_{12} * )</td>
</tr>
<tr>
<td>5</td>
<td>( d_{11} * )</td>
</tr>
</tbody>
</table>
Being a 'final' state problem, it is necessary at this stage to carry the optimization over the initial state, according to equation (C. 4). As the output of the process is fixed, the state input is decided by the selection of decision variable, % acetone conversion, (also refer to equation (3. 6)). The optimum decision will be that one which gives the highest profit for the eight stage process. This state decision variable combination has been denoted by the double starred value in Table (C. VII). The optimal decisions also give the optimal stage 8 output i.e., optimal stage 7 input state. Suppose, this is the one denoted by double starred in Table (C. V I).

The table also indicates that for this input, the optimal stage 7 decision is $D_7^* (X_7^*) = d_7^{1*}$, This stage 7 decision yields the optimal stage 6 input, as again shown by the double starred value in Table (C. V). The table reveals that for this input, the optimal stage 6 decision is $d_6^{*}$. At this stage, we also know the optimal acetone column-quench recycle state and optimal stage 5 input ($X_5^{13**}, X_5^{23**}$ of Table (C. IV)). From this table it can be seen that for this input, the optimal stage 5 decisions are $D_5^* (X_5^*) = d_5^{14**}, d_5^{22**}$. This procedure is continued until stage 2, i.e., acetone column. At stage 2, the optimal distillate rate corresponding to the optimal input is known. The optimal process input (stage 8 input) is already computed in stage 8 analysis. The subtraction of the former quantity from the latter yields the optimal fresh feed required. Table (C. II) also reveals the optimal stage 2 output. However, this output is divided into two parts, the first part is recycled to the quench unit and second part becomes stage 1 input. The optimal quench unit recycle state has been computed in stage 3 analysis. Therefore, the optimal stage 1 input can be determined, this is, say, denoted by double starred value in Table (C. I). This table also gives the optimal stage 1 decision for the optimal stage input.

The optimal plant decision is then the stages operated at the state and decision variables denoted by double starred values.
Limitations of dynamic programming analysis

In the flowsheet problem of the acetic anhydride process, there are relatively few decision variables per stage. However, for most of the stages, the input contains as many as nine elements. This makes dynamic programming analysis much more difficult than it appears theoretically. For most practical purposes, vector $X_n$, with at most three or under some circumstances, four components is the largest that is computationally feasible.

The other drawback of dynamic programming is that it generally requires to compute interpolation of two stored values. For example, suppose, we have optimal stage 4 input from stage 5 analysis, say $X_{4n}^{**}$, and this value lies between the stored values $X_{4}^{13}$ and $X_{4}^{14}$, then it is necessary to carry out interpolation to obtain optimal decision, $D_{4}^{**}$ ($X_{4}^{1n**}$).

The presence of multidecisions at each stage is not very uncommon in process designs. Optimum seeking methods, such as direct search, can be profitably incorporated into dynamic programming to solve such problems.

In the present flowsheet problem, the recycle computations are much more simplified. The utility of dynamic programming becomes very limited in situations involving multiple recycles.
### Card Set 1

<table>
<thead>
<tr>
<th>Number</th>
<th>Format</th>
<th>Variables</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8 I 4</td>
<td>-</td>
<td>Constants to calculate the operating line of absorption unit.</td>
</tr>
<tr>
<td>2</td>
<td>6 F 10.4</td>
<td>-</td>
<td>Constants to calculate physical properaties of the components.</td>
</tr>
</tbody>
</table>

Card set 2 is provided for each component

<table>
<thead>
<tr>
<th>Number</th>
<th>Format</th>
<th>Variables</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>8 F 10.4</td>
<td>RWR</td>
<td>Water rate to absorber-cooler, (lb/hr).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ABP</td>
<td>Wt. fr. of acetone in bottom product of acetone column.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ATP</td>
<td>Wt. fr. of acetone in top product of acetone column.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ACIDBP</td>
<td>Wt. fr. of ac. acid in bottom product of anhydride column.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ACIDIP</td>
<td>Wt. fr. of ac. acid in top product of anhydride column.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RMINJA</td>
<td>Minimum wt. fr. of anhydride in acetone column distillate.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RMAXA</td>
<td>Maximum wt. fr. of acetone in acetone column distillate.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EXWT</td>
<td>Exit water temp. for condenser-cooler, (°F).</td>
</tr>
<tr>
<td>4</td>
<td>8 F 10.4</td>
<td>VVA</td>
<td>Yearly acetone cost, (£/year).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VVJ</td>
<td>Yearly ac. acid cost, (£/year).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VVJA</td>
<td>Yearly product value, (£/year).</td>
</tr>
</tbody>
</table>
### Card Set Format Variables

<table>
<thead>
<tr>
<th>Card Set Number</th>
<th>Format</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.</td>
<td>3 F 10.4</td>
<td><strong>RMFL</strong> Max. loading rate for quench tower, (lb/hr ft(^2)).</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>RMINL</strong> Min. liquid rate for quench tower, (lb/hr ft(^2)).</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>EXMIN</strong> Min. exit liquid temp for quench unit, (°F).</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>EXMAX</strong> Max. exit liquid temp. for quench unit, (°F).</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>HTMAX</strong> Max. height of packing for quench tower, (Ft).</td>
</tr>
<tr>
<td>6</td>
<td>F 10.0</td>
<td><strong>STEP</strong> Initial value for step size control parameter.</td>
</tr>
<tr>
<td></td>
<td>5 I 10</td>
<td><strong>RHO</strong> Minimum allowable value for &quot;STEP&quot;.</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>EPSILN</strong> Factor by which the step size is to be reduced following failure of both moves.</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>DELTTA</strong> Quantity by which the difference between the maximum and minimum limits of each variable is multiplied to form the step size array.</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>IOPSHN</strong> Option for using &quot;OPBIT&quot; subroutine.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>= 0, if subroutine is not reqd.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>=1 , if subroutine is reqd.</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>NVAR</strong> Total number of decision variables.</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>MAXNR</strong> Maximum number of iterations permitted for optimization.</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>INDEX</strong> Total number of starting points.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>= 0, for IOPSHN = 0.</td>
</tr>
</tbody>
</table>
### Card Set 7 is only required if IOPSHN = 0

<table>
<thead>
<tr>
<th>Number</th>
<th>Format</th>
<th>Variables</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>5F 10.8</td>
<td>X (IT)</td>
<td><strong>Initial values of the decision variables.</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(IT=1, NVAR)</td>
<td></td>
</tr>
</tbody>
</table>

Card set 8 is only required if IOPSHN = 1

<table>
<thead>
<tr>
<th>Number</th>
<th>Format</th>
<th>Variables</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>5 F 10.0</td>
<td>(XX(IB, IA), IB = 1, NVAR)</td>
<td><strong>Initial values of the decision variables.</strong> provided</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(IA = 1, INDEX)</td>
<td></td>
</tr>
</tbody>
</table>

Card set 9 must be provided for given number of starting points.

<table>
<thead>
<tr>
<th>Number</th>
<th>Format</th>
<th>Variables</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>2 F 10.4</td>
<td>(P(IT), Q(IT))</td>
<td><strong>Maximum and minimum limits for each decision-variable.</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(IT = 1, NVAR)</td>
<td></td>
</tr>
</tbody>
</table>

Card set 9 must be provided for each decision variable.
D. 2 Program listing in Basic Fortran IV
OPTIMIZATION OF ACETIC ANHYDRIDE PROCESS DESIGN

PROGRAM CONTAINS THREE SUBROUTINES:
SUBROUTINE OPTBIT CHOOSES THE BEST STARTING POINT, IF ASKED.
SUBROUTINE DESIGN EVALUATES THE PROCESS DESIGN FOR A GIVEN SET OF
DESIGN VARIABLES
SUBROUTINE VPRESS CALCULATES THE VAPOUR PRESSURES OF COMPONENTS

WRITTEN BY S.V. DHARMADHIKARI

1. IF IPRINT=-1 FINAL RESULTS ONLY
2. IF IPRINT=0 ALL INTERATIONS
3. IF IPRINT=1 ALL INTERATIONS AND DETAIL RESULTS AT FINAL ITERATION

COMMON IPRINT, IREAD, IRITE, INDEX, NR, NVAR
COMMON NA(9), TBB(9), VIS(9), AA(9), B(9), C(9), AMW(9), RWR, ABP, ATP,
ACIDTP, RMINJA, RMAXA, VVA, VVJ, VFJA, RFML, RMINL, EXMIN, EXMAX, HTMAX, EXWT, ACIDBP
COMMON IDATA, IREAD, 2)(NA(1), IT), IT=1, 8
DO 52 IT=1, 9
READ(IREAD, 10) NAt(1), IT=1, 8
52 READ(IREAD, 3) TBB(IT), VIS(IT), AA(IT), B(IT), C(IT), AMW(IT)
READ(IREAD, 7) RWR, ABP, ATP, ACIDTP, ACIDBP, ACIDTP, RMINJA, RMAXA, EXWT
READ(IREAD, 7) VVA, VVJ, VFJA, RFML, RMINL, EXMIN, EXMAX, HTMAX

COMMON IPRINT, IREAD, IRITE, INDEX, NR, NVAR
COMMON NA(9), TBB(9), VIS(9), AA(9), B(9), C(9), AMW(9), RWR, ABP, ATP,
ACIDTP, RMINJA, RMAXA, VVA, VVJ, VFJA, RFML, RMINL, EXMIN, EXMAX, HTMAX, EXWT, ACIDBP
COMMON IDATA, IREAD, 2)(NA(1), IT), IT=1, 8
DO 52 IT=1, 9
READ(IREAD, 10) NAt(1), IT=1, 8
52 READ(IREAD, 3) TBB(IT), VIS(IT), AA(IT), B(IT), C(IT), AMW(IT)
READ(IREAD, 7) RWR, ABP, ATP, ACIDTP, ACIDBP, ACIDTP, RMINJA, RMAXA, EXWT
READ(IREAD, 7) VVA, VVJ, VFJA, RFML, RMINL, EXMIN, EXMAX, HTMAX

INPUT DATA FOR SPECIFIED VARIABLES, IMPLICIT CONSTRAINT VALUES,
PHYSICAL CONSTANTS FOR COMPONENTS

READ(IREAD, 2)(NA(1), IT=1, 8)
DO 52 IT=1, 9
52 READ(IREAD, 3) TBB(IT), VIS(IT), AA(IT), B(IT), C(IT), AMW(IT)
READ(IREAD, 7) RWR, ABP, ATP, ACIDTP, ACIDBP, ACIDTP, RMINJA, RMAXA, EXWT
READ(IREAD, 7) VVA, VVJ, VFJA, RFML, RMINL, EXMIN, EXMAX, HTMAX

DOUBLE PRECISION S, S1, S2
1 FORMAT(4F15.8)
2 FORMAT(814)
3 FORMAT(6F10.4)
4 FORMAT(M1)
5 FORMAT(118, *OPTIMIZATION OF ACETIC ANHYDRIDE PROCESS DESIGN USING
1 DIRECT SEARCH METHOD*
6 FORMAT($T6, 'ITERATION', 5X, 'ACETONE', 5X, 'QUENCH UNIT', 5X, 'QUENCH U
INIT', 5X, 'ACID/ANHYDRIDE', 5X, 'WATER RATE', 5X, 'YEARLY', '7X, 'NUMBER', 4
2X, 'CONVERSION', 5X, 'INLET GAS', 7X, 'EXIT GAS', 10X, 'RATIO IN', 11X, 'TO
5R')
7 FORMAT(8F10.4)
8 FORMAT(6X, I4, 7X, F10.8, 2X, F10.4, 7X, F10.5, 8X, F10.7, 8X, F10.3, F13.2)
9 FORMAT(3F10.4)
10 FORMAT(F10.0, 5I10)
15 FORMAT(F10.0, 5I10)
9079 FORMAT(/10X, 'OPTIMUM IS REACHED')
9080 FORMAT(/10X, 'OPTIMUM IS NOT REACHED')
9081 FORMAT(/48X, 'VALUES AT OPTIMUM POINT')
STEP SIZE CONTROL PARAMETERS
READ (IREAD, 9) STEP, RHO, EPSLN

OPTION PARAMETERS
READ (IREAD, 10) DELTTA, IOPSHN, NVAR, MAXNR, INDEX, IPRINT
    NR=0
    IF (IOPSHN) 30, 30, 31
    30 READ (IREAD, 15) (X(IT), IT=1, NVAR)
    CALL DESIGN (X(1), X(2), X(3), X(4), X(5), S1)
    GO TO 35

    31 WRITE (IRITE, 4)
    WRITE (IRITE, 5)
    WRITE (IRITE, 6)
    CALL OPB1IT (X(1), X(2), X(3), X(4), X(5), S1)

    35 DO 36 IT=1, NVAR
    36 READ (IREAD, 9) P(IT), Q(IT)
    DO 38 IT=1, NVAR
        DELTAA(IT) = DELTTA * (P(IT) - Q(IT))
    IF (DELTAA(IT)) 37, 37, 38
    37 DELTAA(IT) = DELTTA
    38 CONTINUE

    39 IF (IPRINT) 42, 40, 40
    40 DO 41 IT=1, 15
    41 NNR(IT) = 35 * IT + 1
    42 WRITE (IRITE, 4)
    WRITE (IRITE, 5)
    WRITE (IRITE, 6)
    WRITE (IRITE, 8) NR, (X(IR), IR=1, NVAR), S1
    S = S1
    DO 53 IS=1, NVAR
    DELTAA(IS) = DELTAA(IS)
    53 CONTINUE

    54 Y(IS) = X(IS)

TYPE I EXPLORATORY SEARCH
    I=1
    55 Y(I) = Y(I) + DELTAA(I)
    IF (Y(I) - P(I)) 56, 56, 58
    56 IF (Y(I) - Q(I)) 56, 556, 556
    556 CALL DESIGN (Y(1), Y(2), Y(3), Y(4), Y(5), S2)
    NR=NR+1
    IF (IPRINT) 557, 1055, 1055
    1055 DO 1057 IT=1, 15
    1056 WRITE (IRITE, 4)
    WRITE (IRITE, 5)
    WRITE (IRITE, 6)
    GO TO 1056
    1057 CONTINUE
    1058 WRITE (IRITE, 8) NR, (Y(IR), IR=1, NVAR), S2
    557 IF (S2-S) 58, 58, 57
57 \text{DELTA(I)} = (S2/S) \times \text{DELTA(I)} \\
I = I + 1 \\
S = S2 \\
58 Y(I) = Y(I) - 2.0 \times \text{DELTA(I)} \\
59 \text{IF}(Y(I) - Q(I)) < 61, 59, 59 \\
59 \text{IF}(Y(I) - P(I)) < 559, 559, 61 \\
559 \text{CALL DESIGN (Y(1), Y(2), Y(3), Y(4), Y(5), S2)} \\
560 \text{NR} = \text{NR} + 1 \\
560 \text{IF}(\text{IPRINT}) = 1062, 560, 560 \\
560 \text{DO 1060 IT} = 1, 15 \\
560 \text{IF}(! \text{NR} = \text{NNR}(IT)) = 1060, 1059, 1060 \\
1059 \text{WRITE(IRITE,4)} \\
1059 \text{WRITE(IRITE,5)} \\
1059 \text{WRITE(IRITE,6)} \\
1059 \text{GO TO 1061} \\
1060 \text{CONTINUE} \\
1060 \text{WRITE(IRITE,8) NR, (Y(IR), IR = 1, NVAR), S2} \\
1062 \text{IF}(S2 - S) = 61, 61, 60 \\
60 \text{DELTA(I)} = -(S2/S) \times \text{DELTA(I)} \\
60 \text{I} = I + 1 \\
60 S = S2 \\
61 \text{IF}(I - \text{NVAR}) < 55, 55, 62 \\
61 \text{Y(I)} = \text{Y(I)} + \text{DELTA(I)} \\
61 \text{DELTA(I)} = \text{DELTA(I)} \times \text{EPSILN} \\
61 \text{I} = I + 1 \\
61 \text{IF}(I - \text{NVAR}) < 55, 55, 62 \\
62 \text{IF}(S - S1) = 76, 76, 63 \\
63 I = 1 \\
64 \text{IF}(Y(I) - X(I)) = 901, 901, 900 \\
900 \text{IF}(\text{DELTA(I)}) = 902, 902, 903 \\
901 \text{IF}(\text{DELTA(I)}) = 903, 903, 902 \\
902 \text{DELTA(I)} = -\text{DELTA(I)} \\
C \text{PATTERN MOVE} \\
C 903 \text{ZZ(I)} = X(I) \\
903 \text{X(I)} = Y(I) \\
903 \text{Y(I)} = 2.0 \times Y(I) - ZZ(I) \\
80 \text{IF}(Y(I) - Q(I)) = 65, 80, 80 \\
80 \text{IF}(Y(I) - P(I)) = 66, 66, 65 \\
65 \text{Y(I)} = X(I) \\
65 \text{I} = I + 1 \\
66 \text{I} = I + 1 \\
66 \text{IF}(I - \text{NVAR}) < 64, 64, 67 \\
67 \text{S1} = S \\
67 \text{IF}(\text{NR} = \text{MAXNR}) = 967, 85, 85 \\
967 \text{CALL DESIGN (Y(1), Y(2), Y(3), Y(4), Y(5), S)} \\
967 \text{NR} = \text{NR} + 1 \\
967 \text{IF}(\text{IPRINT}) = 568, 1066, 1066 \\
1066 \text{DO 1068 IT} = 1, 15 \\
1066 \text{IF}(\text{NR} = \text{NNR}(IT)) = 1068, 1067, 1068 \\
1067 \text{WRITE(IRITE,4)}
WRITE(IRITE,5)
WRITE(IRITE,6)
GO TO 1069

1068 CONTINUE
1069 WRITE(IRITE,8) NR,(Y(IR),IR=1,NVAR),S

TYPE 2 EXPLORATORY MOVE

568 I=1
68 Y(I)=Y(I)+DELTA(I)
69 IF(Y(I)-P(I)) 69,69,71
69 IF(Y(I)-Q(I)) 71,569,569
569 CALL DESIGN (Y(1),Y(2),Y(3),Y(4),Y(5),S2)
      NR=NR+1
      IF(IPRINT) 670,570,570
570 DO 1071 IT=1,15
      IF(NR-NNR(IT)) 1071,1070,1071
1070 WRITE(IRITE,4)
      WRITE(IRITE,5)
      WRITE(IRITE,6)
      GO TO 1072
1071 CONTINUE
1072 WRITE(IRITE,8) NR,(Y(IR),IR=1,NVAR),S2
670 IF(S2-S) 71,71,70
70 DELTA(I)=(S2/S)*DELTA(I)
      I=I+1
      S=S2
      IF(I-NVAR) 68,68,75
71 Y(I)=Y(I)-2.0*DELTA(I)
    IF(Y(I)-Q(I)) 74,72,72
72 Y(I)=Y(I)-2.0*DELTA(I)
    IF(Y(I)-P(I)) 74,72,72
572 CALL DESIGN (Y(1),Y(2),Y(3),Y(4),Y(5),S2)
      NR=NR+1
      IF(IPRINT) 1076,573,573
573 DO 1074 IT=1,15
      IF(NR-NNR(IT)) 1074,1073,1074
1073 WRITE(IRITE,4)
      WRITE(IRITE,5)
      WRITE(IRITE,6)
      GO TO 1075
1074 CONTINUE
1075 WRITE(IRITE,8) NR,(Y(IR),IR=1,NVAR),S2
1076 IF(S2-S) 74,74,73
73 DELTA(I)=-(S2/S)*DELTA(I)
      I=I+1
      S=S2
      IF(I-NVAR) 68,68,75
74 Y(I)=Y(I)+DELTA(I)
      DELTA(I)=DELTAA(I)*EPSILN
      I=I+1
      IF(I-NVAR) 68,68,75
75 IF(S-S1) 53,53,975
975 DO 980 IR=1,NVAR
      T1=ABS(Y(IR)-X(IR))
26/11/70  FORTMAIN

T2=0.5*ABS(DELTA(IR))
IF(T1-T2) 980,980,63
980 CONTINUE
76 CONTINUE

C  C  C  C
C  C  C  C

STEP SIZE REDUCTION

C  C  C  C
C  C  C  C

IF(STEP-RHO) 79,79,77
77 IF(NR-MAXNR) 977,85,85
977 STEP=STEP*EPSILN
DO 78 IT=1,NVAR
78 DELTA(IT)=DELTAA(IT)*EPSILN
GO TO 53

C  C  C  C
C  C  C  C

FINAL RESULTS PRINTOUT

C  C  C  C
C  C  C  C

79 WRITE(IRITE,9079)
   WRITE(IRITE,4)
   WRITE(IRITE,5)
   WRITE(IRITE,6)
   WRITE(IRITE,9081)
   IF(IPRINT) 83,83,84
58 IPRINT=1
   GO TO 585
84 IPRINT=IPRINT+1
585 CALL DESIGN(X(1),X(2),X(3),X(4),X(5),S2)
   WRITE(IRITE,8) NR,(X(IR),IR=1,NVAR),S1
   GO TO 81
85 CONTINUE
   WRITE(IRITE,9080)
   WRITE(IRITE,8) NR,(X(IR),IR=1,NVAR),S1
81 CONTINUE
STOP
END.
SUBROUTINE OPBIT(X1,X2,X3,X4,X5,S1)

OUTPUT VARIABLES
X1,X2,X3,X4,X5 = VALUES OF 'BEST' STARTING INDEPENDENT VARIABLES
S1 = VALUE OF OBJECTIVE FUNCTION AT ABOVE STARTING POINTS

COMMON IPRINT,IREAD,IRITE,INDEX,NR,NVAR
COMMON NA(9),TBB(9),VJS(9),AA(9),B(9),C(9),AMW(9),RWR,ABP,ATP,
1  ACIDTP,RMINJA,RMAXA,VVA,VVJ,VVJA,RMFL,RMINL,EXMIN,EXMAX,HTMAX,EX
2WTV,ACIDBP
DOUBLE PRECISION VALUE(10)
DIMENSION X(50)
COMMON NA(9),TBB(9),VJS(9),AA(9),B(9),C(9),AMW(9),RWR,ABP,ATP,
1  ACIDTP,RMINJA,RMAXA,VVA,VVJ,VVJA,RMFL,RMINL,EXMIN,EXMAX,HTMAX,EX
2WTV,ACIDBP
DOUBLE PRECISION VALUE(10)
DIMENSION X(50)

8 FORMAT(6X,I4,9X,F10.8,3X,F10.4,8X,F10.5,11X,F10.7,5X,F10.3,F20.2)
15 FORMAT(5F10.0)

DO 20 IA=1,INDEX

READ(IREAD,15) (XX(IB,IA),IB=1,NVAR)

DO 20 IB=1,NVAR
20 CONTINUE

CONTINUE
DO 22 IB=1,NVAR
22 X(IB)=XX(IB,1)
CALL DESIGN(X(1),X(2),X(3),X(4),X(5),VALUE(1))
S1=VALUE(1)
WRITE(IRITE,8) NR,(XX(IB,IB),IB=1,NVAR),S1

SELECTION OF 'BEST' STARTING POINT

DO 30 IA=2,INDEX
CALL DESIGN(XX(1,IA),XX(2,IA),XX(3,IA),XX(4,IA),XX(5,IA),VALUE(IA))
WRITE(IRITE,8) NR,(XX(IB,IA),IB=1,NVAR),VALUE(IA)
1 IF(VALUE(IA)-S1) 30,30,26
26 DO 27 IB=1,NVAR
27 X(IB)=XX(IB,IA)
S1=VALUE(IA)
30 CONTINUE
X1=X(1)
X2=X(2)
X3=X(3)
X4=X(4)
X5=X(5)
RETURN
SUBROUTINE DESIGN (CONV, GT, TEG, RT, HR, PROFIT)

INPUT VARIABLES
CONV = ACETONE CONVERSION IN FRACTION
GT = QUENCH UNIT INLET GAS TEMPERATURE DEGF.
GT = QUENCH UNIT EXIT GAS TEMPERATURE DEGF.
RT = ACID/ANHYDRIDE RATIO IN RECYCLE
WR = WATER RATE TO CONDENSER LBS/HR.

OUTPUT VARIABLES
PROFIT = ANNUAL PROFIT £/YEAR

Y = 0.95 - CONV
Z = (6000.0*58.0)/(102.0*CONV*Y)

FURNACE DESIGN
A(1) = (1.0 - CONV)*Z
BB(1) = (CONV*Y*Z*42.0)/58.0
CONV = CONV*100.0

COMPOSITION OF EFFLUENT GASES


```
U = (-0.00445 + 0.01*CONV + 1.7E-04*CONV*CONV) / 100.0
D = (0.305 - 0.01*CONV + 0.001*CONV*CONV) / 100.0
E = (4.575 + 0.05*CONV + 6.667E-3*CONV*CONV) / 100.0
F = (4.695 + 0.045*CONV + 6.667E-3*CONV*CONV) / 100.0
G = (1.605 - 0.005*CONV + 0.007*CONV*CONV) / 100.0
H = (Z*U*G*2.0) / 58.0
AI = Z - (A(1) + BB(1) + D + EK + F + G)

HEAT DUTY OF FURNACE

\[ H_1 = Z \times (781.3479 + 5.8966 \times CONV) \]
\[ W_E = 58000.0 / (946.0042 + 19.432528 \times CONV - 0.499952 \times CONV^2 + 0.0106658 \times CONV^3) \]
\[ H_3 = \left( \frac{Z^*1.8}{W_E} \right) \times \left\{ \frac{(6.3439 - 0.04498 \times CONV + 4.191E-04 \times CONV^2) \times 110.0}{1 + ((431.113 - 0.40053 \times CONV - 4.796E-04 \times CONV^2) \times (110.0 \times 1.954) / 2.0) + ((2 - 10.9524 + 0.10646 \times CONV - 2.564E-4 \times CONV^2) \times 317.0) / 3.0) + H_1 \right\} \]

QUENCH UNIT DESIGN

\[ DMGT = 0.5 \times (TEG + GT) + 460.0 \]
\[ Q = (Z \times 359.0 \times DMGT) / (WET \times 492.0) \]
\[ GA = (19800.0 \times SQRT(WET / 29.0)) \]
\[ AQ = Q / GA \]
\[ DQ = SQRT(AQ / 0.785) \]
\[ NDQ = I\text{FIX}(DQ) \]
\[ RDQ = NDQ \]
\[ Q = 2.785 \times DQ \times DQ \]

CALCULATION OF IRRIGATION RATE

\[ RTLIQ = 2.161E+05 / (DQ \times DQ) \]
\[ RTLIQ = 10000.0 \]
\[ DG = (WET \times 492.0) / (359.0 \times DMGT) \]
\[ GG = Z / (3600.0 \times AQ) \]
\[ BLP1 = \left( \frac{GG \times GG \times 25.0 \times 0.94 \times 0.94 \times (0.63 \times 0.2)}{DG \times (0.76 \times 3) \times 66.7 \times 32.2} \right) \]
\[ BLP2 = \left( \frac{RTLIQ / (3600.0 \times GG)}{SQRT(DG / 66.7)} \right) \]
\[ IF(BLP1 = 0.1) \]
\[ IF(BLP2 = 0.006281 \times (BLP1**(-1.3406))) \]
\[ GO TO 106 \]
\[ IF(BLP3 = 0.85117 \times (EXP(-16.6871 \times BLP1))) \]
\[ FL = (BLP2 / BLP3) \times 100.0 \]
\[ IF(FL < RMFL) \]
\[ RTLIQ = RTLIQ - 500.0 \]
\[ GO TO 103 \]
\[ IF(RTLIQ < RMINL) \]
\[ RTLIQ = RTLIQ + 500.0 \]
\[ GO TO 103 \]
```
TOTAL LIQUID RATE TO QUENCH SPRAY

\[
X_1 = 0.535 \times 149.0 + 96.75 \times 1.8 \times (T_1 - 392.0) \times (9.88 + 1.343 \times (T_1 + 392.0) / 102.0)
\]

\[
X_2 = 0.434 \times 184.0 + 92.2 \times 1.8 \times (T_1 - 410.0) \times (18.3 + 1.64 \times (T_1 + 410.0) / 102.0)
\]

DELH = \[
Z \times 1.8 \times (1032.0 - T_1) \times ((5.48 + 1.64 \times (T_1 + 392.0)) / (1032.0 + 1032.0 \times (T_1 - 3.0)) / WET)
\]

\[
X = \frac{DELH}{(X_1 + X_2)}
\]

BM1 = \[
(1.00 + (0.25 \times (BIP_1 + BIP_2 + 1.63)) / 60.0)
\]

PD = \[
1.00 / (((Z/WET) + (AJ(1) \times 1.1) / 60.0))
\]

AK = \[
(48.6 \times 1.4 \times 0.6 \times 0.168 \times (VG - 0.5) \times 0.75) \times PD \times TF
\]

BK = \[
(48.6 \times 1.4 \times 0.6 \times 0.284 \times (VG - 0.5) \times 0.75) \times PD \times TF
\]

W = \[
Z / AQ
\]

BJ = \[
AJ(1) / Z
\]

S = \[
((5.48 + 3.28 \times 2 \times DMGT / 1.8) - (8.45 \times E - 6 \times (DMGT / 1.8) \times 2)) / WET) + 0.13825
\]

PI = \[
0.5 \times (BIP_1 + BIP_2)
\]

BK1 = \[
BK \times PI / WET / 102.0
\]

AK1 = \[
(AK \times PI / WET) / 60.0
\]

PIV = \[
AK1 \times 25.0 / W
\]

VIP = \[
-BK1 \times 25.0 / W
\]

TIP = \[
-150.0 / (W \times 5)
\]

FORMAT(3F20.7)

SH = (RT \times 0.535 + 0.435) / (RT + 1.0)

T1 = (96.75 \times 1.8 \times W) / (RTLIOQ \times SH)

T2 = (92.2 \times 1.8 \times W) / (RTLIOQ \times SH)

T3 = W \times S / (RTLIOQ \times SH)

NNT = 185

IF(NNT = 215) 113, 112, 113

NNT = NNT - 5

CALCULATION OF TOWER HEIGHT

113 NNT = NNT + 15

TLO = NNT

IF(NNT = 230) 114, 114, 135

114 HHA = X / Z

HHB = HHA

TGO = GT

JRV1 = -1

115 JRIV = JRIV + 1

IF(TLO = 100.0) 4115, 4116, 4116

4115 HAI = 0.00009 \times TLO + 0.025

HBI = 0.00015 \times TLO + 0.0075
GO TO 4117

4116 CONTINUE

HAI = 0.9057441 - TLO * 0.1534549E-01 + TLO * TLO * 0.6781323E-04
HBI = 0.4607232 - TLO * 0.7902984E-02 + TLO * TLO * 0.3464325E-04

4117 CONTINUE

N = 1
DHA(N) = PIV * (HHA - HAI)
HAI(N) = HHA + DHA(N)
DHB(N) = VIP * (HHB - HBI)
HBI(N) = HHB + DHB(N)
DTG(N) = TIP * (TGO - TLO)
TG(N) = (TGO + DTG(N))
DTL(N) = (T1 * DHA(N)) + (T2 * DHB(N)) + (T3 * DTG(N))
TL(N) = TLO + DTL(N)

7054 WRITE (IRITE, 50) JIRIV, TGO, TLO, HHA, HHB

7053 TTEG = 0.8 * TEG
TEGR = 1.2 * TEG

116 IF (TGO - TEGG) 117, 117, 119
117 TQ1 = TGO
HQ1 = JIRIV
IF (NNT - 215) 119, 118, 119
118 TS1 = HHB
119 IF (TTEG - TGO) 120, 120, 123
120 IF (TGO - TEG) 121, 121, 123
121 TQ2 = TGO
HQ2 = JIRIV
IF (NNT - 215) 123, 122, 123
122 TS2 = HHB
123 IF (JIRIV) 9123, 9123, 9122
9122 HHHA(JIRIV) = HHA
9123 BBJ = 0.6 * BJ
BJJ = 1.34 * BJ
IF (BJ - HHA) 124, 124, 126
124 IF (HHA - BJJ) 125, 125, 126
125 TTQ1 = HHA
HM1 = JIRIV
126 IF (BJH - HHA) 127, 127, 129
127 IF (HHA - BJH) 128, 128, 129
128 TTQ2 = HHA
HM2 = JIRIV
129 N = N + 1

1400 CONTINUE

HAI = 0.9057441 - TNL(N-1) * 0.1534549E-01 + TNL(N-1) * TNL(N-1) * 0.6781323E-04
HBI = 0.4607232 - TNL(N-1) * 0.7902984E-02 + TNL(N-1) * TNL(N-1) * 0.3464325E-04

4130 CONTINUE

DHA(N) = PIV * (HAI(N-1) - HAI)
DHB(N) = VIP * (HHB(N-1) - HBI)

903 DHAM = 0.5 * (DHA(N) + DHA(N-1))
DHBM = 0.5 * (DHB(N) + DHB(N-1))
DTGN = TIP * (TG(N-1) - TL(N-1))
DTGM = 0.5 * (DTG(N) + DTG(N-1))
DTL(N) = ((T1*DHAM) + (T2*DHBM) + (T3*DTGM))

TL(N) = TLO + DTL(N)
TG(N) = TG0 + DTGM
HHA = HHA + DHAM
HHB = HHB + DHBM
TGO = TGN
TL0 = TL(N)

IF(TGO < 200.0) I = 130, 130, 115

DO 9126 IIR = 1, JRI
IF(BJ - HHHA(IIR)) 9124, 9124, 9126
9124 IF(HHHA(IIR) - BJ) 9125, 9125, 9126
9125 I = 1
9126 CONTINUE
IF(I) 9127, 9127, 9132
9127 DO 9131 IIR = 1, JRI
IF(BJ - 0.01 - HHHA(IIR)) 9129, 9129, 9131
9129 IF(HHHA(IIR) - BJ) 9130, 9130, 9131
9130 TTQ1 = HHHA(IIR)
HM1 = JRI
9131 CONTINUE
9132 CONTINUE
CMQ = (TTQ1 - TTQ2) / (HM1 - HM2)
CQ = (TTQ1 - (CMQ * HM1))
HP = (TEG - CQ) / CMQ
IF(I) 9135, 9135, 9136
9133 HHP = HM1
GO TO 9135
9134 CMQ = (TTQ1 - TTQ2) / (HM1 - HM2)
CQ = (TTQ1 - (CMQ * HM1))
HHP = (BJ - CQ) / CMQ
9135 IF(NNT - 200) 131, 131, 132
131 HP1 = HP
HHP1 = HHP
GO TO 111
132 IF(NNT - 215) 133, 133, 134
133 HP2 = HP
HHP2 = HHP
CMQ = (TQ1 - TQ2) / (TS1 - TS2)
CQ = TQ1 - (CMQ * TS1)
BH = (TEG - CQ) / CMQ
GO TO 111
134 HP3 = HP
HHP3 = HHP
GO TO 111

C  INTERPOLATION METHOD TO CALCULATE HEIGHT OF PACKING
C
CMP1 = 0.1 * (HP3 - HP2)
CP1 = HP1 - (CMP1 * 200.0)
CMP2 = 0.1 * (HHP3 - HHP2)
CP2=HHPl-(CMP2*200.0)
EXT=(CP2-CP1)/(CMP1-CMP2)
IF(EXT=EXMIN) 136,136,137
136 WRITE (IRITE,52)
   EXT=EXMIN
   GO TO 139
137 IF(EXT=EXMAX) 139,139,138
138 WRITE (IRITE,53)
   EXT=EXMAX
139 HEIGHT=(CMP1*EXT+CP1)
   IF(HEIGHT=HTMAX) 61,61,140
140 WRITE (IRITE,55)
   HEIGHT=HTMAX
   CC1=0.62*(138.45/105.3)*(HEIGHT*1.2+1.0)*((DQ+10.0)**2.19)+1.0585*0.785*DQ*DQ*HEIGHT
   AJA(I)=Z*BJ
   QUENCH UNIT HEAT EXCHANGER DESIGN
   HEAT=(((RT/(RT+1.0))*AQ*RTLIQ)+X-(Z*BJ))*53.5)+(((1.0/(RT+1.0))*AQ*RTLIQ)+X-(Z*BJ))*43.4)
   RW=(HEAT/30.0)
   DELT1=EXT-103.0
   DELTM=(DELT1-40.0)/(ALCG(DELT1/40.0))
   AREA=HEAT/(100.0*DELM)
   CC2=336.2*((AREA+100.0)**0.46)
   ST=(0.006*((RTLIQ*AQ)+(2.0*X))+(Z*BH)))
   IF(ST-1000.0) 141,141,142
141 CC3=(14.14*(ST**0.66)>GO TO 899
142 CC3 = 1147.0*(ST/1000.0)**0.66)
   GO TO 899
899 FA=7.691E—4*((AQ*RTLIQ)+(2.0*X)-(Z*(BJ+BH)))
   CC4 = 275.0*(FA**0.582)
   CC=CC1+CC2+CC3+CC4
   I=1
   TG(I)=200.0
   KTIM=1
   CONDENSER DESIGN
   CALCULATION OF PHYSICAL PROPERTIES
143 DO 144 N=1,9
   VIC(N)=VIS(N)*(((TG(I)+460.0)/739.8)**1.5)*((411.0+1.47*TBB(N))/
   (((TG(I)+460.0)/1.8)+1.47*TBB(N))
   CP(N)=(AA(N)+B(N))*0.001*(((TG(I)+460.0)/1.8)+C(N)*1.0E-06*(((TG(I)+
   1 460.0)/1.8)*(((TG(I)+460.0)/1.8)))/AMW(N)
144 THK(N)=VIC(N)*2.42*(CP(N)*(2.48/AMW(N)))
   IF(I-2) 145,148,160
145 GS(I)=(AI(I)+BB(I)*AJ(I)+AJA(I)+AI+EK+F+G+D)
   AM(I)=AI(I)/AMW(I)
   AJM(I)=AJ(I)/AMW(I)
   AJAM(I)=AJA(I)/AMW(I)
   BM(I)=BB(I)/AMW(I)
A\text{IM} = A1/\text{AMW}(5)

\text{EM} = EK/\text{AMW}(6)

\text{FM} = F/\text{AMW}(7)

\text{DM} = D/\text{AMW}(8)

\text{GM} = G/\text{AMW}(9)

\text{GGM}(I) = (A\text{IM}1) + BM(I) + AJM(I) + AJAM(I) + A\text{IM} + E\text{M} + F\text{M} + D\text{M} + G\text{M}

\text{NPOT} = 1

146 \text{RM}1 = 2.42 * (\text{AM}\text{I}1 * \text{VIC}(1) * \text{SQRT}(\text{AMW}(1))) + (\text{A}\text{JM}(I) * \text{VIC}(2) * \text{SQRT}(\text{AMW}(2))) + (\text{AJM}(I) * \text{VIC}(3) * \text{SQRT}(\text{AMW}(3))) + (\text{BM}(I) * \text{VIC}(4) * \text{SQRT}(\text{AMW}(4))) + (\text{A}\text{IM} * 2 \text{VIC}(5) * \text{SQRT}(\text{AMW}(5))) + (\text{EM} * \text{VIC}(6) * \text{SQRT}(\text{AMW}(6))) + (\text{FM} * \text{VIC}(7) * \text{SQRT}(\text{AMW}(7))) + (\text{DM} * \text{VIC}(8) * \text{SQRT}(\text{AMW}(8))) + (\text{GM} * \text{VIC}(9) * \text{SQRT}(\text{AMW}(9)))

\text{NPOT} = 1

147 \text{VA} = (A1 * 74.0) + (B1 * 44.2) + (A1 * 63.8) + (A1 * 106.2) / (A1 + B1)

148 \text{A}(I) = \text{A}(I-1)

\text{BB}(I) = \text{BB}(I-1)

\text{AJ}(I) = \text{AJ}(I-1)

\text{AJA}(I) = \text{AJA}(I-1)

\text{AM}(I) = \text{AM}(I-1)

\text{BM}(I) = \text{BM}(I-1)

\text{AJM}(I) = \text{AJM}(I-1)

\text{AJAM}(I) = \text{AJAM}(I-1)

\text{GS}(I) = \text{GS}(I-1)

\text{GGM}(I) = \text{GGM}(I-1)

\text{RM}(I) = \text{RM}(I-1)

\text{NPOT} = 2

\text{GO TO 146}

149 \text{DMV}(I) = \text{GS}(I) / 1.125
\[\text{RE} = \text{DMV(I)} \times 0.082 / \text{PMEU}\]
\[\text{PR} = ((\text{SPHT} \times \text{PMEU}) / \text{THERMI})^{0.33}\]
\[\text{HJ} = 0.3842 \times (\text{RE}^{0.5401})\]
\[\text{HG} = (HJ \times \text{PR} \times \text{THERMI})^{0.082}\]
\[\text{GK} = (\text{HO} \times \text{PR} \times \text{PR}) / (\text{RM(I)} \times \text{SC})\]
\[\text{TF} = 105.0\]
\[\text{WT} = \text{EXWT}\]
\[\text{NUN} = 1\]

**ITERATION FOR HEAT AND MASS BALANCE EQUATION**

\[\text{SL} = 220.0 \times (\text{TF} - \text{WT})\]
\[\text{PC} = ((\text{AM(I)} + \text{AJM(I)} + \text{AJAM(I)}) + (0.9 \times (\text{BB(I)} / 42.0))) / \text{GGM(I)}\]
\[\text{CALL VPRESS(PPA(I),PPJ(I),PPN(I),TG(I),I)}\]
\[\text{PBM} = ((1.0 - \text{PC}) - (1.0 - \text{PF})) / (\text{LOG}(1.0 - \text{PC}) / (1.0 - \text{PF}))\]
\[\text{S2} = \text{HO} \times (\text{TG(I)} - \text{TF}) + (\text{GK} \times 58.7 \times 225.0 \times (\text{PC} - \text{PF}) / \text{PBM})\]
\[\text{SS1} = 0.75 \times \text{S1}\]
\[\text{SS2} = 1.25 \times \text{S1}\]
\[\text{IF(S1-S2) 151,151,153}\]
\[\text{IF(S2-SS2) 152,152,153}\]
\[\text{CONTINUE 152}\]
\[\text{IF(NUN-I) 154,154,164}\]
\[\text{PR} = 0.1\]
\[\text{TF} = \text{TF} + \text{PP1}\]
\[\text{GO TO 150}\]
\[\text{RU(I)} = (\text{S1} + \text{S2}) / 2.0\]
\[\text{Q1(I)} = 0.0\]
\[\text{RESU(I)} = 1.0 / \text{RU(I)}\]
\[\text{CALL VPRESS(PPA(I),PPJ(I),PPN(I),TG(I),I)}\]
\[\text{SUM} = 0.0\]
\[\text{I} = \text{I} + 1\]
\[\text{TG(I)} = \text{TG(I-1)} - 20.0\]
\[\text{JTOP} = 20\]
\[\text{CALL VPRESS(PPA(I),PPJ(I),PPN(I),TG(I),I)}\]
\[\text{DEL(I)} = \text{PPA(I-1)} - \text{PPA(I)}\]
\[\text{DELJ(I)} = \text{PPJ(I-1)} - \text{PPJ(I)}\]
\[\text{DELN(I)} = \text{PPN(I-1)} - \text{PPN(I)}\]
\[\text{AMR(I)} = (\text{DEL(I)} \times \text{AM(I-1)}) / \text{PPA(I-1)}\]
\[\text{ACMR(I)} = (\text{DELJ(I)} \times \text{AJM(I-1)}) / \text{PPJ(I-1)}\]
\[\text{ANMR(I)} = (\text{DELN(I)} \times \text{AJAM(I-1)}) / \text{PPN(I-1)}\]
\[\text{AM(I)} = \text{AM(I-1)} - \text{AMR(I)}\]
\[\text{AJM(I)} = \text{AJM(I-1)} - \text{ACMR(I)}\]
\[\text{AJAM(I)} = \text{AJAM(I-1)} - \text{ANMR(I)}\]
\[\text{IF(KTIM-I) 157,157,158}\]
\[\text{HT} = (\text{ACMR(I)} \times 11500.0)\]
\[\text{BM(I)} = \text{BM(I-1)} - \text{ACMR(I)}\]
\[\text{GO TO 159}\]
\[\text{BM(I)} = \text{BM(I-1)}\]
\[\text{HT} = 0.0\]
\[\text{AI(I)} = \text{AM(I)} \times 58.0\]
\[\text{AJ(I)} = \text{AJM(I)} \times 60.0\]
\[\text{AJAM(I)} = \text{AJAM(I-1)} \times 102.0\]
\[\text{BB(I)} = \text{BM(I)} \times 42.0\]
\[\text{HL(I)} = ((\text{AMR(I)} \times 13050.0) + (\text{ACMR(I)} \times 11400.0) + (\text{ANMR(I)} \times 17034.0) + (\text{AI(I)} *}
1CP(I)*JTOP)+(AJ(I)*CP(2)*JTOP)+(AJA(I)*CP(3)*JTOP)+(BB(I)*CP(4)*
2JTOP)+(AI*CP(5)*JTOP)+(EK*CP(6)*JTOP)+(F*CP(7)*JTOP)+(N*CP(8)*JTOP
.3I+(G*CP(9)*JTOP))=HT
Q(I)=Q(I-1)+HL(I)
WT=(EXWT-(Q(I-1)/WR))
GS(I)=AI+BB(I)+AJ(I)+AJA(I)+AI+EK+F+D+G
GGM(I)=AM(I)+BM(I)+AJM(I)+AJAM(I)+EM+FM+GM+DM+AIM
RM(I)=GS(I)/GGM(I)
DMV(I)=GS(I)/1.125
GO TO 143
160 NPOT=3
GO TO 146
161 RE=(0.082*DMV(I))/PMEU
PR=((SPHT*PMEU)/THERMK)**0.33
HJ=0.3842*(RE**0.5401)
HO=0.082
GK=(HJ*PR/THERMK)/0.082
NUNI=NUNI+1
TF=90.0
IF(NUNI-2) 150,163,162
162 TF=60.0
GO TO 150
163 TF=80.0
GO TO 150
C
C NUMERICAL INTEGRATION TO CALCULATE EXCHANGER AREA
C
164 RU(I)=(S1+S2)/2.0
RESU(I)=1.0/RU(I)
RESUM(I)=(RESU(I)+RESU(I-1))/2.0
VALUE(I)=(HL(I)*RESUM(I))
SUM=SUM+VALUE(I)
C
FINAL ADJUSTMENTS FOR STEPWISE PROCEDURE
C
BBB=BM(I)*0.1+2.0
IF(BM(I)-BBB) 165,165,155
165 BBBB=0.1*BM(I)+0.005
IF(BM(I)-BBBB) 167,167,166
166 VP=PPJ(I)-(BM(I)-(BM(I)*0.1))*PPJ(I)/AJM(I)
TG(I)=(-4864.607*1.8)/(ALOG(VP/249327.8))-460.0
GO TO 156
167 IF(WT-73.5) 169,169,290
290 IF(KTIM-1) 168,168,169
168 I=I+1
TG(I)=TG(I-1)-5.0
JTOP=5
KTIM=KTIM+1
GO TO 156
169 CC1=672.5*((SUM+100.0)**0.46)
C
ABSORPTION UNIT DESIGN
GMOL(1)={AM(1)+BM(1)+AJM(1)+AJAM(1)+AIM+EM+FM+DM+GM}
ECOAT=A(1)-A(1)
ECOAC=AJM(I)-AJM(I) - (60.05*(BM(I)-BM(I))
ECOAN=(BB(1)-BB(I))*(60.05*(BM(I)-BM(I))+(AJA(I)-AJA(I))

TKT=(0.99*BB(I))
TAC=1.43*TKT
FOAN=(TKT*TAC)
ANST=(FOAN+ECOAN)
ACST=RT*ANST
ACRATE=(ACST-ECOAC)

TP=TG(I)
AM(I)=AM(I)
BM(I)=BM(I)
AJM(I)=AJM(I)
AJAM(I)=AJAM(I)
I=0

170 I=I+1
IF(I<9) 171,178,178

CALCULATION OF OPERATING LINE

171 NN=NA(I)
IF(NN) 172, 172, 173
172 GL(I)=GMOL(1)
ANA=0.0
GO TO 9173
173 ANAL=NN
ANA=ANA/100.0
GL(I)=GMOL(I) - (ANA*AM(I)) - BM(I)

9173 AMN(I)=(AM(I)-(ANA*AM(I)))
YA(I)=AMN(I)/GL(I)
IF(NN<99) 175, 174, 174
174 FOAT=58.08*(AM(I)-(GL(I)*YA(I)))
XAI(I)=0.0
AAM=0.0
DLM(I)=(ACRATE/60.05)+BM(I)
IF(1PRINT-1) 170, 170, 7170
7170 WRITE(1RITE,50) NN, GL(I), YA(I), DLM(I), XA(I), AAM
GO TO 170
175 IF(NN) 176, 176, 177
176 AAM=0.0
DLM(I)=DLM(I-1)+(GL(I)-GL(I-1))-BM(I)
XA(I)=(DLM(I)-DLM(I-1))/DLM(I)
IF(1PRINT-1) 170, 170, 7176
7176 WRITE(1RITE,50) NN, GL(I), YA(I), DLM(I), XA(I), AAM
GO TO 170
177 AAM=(1.0-ANA)*100.0
DLM(I)=DLM(I-1)+(GL(I)-GL(I-1))
XA(I)=(GL(I)-GL(I))/DLM(I)
IF(1PRINT-1) 170, 170, 7177
7177 WRITE(1RITE,50) NN, GL(I), YA(I), DLM(I), XA(I), AAM
GO TO 170
178 YAI(I)=YA(I)
XX(I)=XA(I)
I=1

\[ XH(1) = XX(1) \]
\[ YH(1) = \{1.3172E-4 \times XH(1) + (0.477194 \times XH(1) \times XH(1))\} \]
\[ YM = 0.5 \times \{YY(1) - YH(1)\}\]

179 I=I+1

\[ YY(I) = YY(I-1) - YM \]

IF(YY(I)-YA(I)) 185,185,180.

180 DD 183 NRIP=2,9

IF(YY(I)-YA(NRIP-1)) 181,183,183

IF(YY(I)-YA(NRIP-2)) 183,182,182

182 P1=YA(NRIP-2)

QO1=XA(NRIP-2)
P2=YA(NRIP-1)

QO2=XA(NRIP-1)

183 CONTINUE

\[ DM1 = \frac{(QO2-QO1)}{(P2-P1)} \]
\[ XX(I+1) = \{DM1 \times YY(I) + (QO2-DM1 \times P2)\} \]
\[ XH(I+1) = XX(I+1) \]

IF(XH(I+1)-0.0025) 185,185,184

184 \[ YH(I) = \{1.3172E-4 \times XH(I+1) + (0.477194 \times XH(I+1) \times XH(I+1))\} \]

YM=0.5*(YY(I)-YH(I))

GO TO 179

185 N=1

TT=TP

CCC=GM+FM+DM+AIM+EM

CAK=0.056*CCC

ANK=0.01718*CCC

IF(CAK-AM(1)) 186,186,187

186 AJM(1)=CAK

187 IF(ANK-AM(1)) 188,188,9189

188 AJAM(1)=ANK

9189 GR(N) = CCC+AJM(1)+AJAM(1)

C COLUMN DIMENSIONS

GMN(1) = (AM(1)+BM(1)+AJM(1)+AJAM(1)+CCC)

GSN(1) = ((AM(1)*58.08)+(BM(1)*42.0)+(AJM(1)*60.05)+(AJAM(1)*102.09)

1+(FM*2.0)+(EM*1.0)+2.18.0) + (FM*16.0)+(EM*39.0))

AMM=GSN(1)/GMN(1)

DENV=2.43E-3*AMM

VG=0.15*SQRT((65.3-DENV)/DENV)

SV=3.4/SQRT(DENV)

SA=GSN(1)/3600.0*DEI

DM1=SQRT((GMN(1)*0.1456)/VG)

DIA=NDIA

IF(DIA-RDIA-0.5) 189,189,190

189 DIA=RDIA+0.5

GO TO 191

190 DIA=RDIA+1.0

191 HOLD=(0.1742*CIA*DIA)

ALPHA=GR(1)*48.04/ACRATE
BETA=HOLD*337.5/GR(1)
QP=((-1.6)-(ALPHA*(BETA+1)))
PQ=(0.5*(1.0+(ALPHA*BETA)))*ALPHA
Z1=0.5*-(QP*SQRTP(QP*QP-(4.0*PQ)))
Z2=0.5*-(QP*SQRTP(QP*QP-(4.0*PQ)))
Y0=8M(1)/GR(1)
Y2=0.01*Y0
AH=HOLD
Y1=(Y2*{(AH*270.0)+(ACRATE/60.05)+(0.8*GR(1))})/(0.6*{(AH*270.0)+1(ACRATE/60.05)+(0.8*GR(1))})
PLATES=ALOG((Y0*{(1.0/Z1)-(1.0/Z2)})/(Y1-(Y2/Z2)))/ALOG(1.0/Z1)
NPLATE=1FIX(PLATES)
PPP=NPLATE
IF(PLATES-PPP)) 193,193,192
PLATES=PPP+1.0
193 CC2=1(PLATES*1.67+5.0)*0.3943*((DIA+10.0)**2.35)+1(PLATES*0.1117*1((DIA+5.0)**3.45))
N=N+1
NRIV=1
194 IF(yy(N)-YA(1)) 206,206,195
195 DO 198 NRIP=2,9
196 IF(yy(N)-YA(NRIP-1)) 196,198,198
197 P1=YA(NRIP-2)
Q1=GL(NRIP-2)
P2=YA(NRIP-1)
QQ2=GL(NRIP-1)
198 CONTINUE
C
C ABSORPTION COLUMN PLATE HEAT EXCHANGER
C
DM1=(QQ2-QQ1)/(P2-P1)
GMOL(N)=(DM1*YY(N))+(QQ2-(DM1*P2))
AM(N)=GMOL(N)*YY(N)
ABAC(N)=AM(N-1)-AM(N)
BM(N)=0.0456*(0.543**N)*GR(1)
ABKT(N)=BM(N-1)-BM(N)
HLAC=ABAC(N)*19050.0
HLKT=ABKT(N)*119050.0
IF(N=199,201)
NRIV=NRIV+1
199 AJM(N)=AJM(N-1)
AJAM(N)=AJAM(N-1)
AMB=1(AHM(N-1)*6.36)+1(9.88*AJM(N-1))+18.3*AJAM(N-1)+4.79*BM(N-1)
1+6.95*GM)+6.35*FM)+6.34*DM)+(3.2*AIM)+(3.02*EM))/GMOL(N-1)
BMB=1(AHM(N-1)*43.7)+(26.78*AJM(N-1))+32.78*AJAM(N-1)+22.59*BM(N
1-1)-10.2*GM)+(1.81*FM)+(10.14*DM)+(18.41*AIM)+(28.21*EM))/(GMOL(N-
21)*1.0E+03)
CMB=1(-10.96*AM(N-1))-1(5.89*AJM(N-1))-1(1.13*AJAM(N-1))-17.19*B
M(N-1))+10.48*GM)+10.27*FM)+3.42*DM)+(18.41*AIM)+(8.54*EM))/(GMOL(N-
21)*1.0E+06)
TF1=1(TF+460.0))/1.8
IF(NRIV=3) 500,200,500
500 DELHA=GMOL(N-1)*(TF1-320.0)+1.8*(AMB+(BMB*(TF1+320.0)))*(CMB*(TF1*
1TF1=(TF1*320.0)+(102400.0))
TOTH(N)=(HLAC+HLKT+DELHA)
MT=1
AR=57.5*AM(MT)
RLIQ(MT)=FOAN+ACRATE+AR
MT=MT+1
RLIQ0(MT)=RLIQ(MT-1)-(ABAC(MT)*58.0)-(ABKT(MT)*44.0)
N=N+1
GO TO 194
200 DELHA=GMOL(N)*12.6*(AMB+(633.0*BMB)+(3.01E+5*CMB))
TOTH(N)=(HLAC+HLKT+DELHA)
RLIQ(N)=(RLIQ(N-1)-(ABAC(N)*58.0)-(ABKT(N)*44.0))
SLIQ=(RLIQ(N)+RLIQ(N-1))/2.0
DELT=N=TOTH(N)*2.0/SLIQ
EXLIQT=(85.0+DELT(N))
WT=73.0+(TOTH(N)/RWR)
DELT1=(EXLIQT-WT)
ALMTD=(DELT1-12.0)/ALOG(DELT1/12.0)
DNT=TOTH(N)/(1458.0*ALMTD)
JDIP=1.
N=N+1
GO TO 194
201 TOTH(N)=(HLAC+HLKT)
RLIQ(N)=(RLIQ(N-1)-(ABAC(N)*58.0)-(ABKT(N)*44.0))
SLIQ=(RLIQ(N)+RLIQ(N-1))/2.0
DELT(N)=TOTH(N)*2.0/SLIQ
IF(DELT(N)-5.0) 203,203,202
202 EXLIQT=(85.0+DELT(N))
WT=73.0+(TOTH(N)/RWR)
DELT1=(EXLIQT-WT)
ALMTD=(DELT1-12.0)/ALOG(DELT1/12.0)
TNN(N)=TOTH(N)/(1080.0*ALMTD*1.35)
DNT=TNN(N)+DNT
JDIP=JDIP+1
203 IF(TOTH(N)-4500.0) 206,204,204
204 IF(N=1) 205,206,206
205 N=N+1
GO TO 194
206 DNT=DNT*1.2
RDIP=JDIP
CC3=((RDIP*232.0)+(DNT*7.0))
CC=CC+CC1+CC2+CC3
RH=RW+WR+(RDIP*12500.0)
TAC=TAC+ACRATE
ACETONE COLUMN DESIGN
A(1)=(ECOAT+FOAT)
AJ(1)=ACST
AJA(1)=ANST
DW=(A(1)-(ABP*(A(1)+AJ(1)+AJA(1)))/(ATP-ABP)
WW=A(1)+AJ(1)+AJA(1)-DW
AD=ATP+DW
ACD=(1.0-ATP)*DW
AB=A(1)-AD  
ACB=AJ(1)-ACD  
ANB=AJA(1)  
NKIT=1

207 IF(NKIT-1) 208,209,208  
208 ANDM=0.0  
GO TO 210.  
209 ACB=WW*ACIDBP  
ANB=WW*1.0-ACIDBP  
ACD=DW*ACIDTP  
ANAD=AJA(1)-ANB  
AD=DW-ANAD-ACD  
ANDM=ANAD/102.09  
210 AFM=A(1)/58.08  
ACFM=AJ(1)/60.05  
ANFM=AJA(1)/102.09  
FM=AFM+ACFM+ANFM  
AFMF=AFM/FM  
ACFMF=ACFM/FM  
ANFMF=ANFM/FM  
FM = AFM + ACFM + ANFM  
ACMF=ACMF/FM  
ANDMF=ANDMF/FM  
BAM=AFM-ADM  
BJM=ACFM-ACDM  
BJAM=ANFM-ANDM  
WM=FM-DM  
ABM=BAM/WM  
ACBM=BJM/WM  
ANBM=BJAM/WM  
DD=DM*100.0/FM  
WD=WM*100.0/FM  
FD=100.0  
IF(NKIT-2) 211,249,249  
211 I=1  

CALCULATION OF STILL TEMPERATURE  

TA(I)=115.0  
212 CALL VPRESS(PPA(I),PPJ(I),PPN(I),TA(I),2)  
XP(I)=(PPA(I)*ABM+PPJ(I)*ACBM+PPN(I)*ANBM)  
IF(0.99-XP(I)) 213,213,215  
213 IF(XP(I)-1.01) 214,214,215  
214 ALPHLK=PPA(I)/PPJ(I)  
ALPHA=PPN(I)/PPJ(I)  
TEMST=TA(I)  
GO TO 216  
215 TA(I)=TA(I)+0.5  
GO TO 212  
216 TOT=50.0  
217 CALL VPRESS(PAA,PJA,PNP,TOT,2)
XR1 = (ADMF/PAA + ACDMF/PJA)

IF(0.99-XR1) 218, 218, 220

IF(XR1=1.01) 219, 219, 220

ALPHAB=PAA/PJA

TOPTM=TOT

GO TO 221

TDT=TOT+0.5

GO TO 217

ALPAV=SQRT(ALPHLK*ALPHAB)

XNM=(ALOG((ADMF/ACDMF)*(ACBM/ABM)))/ALOG(ALPAV) = 1.0

BV=-{(ALPAV*AFMF*(1.0+ALPHAH))+(ACFMF*(ALPAV+ALPHAH))*(ALPHAH*AMF)}

CV=ALPHAH*ALPAV

THETA=-(BV+SQRT((BV-BV-(4.0*AV*CV)))/(2.0*AV)

IF(1.0-THETA) 224, 224, 222

THETA = -(BV+SQRT((BV-BV-(4.0*AV*CV)))/(2.0*AV)

MINIMUM REFLUX RATIO

RR=((ALPHLK*ADMF)/(ALPHLK-THETA))+(ACDMF/THETA)-1.0

R(1)=1.0*RR

CALCULATION OF OPTIMUM REFLUX RATIO

DO 246 NNN=2,8

R(NNN)=R(NNN-1)+0.4*RR

OM=(R(NNN)*DD+FD)

VM=DD*(R(NNN)+1.0)

TA(I)=TEMST

TOT=TOPTM

AX(I)=ABM

ACX(I)=ACBM

ANX(I)=ANBM

AXP=PPA(I)*AX(I)

ACXP=PPJ(I)*ACX(I)

ANXP=PPN(I)*ANX(I)

AY(I)=AXP/XP(I)

ACY(I)=ACXP/XP(I)

ANY(I)=ANXP/XP(I)

IF(IPRINT-1) 225, 225, 7224

WRITE(RITE,60) AX(I), PPA(I), AXP, AY(I), TA(I)

WRITE(RITE,65) ACX(I), PPJ(I), ACXP,ACY(I)

WRITE(RITE,65) ANX(I), PPN(I), ANXP, ANY(I)

FEED PLATE CALCULATION

AX(I)=(VM/OM)*AY(I-1)+(WD*ABM)/OM

ACX(I)=(VM/OM)*ACY(I-1)+(WD*ACBM)/OM

ANX(I)=(VM/OM)*ANY(I-1)+(WD*ANBM)/OM

RRR=ABS((AX(I)/ACX(I))-(AFMF/ACFMF))

SSS=ABS((AX(I-1)/ACX(I-1))-(AFMF/ACFMF))
26/11/70 DESIGN

IF(RRR-SSS)226,227,227
226 JPIV=1
N=2
GO TO 229
227 JPIV=2
GO TO 241
229 T(A(N)=T(A(N-1))-5.0
230 CALL VPRESS(PPA(I),PPJ(I),PPN(I),TA(N),2)
XP(N)=PPA(I)*AX(I)+PPJ(I)*ACX(I)+PPN(I)*ANX(I)
IF(0.99-XP(N))231,231,232
231 IF(XP(N)-1.01)235,235,232
232 IF(N=2)233,233,234
233 N=N+1
GO TO 229
234 CMD=(XP(N-1)-XP(N))/(TA(N-1)-TA(N))
9234 C1=XP(N)-[CMD*TA(N)]
N=N+1
9235 T(A(N)=([1.0-C1]/CMD))
GO TO 230
235 T(A(1)=T(A(N))
AXP=(PPA(I)*AX(I))
ACXP=PPJ(I)*ACX(I)
ANXP=PPN(I)*ANX(I)
AY(I)=AXP/XP(N)
ACY(I)=ACXP/XP(N)
ANY(I)=ANXP/XP(N)
IF(ANY(I)-RMINJA)236,237,237
236 ANY(I)=0.0
237 IF(JPIV-1)238,238,9239
238 TEMPF=T(A(N)
9239 IF(IPRINT-1)7240,7240,7239
7239 WRITE(IRTRE,60)AX(I),PPA(I),AXP,AY(I),TA(N)
WRITE(IRTRE,65)ACX(I),PPJ(I),ACXP,ACY(I)
WRITE(IRTRE,65)ANX(I),PPN(I),ANXP,ANY(I)
7240 IF(AY(I)-RMAXA)239,242,242
239 IF(JPIV-1)225,225,240
240 I=I+1
241 AX(I)=(R(NNN)+1.0)*AY(I-1)/R(NNN)-ADMF/R(NNN)
ACX(I)=(R(NNN)+1.0)*ACY(I-1)/R(NNN)-ACDMF/R(NNN)
ANX(I)=(R(NNN)+1.0)*ANY(I-1)/R(NNN)
N=2
GO TO 229
C
C COLUMN DIMENSIONS

C 242 T(A(1)=T(A(1)+273.0
DENL=62.4*[(AB*0.797*[((508.0-TA(1))/215.0)**0.33]+ACB*1.05*[((5941.6-TA(1))/301.6)**0.33]+ANB*1.08*[((569.0-TA(1))/276.0)**0.33])/
2WW)
DENV=(WW*0.7605)/(WM*TA(1))
UU=0.15*SQR{(DENL-DENV)/DENV}
DIAB=SQR{(WW*(R(NNN)+1.0)*DM)/(WM*DENV*UU*2828.0)}
TOT=TOT+273.0
DENL=49.42*[((508.0-TOT)/215.0)**0.33]
DENV = (DW * 0.7605) / (DM * TOT)
UU = 0.15 * SQRT (DENL - DENV) / DENV
DIAT = SQRT ((R (NNN) + 1.0) * DW / (DENV * 28280 * UU))
DIA = 0.5 * (CIAB + DIAT)
NDIA = FIX (DIA)
RDIA = DIA
IF (DIA - RDIA - 0.5) 243, 243, 244.
243 DIA = RDIA + 0.5
GO TO 245
244 DIA = RDIA + 1.0
245 RNUM = FLOAT (1 - 1)
RNUM1 = 3.34 * RNUM
SNUM = 0.2236 * RNUM
CC1 = (RNUM1 + 5.0) * 1.211 * ((DIA + 10.0) ** 2.1) + (SNUM * (DIA + 5.0) ** 3.45)
DELH1 = 225.0 * DW * (R (NNN) + 1.0)
TOPT = (TOT + 1.8) - 460.0
DELH2 = DW * 0.55 * (TOPT - 86.0)
WAT1 = (DELH1 + DELH2) / 46.0
WT2 = 74.0 * (DELH2 / WAT1)
DEL1 = (TOPT - WT2)
DELT1 = (DEL1 - 12.0) / ALOG (DELT1 / 12.0)
AREA = DEL1 / (100.0 * DELTM)
CC2 = 336.2 * ((AREA + 100.0) ** 0.46)
WT3 = WT2 + (DELH2 / WAT1)
DELT1 = 133.0 - WT2
DELT2 = 133.0 - WT3
DELTM = (DELT1 - DELT2) / ALOG (DELT1 / DELT2)
AREA = DELH1 / (DELTM * 150.0)
CC3 = 336.2 * ((AREA + 100.0) ** 0.46)
TEMPF = TEMPF + 1.8 + 32
DELH4 = (TA (1) + AJ (1) + AJ (1)) * 0.57 * (TEMPF - 32.0)
DELH5 = WM * 0.47 * (TA (1) - 32.0)
QR = (DELH1 + DELH4 + DELH5 - DELH3)
AREA = QR / 12000.0
CC4 = 336.2 * ((AREA + 100.0) ** 0.46)
SM1 = QR / 832.0
DELH6 = (0.47 * (RT + 1.0) * Z * BH * (TA (1) - 95.0))
WAT2 = (DELH6 / 46.0)
DELT1 = (TA (1) - 120.0)
DELTM = (DELT1 - 21.0) / ALOG (DELT1 / 21.0)
AREA = DELH6 / (DELTM * 50.0)
CC5 = 336.2 * ((AREA + 100.0) ** 0.46)
ST2 = 0.00671 * DW * (R (NNN) + 1.0)
CC7 = 14.22 * ((ST2) ** 0.66)
CR = (WAT1 * WAT2) * 0.011 + (SM1 ** 4.4)
CRA (NNN - 1) = CR
COST (NNN - 1) = (CC1 + CC2 + CC3 + CC4 + CC5 + CC7) + CR
CONTINUE
OPTC = COST (1)
CRAC = CRA (1)
OPTR = R (2)
DO 248, NNN = 2, 7
26/11/70 DESIGN

IF (COST(NNN)-OPTC) 247,248,248
247 OPTC= COST(NNN)
CRAC=CRA(NNN)
OPTR=R(NNN+1)
248 CONTINUE
OPTC=OPTC-CRAC
IF (PRINT-1) 4248,4247,4247
4247 WRITE(IRITEN,70) OPTR
4248 SG=((A(1)*0.78)+(AJ(1)*1.048)+(AJA(1)*1.081))/(A(1)+AJ(1)+AJA(1))
STI=0.36*(A(1)+AJ(1)+AJA(1))/SG
CC6=1349.0*STI
FRATE=Z-DW
ST4=(FRAT*76.37)
CC8=20.67*(((5.0E-4*ST4)+100.0)**1.01)
H4=((H3+(A(1)*0.54)+(0.505*AJA(1))+(0.434*AJA(1)))*1.8*(TEMPF-40.0)
1)/1.0E6
CC9=3373.0*(H4**0.786)
CC=CC+OPTC+CC6+CC8+CC9
FW=(WW-((RT+1.0)*Z*BH))
ACETIC ANHYDRIDE COLUMN
.A(1)=(FW/WW)*AB
.AJ(1)=(FW/WW)*ACB
.AJAL(1)=(FW/WW)*ANB
EXAC=(Z*BHAJ(1)-ACB
XF=AJJ(1)/(A(1)+AJ(1)+AJA(1))
DW=FW*(X FCIDBP)/(ACIDTP-ACIDBP)
WW=FW-DW
NKIT=NKIT+1
GO TO 207
249 XF=ACMF
XD=ACDMF
XX=ACBM
YD=XD
XM= XF
YM=(-6.2E-4+2.59104*XM-2.84138*XM*XM+1.2537*XM*XM*XM)
MINIMUM REFLUX RATIO
CMD=ABS((YD-YM)/(XD-XM))
RR=CMD/(1.0-CMD)
R(1)=1.0*RR
CALCULATION OF OPTIMUM REFLUX RATIO
DO 276 NNN=2,8
R(NNN)=R(NNN-1)+0.4*RR
ON=R(NNN)*DD
VN=ON+DD
I=1
PLATE TO PLATE CALCULATIONS
N=1
YAN(I)=YD
IF(YAN(I)-0.985) 250,251,251
250 XAN(I)=10.00157+0.46285*YAN(I)-0.39462*(YAN(I)*YAN(I))\+0.94681*(YAN(I)**3))
   GO TO 9251
251 XAN(I)=(YAN(I)-0.461)/0.54
9251 IF(IPRINT=I) 252,252,7252
7252 WRITE(IRITE,80) XAN(I),YAN(I),N
252 I=I+1
N=N+1
   YAN(I)=((R(NNN)/(R(NNN)+1.0))*XAN(I-1)+XD/(R(NNN)+1.0))
   IF(YAN(I)-0.985) 253,254,254
253 XAN(I)=10.00157+0.46285*YAN(I)-0.39462*(YAN(I)*YAN(I))\+0.94681*(YAN(I)**3))
   GO TO 5255
254 XAN(I)=(YAN(I)-0.461)/0.54
9255 IF(IPRINT=I) 255,255,7255
7255 WRITE(IRITE,80) XAN(I),YAN(I),N
255 IF(XAN(I)-XF) 256,256,256
256 OM=ON+FD
   VM=VN
257 I=I+1
   YAN(I)=(((OM/VM)*XAN(I-1))-((WD*XW)/VM))
   IF(YAN(I)-0.228) 258,258,259
258 XAN(I)=(YAN(I)/2.28)
   GO TO 260
259 XAN(I)=(0.00157+0.46285*YAN(I)-0.39462*(YAN(I)*YAN(I))\+0.94681*(YAN(I)**3))
260 IF(XAN(I)-XF) 262,262,261
261 N=N+1
   IF(IPRINT=I) 257,257,7261
7261 WRITE(IRITE,80) XAN(I),YAN(I),N
   GO TO 257
262 TP=110.0
263 CALL VPRESS(ZPA,ZPJ,ZPN,TP,2)
   RX1=ADMF/ZPA
   RX2=ACDMF/ZPJ
   RX3=ANDMF/ZPN
   RX4=(RX1+RX2+RX3)
   IF(RX4<0.99) 265,265,264
264 IF(RX4<1.01) 266,266,265
265 TP=TP+0.5
   GO TO 263
266 TB=130.0
267 CALL VPRESS(ZPA,ZPJ,ZPN,TP,2)
   RX4=ZPJ*ACBM+ZPN*ANBM
   IF(RX4<0.99) 269,269,268
268 IF(RX4<1.01) 270,270,269
269 TB=TB+0.5
   GO TO 267
270 CONTINUE
C COLUMN DIMENSIONS
DESIGN

26/11/70

C

DENL= (ACB*1.05*(((594.6-(TB+273.0))/301.6)*0.33)) + (ANB*1.08*(((1569.0-(TB+273.0))/276.0)*0.33)) * 62.4/WW
DENV=WW*0.7605/(WW*(TB+273.0))
UU=0.15*SQRT ((DENL-DENV)/DENV)
DAB=SQRT(((WW*(R(NNN)+1.0)*DM)/(WW*DENV*2828.0*UU)))
DENV=DW*0.7605/(DM*(TB+273.0))
UU=0.15*SQRT ((DENL-DENV)/DENV)
DIA=0.5*(DAB+DIAT)
NDIA=IF (DIA+RDIA=0.5) 271, 272, 272
271 DIA=RDIA+0.5
GO TO 273
272 DIA=RDIA+1.0
GO TO 274
273 IF (DIA=5.0) 274, 274, 275
274 QP=0.62
GO TO 9275
275 QP=0.92
GO TO 273
9275 TRT=FLOAT (N-1)
CCL=((12.27+TP+5.0)*1.315*QP*1.0+10.0)*TRT*15.0**3.45)
TP=TP*1.8+32.0
DELH1=DW*0.54*(TP-104.0)
DELH2=174.15*(R(NNN)+1.0)*DW
WAT=(DELH1+DELH2)/46.0
WAT1=WAT
WT2=74.0*DELH1/WAT
DELT1=(TP-WT2)
DELTM=(DELT1-30.0)/ALOG(DELT1/30.0)
AREA=DELH1/(DELTM*50.0)
CC3=336.2*(AREA+100.0)**0.46)
WT3=WT2+(DELH2/WAT)
DELT1=(TP-WT2)
DELT2=(TP-WT3)
DELTM=(DELT1-DELT2)/ALOG(DELT1/DELT2)
AREA=DELH2/(DELTM*50.0)
CC5=336.2*(AREA+100.0)**0.46)
TB=TB+1.8+32.0
DELH1=FW*C.47*(TA(1)-32.0)
DELH3=DW*0.54*(TP-32.0)
DELH4=WW*0.434*(TB-32.0)
QR=(DELH2+DELH3+DELH4-DELH1)
AREA=QR/12000.0
CC6=336.2*(AREA+100.0)**0.46)
SM2=QR/832.0
DELH5=WW*0.434*(TB-86.0)
WAT=DELH5/46.0

(302)
\[ WAT = WAT + WAT1 \]
\[ DELT1 = TB - 120.0 \]
\[ DELTM = (DELT1 - 12.0) / \log_{10}(DELT1 / 12.0) \]
\[ AREA = DELT1 / (DELT1 * 50.0) \]
\[ CC2 = 336.2 \times (\text{AREA} + 100.0) \times 0.46 \]
\[ ST3 = 0.0055 \times DW \times (R(NNN) + 1.0) \]
\[ CC4 = 14.22 \times (ST3 \times 0.66) \]
\[ CR = [WAT \times 0.011] + (SM2 \times 4.4) \]
\[ CRB(NNN - 1) = CR \]
\[ COST(NNN - 1) = (CC1 + CC2 + CC3 + CC4 + CC5 + CC6) + CR \]

276 CONTINUE

OPTC = COST(1)
CRAN = CRB(1)
OPTR = R(2)
DO 278 NNN = 2, 7
IF (COST(NNN) - OPTC) 277, 278, 278

277 OPTC = COST(NNN)
CRAN = CRB(NNN)
OPTR = R(NNN + 1)

278 CONTINUE

OPTC = OPTC - CRAN
IF (IPRINT - 1) 4279, 4278, 4278

4278 WRITE (IWRITE, 90) OPTR
4279 CONTINUE

FRAC = TAC + EXAC - DW
ST5 = 58.93 \times FRAC
ST6 = 56.01 \times WW
CC7 = 54.11 \times ((ST5 / 4.0) \times 0.57)

C OPERATING COST AND PROFIT
C

CR2 = 0.01887 \times 4.4 \times FRAC
ST6 = ST6 / 6.0E3
IF (ST6 > 100.0) 279, 279, 280

279 CC8 = 3267.0 \times \sqrt{ST6}
GO TO 281

280 CC8 = 155.0 \times (ST6 + 100.0) \times 1.01
281 CC = CC + OPTC + CC7 + CC8
CR1 = 0.011 \times RW
CR = CR1 + CR2 + CRAC + CRAN
CD = (0.5 \times CC) \times CR
PROFIT = (WW \times VVJA) - (CO + (FRAT \times VVA) + (FRAC \times VVJ))
CONV = CONV / 100.0
RETURN
END
SUBROUTINE VPRESS (PAP, PJP, PNP, TTT, K)
C THIS SUBROUTINE CALCULATES VAPOUR PRESSURE OF ACETONE, ACETIC ACID &
C AC. ANHYDRIDE FOR GIVEN TEMP (IF K=1, GIVEN TEMP IS IN DEG F, K=2 TEM
C P IS IN DEG C.)
GO TO (1,2), K
1 TTR = 1.8 / (TTT + 460.0)
GO TO 3
2 TTR = 1.0 / (TTT + 273.0)
3 PAP = 100000.1 * EXP(-3799.231 * TTR)
PJP = 249327.8 * EXP(-4864.607 * TTR)
PNP = 448095.7 * EXP(-5355.908 * TTR)
RETURN
END
D. 3 Error Messages

The following errors cause the error message to be printed. However, the program allows the design to be continued taking the maximum (or minimum) specified value.

1. *** EXIT LIQUID TEMPERATURE IS TOO LOW. CALCULATION CONTINUES ***.

2. *** EXIT LIQUID TEMPERATURE IS TOO HIGH. CALCULATION CONTINUES ***.

3. *** LINEAR INTERPOLATION METHOD FAILED TO FIND HEIGHT OF PACKING. MAXIMUM SPECIFIED HEIGHT IS TAKEN ***.

All above three error messages are generated during the quench unit design calculations.
APPENDIX D (Continued)

D. 4  Program Output

(with I OPHN = 0. and I PRINT = 0)
<table>
<thead>
<tr>
<th>ITERATION NUMBER</th>
<th>ACETONE CONVERSION</th>
<th>QUENCH UNIT INLET GAS TEMPERATURE (DEG F)</th>
<th>QUENCH UNIT EXIT GAS TEMPERATURE (DEG F)</th>
<th>ACID/ANHYDRIDE RATIO IN RECYCLE</th>
<th>WATER RATE TO CONDENSER (LBS/HR)</th>
<th>YEARLY PROFIT (£/YEAR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.25000000</td>
<td>950.0000</td>
<td>300.0000</td>
<td>1.0000000</td>
<td>778000.000</td>
<td>1083227.18</td>
</tr>
<tr>
<td>1</td>
<td>0.25999981</td>
<td>950.0000</td>
<td>300.0000</td>
<td>1.0000000</td>
<td>778000.000</td>
<td>1066063.10</td>
</tr>
<tr>
<td>2</td>
<td>0.23999965</td>
<td>959.9998</td>
<td>300.0000</td>
<td>1.0000000</td>
<td>778000.000</td>
<td>1098276.10</td>
</tr>
<tr>
<td>3</td>
<td>0.23999935</td>
<td>959.9998</td>
<td>300.0000</td>
<td>1.0000000</td>
<td>778000.000</td>
<td>1100254.75</td>
</tr>
<tr>
<td>4</td>
<td>0.23999923</td>
<td>959.9998</td>
<td>298.9976</td>
<td>1.0000000</td>
<td>778000.000</td>
<td>1099997.37</td>
</tr>
<tr>
<td>5</td>
<td>0.23999906</td>
<td>959.9998</td>
<td>298.9976</td>
<td>0.9600000</td>
<td>778000.000</td>
<td>1100512.76</td>
</tr>
<tr>
<td>6</td>
<td>0.23999888</td>
<td>959.9998</td>
<td>298.9976</td>
<td>0.9600000</td>
<td>778000.000</td>
<td>1098257.63</td>
</tr>
<tr>
<td>7</td>
<td>0.23999876</td>
<td>959.9998</td>
<td>298.9976</td>
<td>0.9600000</td>
<td>778000.000</td>
<td>1101847.69</td>
</tr>
<tr>
<td>8</td>
<td>0.23999858</td>
<td>959.9998</td>
<td>298.9976</td>
<td>0.9600000</td>
<td>792999.938</td>
<td>1101673.11</td>
</tr>
<tr>
<td>9</td>
<td>0.23999831</td>
<td>959.9998</td>
<td>298.9976</td>
<td>0.9600000</td>
<td>762999.838</td>
<td>1102021.64</td>
</tr>
<tr>
<td>10</td>
<td>0.22998710</td>
<td>969.9995</td>
<td>297.9951</td>
<td>0.9199801</td>
<td>747999.000</td>
<td>1121366.30</td>
</tr>
<tr>
<td>11</td>
<td>0.21998605</td>
<td>969.9995</td>
<td>297.9951</td>
<td>0.9199991</td>
<td>747999.000</td>
<td>1136820.29</td>
</tr>
<tr>
<td>12</td>
<td>0.21998573</td>
<td>980.0173</td>
<td>297.9951</td>
<td>0.9199991</td>
<td>747999.000</td>
<td>1137826.28</td>
</tr>
<tr>
<td>13</td>
<td>0.21998575</td>
<td>980.0173</td>
<td>296.9927</td>
<td>0.9199991</td>
<td>747999.000</td>
<td>1138062.75</td>
</tr>
<tr>
<td>14</td>
<td>0.21998573</td>
<td>980.0173</td>
<td>296.9927</td>
<td>0.7999506</td>
<td>732996.625</td>
<td>1140451.19</td>
</tr>
<tr>
<td>15</td>
<td>0.21998574</td>
<td>980.0173</td>
<td>296.9927</td>
<td>0.7999506</td>
<td>702993.063</td>
<td>1140627.57</td>
</tr>
<tr>
<td>16</td>
<td>0.19971615</td>
<td>980.0173</td>
<td>294.9987</td>
<td>0.7999011</td>
<td>702993.063</td>
<td>115766.16</td>
</tr>
<tr>
<td>17</td>
<td>0.18943739</td>
<td>980.0173</td>
<td>294.9987</td>
<td>0.7999011</td>
<td>702993.063</td>
<td>1167221.19</td>
</tr>
<tr>
<td>18</td>
<td>0.18943721</td>
<td>990.0442</td>
<td>293.9829</td>
<td>0.7999011</td>
<td>702993.063</td>
<td>1168125.23</td>
</tr>
<tr>
<td>19</td>
<td>0.18943705</td>
<td>990.0442</td>
<td>293.9829</td>
<td>0.7999011</td>
<td>702993.063</td>
<td>1168310.55</td>
</tr>
<tr>
<td>20</td>
<td>0.18943691</td>
<td>990.0442</td>
<td>293.9829</td>
<td>0.7597865</td>
<td>687988.375</td>
<td>1172115.02</td>
</tr>
<tr>
<td>21</td>
<td>0.18943679</td>
<td>990.0442</td>
<td>293.9829</td>
<td>0.7597865</td>
<td>642979.375</td>
<td>1172286.91</td>
</tr>
<tr>
<td>22</td>
<td>0.15901613</td>
<td>990.0442</td>
<td>290.9731</td>
<td>0.7597865</td>
<td>642979.375</td>
<td>116682.93</td>
</tr>
<tr>
<td>23</td>
<td>0.14861751</td>
<td>990.0442</td>
<td>290.9731</td>
<td>0.7597865</td>
<td>642979.375</td>
<td>1206245.25</td>
</tr>
<tr>
<td>24</td>
<td>0.14861751</td>
<td>990.0437</td>
<td>290.9731</td>
<td>0.7597865</td>
<td>642979.375</td>
<td>1205168.80</td>
</tr>
<tr>
<td>25</td>
<td>0.14861751</td>
<td>990.0437</td>
<td>291.9756</td>
<td>0.7597865</td>
<td>642979.375</td>
<td>1206025.73</td>
</tr>
<tr>
<td>26</td>
<td>0.14861751</td>
<td>990.0437</td>
<td>290.9683</td>
<td>0.7195052</td>
<td>627972.438</td>
<td>1207500.38</td>
</tr>
<tr>
<td>27</td>
<td>0.14861751</td>
<td>990.0437</td>
<td>290.9683</td>
<td>0.7195052</td>
<td>627972.438</td>
<td>1207674.18</td>
</tr>
<tr>
<td>28</td>
<td>0.10779816</td>
<td>990.0432</td>
<td>290.9683</td>
<td>0.7195052</td>
<td>627972.438</td>
<td>1225156.58</td>
</tr>
<tr>
<td>29</td>
<td>0.11827809</td>
<td>990.0432</td>
<td>290.9683</td>
<td>0.7195052</td>
<td>627972.438</td>
<td>1219254.05</td>
</tr>
<tr>
<td>30</td>
<td>0.10779798</td>
<td>985.0432</td>
<td>290.9683</td>
<td>0.7195052</td>
<td>627972.438</td>
<td>1224597.05</td>
</tr>
<tr>
<td>31</td>
<td>0.10779792</td>
<td>995.0430</td>
<td>290.9683</td>
<td>0.7195052</td>
<td>627972.438</td>
<td>1225705.14</td>
</tr>
<tr>
<td>32</td>
<td>0.10779786</td>
<td>995.0430</td>
<td>290.4968</td>
<td>0.7195052</td>
<td>627972.438</td>
<td>1225816.91</td>
</tr>
<tr>
<td>33</td>
<td>0.10779786</td>
<td>995.0430</td>
<td>290.4968</td>
<td>0.7598103</td>
<td>627972.438</td>
<td>1224552.89</td>
</tr>
<tr>
<td>34</td>
<td>0.10779786</td>
<td>995.0430</td>
<td>290.4968</td>
<td>0.7195051</td>
<td>612963.375</td>
<td>1225994.32</td>
</tr>
<tr>
<td>35</td>
<td>0.10779786</td>
<td>995.0430</td>
<td>290.4968</td>
<td>0.7195045</td>
<td>612963.375</td>
<td>1225992.25</td>
</tr>
<tr>
<td>ITERATION NUMBER</td>
<td>ACETONE CONVERSION</td>
<td>QUENCH UNIT INLET GAS TEMPERATURE (DEG F)</td>
<td>QUENCH UNIT EXIT GAS TEMPERATURE (DEG F)</td>
<td>ACID/ANHYDRIDE RATIO IN RECYCLE</td>
<td>WATER RATE TO CONDENSER (LBS/HR)</td>
<td>YEARLY PROFIT (£/YEAR)</td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------</td>
<td>---------------------------------------------</td>
<td>-------------------------------------------</td>
<td>----------------------------------</td>
<td>-----------------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>36</td>
<td>0.10279775</td>
<td>995.0430</td>
<td>290.49683</td>
<td>0.7195045</td>
<td>612963.375</td>
<td>1228439.78</td>
</tr>
<tr>
<td>37</td>
<td>0.10279775</td>
<td>990.0405</td>
<td>290.49683</td>
<td>0.7195045</td>
<td>612963.375</td>
<td>1227873.81</td>
</tr>
<tr>
<td>38</td>
<td>0.10279775</td>
<td>995.0427</td>
<td>290.49683</td>
<td>0.7195045</td>
<td>612963.375</td>
<td>1228315.13</td>
</tr>
<tr>
<td>39</td>
<td>0.10279775</td>
<td>995.0427</td>
<td>290.49634</td>
<td>0.7395044</td>
<td>627974.500</td>
<td>1227766.01</td>
</tr>
<tr>
<td>40</td>
<td>0.10279775</td>
<td>995.0427</td>
<td>290.49634</td>
<td>0.7395044</td>
<td>612962.625</td>
<td>1228260.54</td>
</tr>
<tr>
<td>41</td>
<td>0.10279775</td>
<td>995.0425</td>
<td>290.49585</td>
<td>0.7195036</td>
<td>612962.625</td>
<td>1228437.64</td>
</tr>
<tr>
<td>42</td>
<td>0.10780764</td>
<td>995.0425</td>
<td>290.49585</td>
<td>0.7195036</td>
<td>612962.625</td>
<td>1225990.83</td>
</tr>
<tr>
<td>43</td>
<td>0.10279757</td>
<td>990.0425</td>
<td>290.49585</td>
<td>0.7195036</td>
<td>612962.625</td>
<td>1227872.69</td>
</tr>
<tr>
<td>44</td>
<td>0.10279751</td>
<td>995.0422</td>
<td>290.49585</td>
<td>0.7395036</td>
<td>612962.625</td>
<td>1228317.04</td>
</tr>
<tr>
<td>45</td>
<td>0.10279751</td>
<td>995.0422</td>
<td>290.49561</td>
<td>0.7395036</td>
<td>612962.625</td>
<td>1227767.77</td>
</tr>
<tr>
<td>46</td>
<td>0.10279751</td>
<td>995.0422</td>
<td>290.49561</td>
<td>0.7195035</td>
<td>605466.625</td>
<td>1228818.21</td>
</tr>
<tr>
<td>47</td>
<td>0.10279727</td>
<td>995.0417</td>
<td>290.49561</td>
<td>0.7195024</td>
<td>605466.625</td>
<td>1228517.05</td>
</tr>
<tr>
<td>48</td>
<td>0.10279715</td>
<td>995.0417</td>
<td>290.49561</td>
<td>0.7195024</td>
<td>605466.625</td>
<td>1226083.57</td>
</tr>
<tr>
<td>49</td>
<td>0.10279703</td>
<td>990.0417</td>
<td>290.49487</td>
<td>0.7195024</td>
<td>605466.625</td>
<td>1227955.95</td>
</tr>
<tr>
<td>50</td>
<td>0.10279703</td>
<td>995.0415</td>
<td>290.49487</td>
<td>0.7195024</td>
<td>605466.625</td>
<td>1228407.74</td>
</tr>
<tr>
<td>51</td>
<td>0.10279703</td>
<td>995.0415</td>
<td>290.49463</td>
<td>0.7195024</td>
<td>605466.625</td>
<td>1228785.14</td>
</tr>
<tr>
<td>52</td>
<td>0.10279703</td>
<td>995.0415</td>
<td>290.49463</td>
<td>0.7195024</td>
<td>605466.625</td>
<td>1228843.99</td>
</tr>
<tr>
<td>53</td>
<td>0.10779744</td>
<td>995.0422</td>
<td>290.49561</td>
<td>0.7195023</td>
<td>605466.625</td>
<td>1226085.75</td>
</tr>
<tr>
<td>54</td>
<td>0.10279733</td>
<td>990.0420</td>
<td>290.49561</td>
<td>0.7195035</td>
<td>605466.625</td>
<td>1227957.22</td>
</tr>
<tr>
<td>55</td>
<td>0.10279727</td>
<td>995.0417</td>
<td>290.49536</td>
<td>0.7195035</td>
<td>605466.625</td>
<td>1228407.02</td>
</tr>
<tr>
<td>56</td>
<td>0.10279727</td>
<td>995.0417</td>
<td>290.49512</td>
<td>0.7195035</td>
<td>605466.625</td>
<td>1227849.29</td>
</tr>
<tr>
<td>57</td>
<td>0.10279727</td>
<td>995.0417</td>
<td>290.49512</td>
<td>0.7195035</td>
<td>605466.625</td>
<td>1228436.25</td>
</tr>
<tr>
<td>58</td>
<td>0.10529745</td>
<td>995.0422</td>
<td>290.49561</td>
<td>0.7195035</td>
<td>605466.625</td>
<td>1227582.67</td>
</tr>
<tr>
<td>59</td>
<td>0.10029733</td>
<td>995.0422</td>
<td>290.49561</td>
<td>0.7195035</td>
<td>605466.625</td>
<td>1229947.92</td>
</tr>
<tr>
<td>60</td>
<td>0.10029727</td>
<td>997.5420</td>
<td>290.49561</td>
<td>0.7195035</td>
<td>605466.625</td>
<td>1230213.36</td>
</tr>
<tr>
<td>61</td>
<td>0.10029721</td>
<td>997.5420</td>
<td>290.49536</td>
<td>0.7195035</td>
<td>605466.625</td>
<td>1230157.12</td>
</tr>
<tr>
<td>62</td>
<td>0.10029721</td>
<td>997.5420</td>
<td>290.24536</td>
<td>0.7195035</td>
<td>605466.625</td>
<td>1230267.02</td>
</tr>
<tr>
<td>63</td>
<td>0.10029721</td>
<td>997.5420</td>
<td>290.24536</td>
<td>0.7195035</td>
<td>605466.625</td>
<td>1230945.06</td>
</tr>
<tr>
<td>64</td>
<td>0.10029721</td>
<td>997.5420</td>
<td>290.24536</td>
<td>0.7295035</td>
<td>605466.625</td>
<td>1230591.66</td>
</tr>
<tr>
<td>65</td>
<td>0.10029721</td>
<td>997.5420</td>
<td>290.24536</td>
<td>0.7095035</td>
<td>609212.563</td>
<td>1230545.04</td>
</tr>
<tr>
<td>66</td>
<td>0.10029721</td>
<td>997.5420</td>
<td>290.24536</td>
<td>0.7095035</td>
<td>601712.563</td>
<td>1230633.71</td>
</tr>
<tr>
<td>67</td>
<td>0.10029721</td>
<td>997.5420</td>
<td>290.24536</td>
<td>0.7095035</td>
<td>601712.563</td>
<td>1230633.71</td>
</tr>
<tr>
<td>68</td>
<td>0.10280001</td>
<td>995.0413</td>
<td>290.24536</td>
<td>0.7095035</td>
<td>601712.563</td>
<td>1229225.12</td>
</tr>
<tr>
<td>69</td>
<td>0.10029703</td>
<td>997.5417</td>
<td>290.49536</td>
<td>0.7095035</td>
<td>601712.563</td>
<td>1230371.97</td>
</tr>
<tr>
<td>70</td>
<td>0.10029697</td>
<td>997.5417</td>
<td>290.49536</td>
<td>0.7095035</td>
<td>601712.563</td>
<td>1230580.06</td>
</tr>
<tr>
<td>ITERATION NUMBER</td>
<td>ACETONE CONVERSION (%)</td>
<td>QUENCH UNIT EXIT GAS TEMPERATURE (DEG F)</td>
<td>WATER RATE TO CONDENSER (LBS/HR)</td>
<td>YEARLY PROFIT ($/YEAR)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------------</td>
<td>------------------------------------------</td>
<td>----------------------------------</td>
<td>------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>71</td>
<td>0.1002967</td>
<td>97.453162</td>
<td>0.7695034</td>
<td>1.230391.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>0.1002967</td>
<td>97.453162</td>
<td>0.7695034</td>
<td>1.230391.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>0.1003967</td>
<td>97.453162</td>
<td>0.7695034</td>
<td>1.230391.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>0.1003967</td>
<td>97.453162</td>
<td>0.7695034</td>
<td>1.230391.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>0.1003967</td>
<td>97.453162</td>
<td>0.7695034</td>
<td>1.230391.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>76</td>
<td>0.1003967</td>
<td>97.453162</td>
<td>0.7695034</td>
<td>1.230391.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITERATION NUMBER</td>
<td>ACETONE CONVERSION</td>
<td>QUENCH UNIT INLET GAS TEMPERATURE (DEG F)</td>
<td>QUENCH UNIT EXIT GAS TEMPERATURE (DEG F)</td>
<td>ACID/ANHYDRIDE RATIO IN RECYCLE</td>
<td>WATER RATE TO CONDENSER (LBS/HR)</td>
<td>YEARLY PROFIT (£/YEAR)</td>
</tr>
<tr>
<td>------------------</td>
<td>---------------------</td>
<td>--------------------------------------------</td>
<td>------------------------------------------</td>
<td>----------------------------------</td>
<td>-------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>106</td>
<td>0.10029554</td>
<td>999.7278</td>
<td>290.08862</td>
<td>0.7020027</td>
<td>600773.813</td>
<td>1231155.21</td>
</tr>
<tr>
<td>107</td>
<td>0.10029554</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7020027</td>
<td>600773.813</td>
<td>1231164.48</td>
</tr>
<tr>
<td>108</td>
<td>0.10029554</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7032527</td>
<td>600773.813</td>
<td>1231126.16</td>
</tr>
<tr>
<td>109</td>
<td>0.10029554</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>110</td>
<td>0.10029554</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>111</td>
<td>0.10029554</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>112</td>
<td>0.10029554</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>113</td>
<td>0.10013896</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>114</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>115</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>116</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>117</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>118</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>119</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>120</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>121</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>122</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>123</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>124</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>125</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>126</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>127</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>128</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>129</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>130</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>131</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>132</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>133</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>134</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>135</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>136</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>137</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>138</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>139</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>140</td>
<td>0.10013890</td>
<td>999.7278</td>
<td>290.02612</td>
<td>0.7007527</td>
<td>600773.813</td>
<td>1231207.70</td>
</tr>
<tr>
<td>ITERATION NUMBER</td>
<td>ACETONE CONVERSION</td>
<td>QUENCH UNIT INLET GAS TEMPERATURE (DEG F)</td>
<td>QUENCH UNIT EXIT GAS TEMPERATURE (DEG F)</td>
<td>ACID/ANHYDRIDE RATIO IN RECYCLE</td>
<td>WATER RATE TO CONDENSER (LBS/HR)</td>
<td>YEARLY PROFIT (£/YEAR)</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------</td>
<td>-------------------------------------------</td>
<td>------------------------------------------</td>
<td>---------------------------------</td>
<td>---------------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>141</td>
<td>0.10006022</td>
<td>999.9612</td>
<td>290.00244</td>
<td>0.7004393</td>
<td>600070.625</td>
<td>1231317.97</td>
</tr>
<tr>
<td>142</td>
<td>0.10006022</td>
<td>999.9612</td>
<td>290.00244</td>
<td>0.7001267</td>
<td>600187.750</td>
<td>1231330.02</td>
</tr>
<tr>
<td>143</td>
<td>0.10006022</td>
<td>999.9612</td>
<td>290.00244</td>
<td>0.7001265</td>
<td>600304.375</td>
<td>1231328.42</td>
</tr>
<tr>
<td>144</td>
<td>0.10013825</td>
<td>999.9612</td>
<td>290.00244</td>
<td>0.7001265</td>
<td>600304.375</td>
<td>1231324.37</td>
</tr>
<tr>
<td>145</td>
<td>0.10006005</td>
<td>999.8831</td>
<td>290.00244</td>
<td>0.7001265</td>
<td>600304.375</td>
<td>123137.18</td>
</tr>
<tr>
<td>146</td>
<td>0.10005999</td>
<td>999.9612</td>
<td>290.01025</td>
<td>0.7001265</td>
<td>600304.375</td>
<td>1231326.29</td>
</tr>
<tr>
<td>147</td>
<td>0.10005999</td>
<td>999.9612</td>
<td>290.00244</td>
<td>0.7002826</td>
<td>600304.375</td>
<td>1231318.88</td>
</tr>
<tr>
<td>148</td>
<td>0.10005999</td>
<td>999.9612</td>
<td>290.00244</td>
<td>0.7001263</td>
<td>600187.750</td>
<td>1231322.62</td>
</tr>
<tr>
<td>149</td>
<td>0.10005999</td>
<td>999.9612</td>
<td>290.00244</td>
<td>0.7001267</td>
<td>600187.750</td>
<td>1231326.91</td>
</tr>
<tr>
<td>150</td>
<td>0.10009921</td>
<td>999.9612</td>
<td>290.00244</td>
<td>0.7001267</td>
<td>600187.750</td>
<td>1231318.49</td>
</tr>
<tr>
<td>151</td>
<td>0.1002100</td>
<td>1000.0000</td>
<td>290.00610</td>
<td>0.7001267</td>
<td>600187.750</td>
<td>1231339.34</td>
</tr>
<tr>
<td>152</td>
<td>0.1002095</td>
<td>1000.0000</td>
<td>290.01956</td>
<td>0.7002829</td>
<td>600246.313</td>
<td>1231341.67</td>
</tr>
<tr>
<td>153</td>
<td>0.1002089</td>
<td>1000.0000</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600129.125</td>
<td>1231340.42</td>
</tr>
<tr>
<td>154</td>
<td>0.1002089</td>
<td>1000.0000</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600187.250</td>
<td>1231342.02</td>
</tr>
<tr>
<td>155</td>
<td>0.1002089</td>
<td>1000.0000</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600187.250</td>
<td>1231336.89</td>
</tr>
<tr>
<td>156</td>
<td>0.1002089</td>
<td>1000.0000</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600187.250</td>
<td>1231336.89</td>
</tr>
<tr>
<td>157</td>
<td>0.1002089</td>
<td>1000.0000</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600187.250</td>
<td>1231336.89</td>
</tr>
<tr>
<td>158</td>
<td>0.1005981</td>
<td>1000.0000</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600187.250</td>
<td>1231336.89</td>
</tr>
<tr>
<td>159</td>
<td>0.1002065</td>
<td>999.96609</td>
<td>290.00196</td>
<td>0.7001266</td>
<td>600216.500</td>
<td>1231341.39</td>
</tr>
<tr>
<td>160</td>
<td>0.1002065</td>
<td>1000.0000</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231334.31</td>
</tr>
<tr>
<td>161</td>
<td>0.1002065</td>
<td>1000.0000</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231345.72</td>
</tr>
<tr>
<td>162</td>
<td>0.1002065</td>
<td>1000.0000</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231342.03</td>
</tr>
<tr>
<td>163</td>
<td>0.1002065</td>
<td>1000.0000</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231345.72</td>
</tr>
<tr>
<td>164</td>
<td>0.1002065</td>
<td>1000.0000</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231342.03</td>
</tr>
<tr>
<td>165</td>
<td>0.1004032</td>
<td>1000.0000</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231345.72</td>
</tr>
<tr>
<td>166</td>
<td>0.10000116</td>
<td>1000.0000</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231345.72</td>
</tr>
<tr>
<td>167</td>
<td>0.10000110</td>
<td>999.9802</td>
<td>290.00195</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231345.72</td>
</tr>
<tr>
<td>168</td>
<td>0.10000110</td>
<td>999.9995</td>
<td>290.00366</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231345.72</td>
</tr>
<tr>
<td>169</td>
<td>0.10000110</td>
<td>999.9995</td>
<td>290.00366</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231345.72</td>
</tr>
<tr>
<td>170</td>
<td>0.10000110</td>
<td>999.9995</td>
<td>290.00366</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231345.72</td>
</tr>
<tr>
<td>171</td>
<td>0.10000110</td>
<td>999.9995</td>
<td>290.00366</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231345.72</td>
</tr>
<tr>
<td>172</td>
<td>0.10000110</td>
<td>999.9995</td>
<td>290.00366</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231345.72</td>
</tr>
<tr>
<td>173</td>
<td>0.10000110</td>
<td>999.9995</td>
<td>290.00366</td>
<td>0.7001266</td>
<td>600187.688</td>
<td>1231345.72</td>
</tr>
<tr>
<td>174</td>
<td>0.10002053</td>
<td>999.9990</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600128.313</td>
<td>1231344.37</td>
</tr>
<tr>
<td>175</td>
<td>0.10000092</td>
<td>999.9893</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600128.313</td>
<td>1231348.98</td>
</tr>
<tr>
<td>ITERATION NUMBER</td>
<td>ACETONE CONVERSION</td>
<td>QUENCH UNIT INLET GAS TEMPERATURE (DEG F)</td>
<td>QUENCH UNIT EXIT GAS TEMPERATURE (DEG F)</td>
<td>ACID/ANHYDRIDE RATIO IN RECYCLE</td>
<td>WATER RATE TO CONDENSER (LBS/HR)</td>
<td>YEARLY PROFIT (£/YEAR)</td>
</tr>
<tr>
<td>------------------</td>
<td>---------------------</td>
<td>--------------------------------------------</td>
<td>------------------------------------------</td>
<td>----------------------------------</td>
<td>-----------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>176</td>
<td>0.10000086</td>
<td>999.9988</td>
<td>290.00732</td>
<td>0.7000484</td>
<td>600128.313</td>
<td>1231350.01</td>
</tr>
<tr>
<td>177</td>
<td>0.10000086</td>
<td>999.9988</td>
<td>290.00342</td>
<td>0.7000484</td>
<td>600128.313</td>
<td>1231347.88</td>
</tr>
<tr>
<td>178</td>
<td>0.10000086</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600128.313</td>
<td>1231349.31</td>
</tr>
<tr>
<td>179</td>
<td>0.10000086</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600128.313</td>
<td>1231353.37</td>
</tr>
<tr>
<td>180</td>
<td>0.10000062</td>
<td>999.9980</td>
<td>290.00708</td>
<td>0.7000475</td>
<td>600099.000</td>
<td>1231350.92</td>
</tr>
<tr>
<td>181</td>
<td>0.10001028</td>
<td>999.9980</td>
<td>290.00708</td>
<td>0.7000475</td>
<td>600099.000</td>
<td>1231347.61</td>
</tr>
<tr>
<td>182</td>
<td>0.10000044</td>
<td>999.9883</td>
<td>290.00708</td>
<td>0.7000475</td>
<td>600099.000</td>
<td>1231346.82</td>
</tr>
<tr>
<td>183</td>
<td>0.10000038</td>
<td>999.9978</td>
<td>290.00781</td>
<td>0.7000475</td>
<td>600099.000</td>
<td>1231347.77</td>
</tr>
<tr>
<td>184</td>
<td>0.10000038</td>
<td>999.9978</td>
<td>290.00586</td>
<td>0.700084</td>
<td>600099.000</td>
<td>1231347.56</td>
</tr>
<tr>
<td>185</td>
<td>0.10000038</td>
<td>999.9978</td>
<td>290.00659</td>
<td>0.700084</td>
<td>600099.000</td>
<td>1231351.59</td>
</tr>
<tr>
<td>186</td>
<td>0.10000038</td>
<td>999.9978</td>
<td>290.00659</td>
<td>0.700084</td>
<td>600099.000</td>
<td>1231351.99</td>
</tr>
<tr>
<td>187</td>
<td>0.1001051</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231346.88</td>
</tr>
<tr>
<td>188</td>
<td>0.10000062</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.14</td>
</tr>
<tr>
<td>189</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00610</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231353.15</td>
</tr>
<tr>
<td>190</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00415</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231347.06</td>
</tr>
<tr>
<td>191</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00488</td>
<td>0.700093</td>
<td>600099.000</td>
<td>1231350.97</td>
</tr>
<tr>
<td>192</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00488</td>
<td>0.7000874</td>
<td>600099.000</td>
<td>1231350.33</td>
</tr>
<tr>
<td>193</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00488</td>
<td>0.700084</td>
<td>600099.000</td>
<td>1231350.51</td>
</tr>
<tr>
<td>194</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00488</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231349.71</td>
</tr>
<tr>
<td>195</td>
<td>0.10000563</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.53</td>
</tr>
<tr>
<td>196</td>
<td>0.10000062</td>
<td>999.9937</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231347.12</td>
</tr>
<tr>
<td>197</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00562</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231349.12</td>
</tr>
<tr>
<td>198</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00484</td>
<td>0.7000288</td>
<td>600099.000</td>
<td>1231349.10</td>
</tr>
<tr>
<td>199</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00484</td>
<td>0.7000679</td>
<td>600099.000</td>
<td>1231347.54</td>
</tr>
<tr>
<td>200</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00484</td>
<td>0.7000473</td>
<td>600099.000</td>
<td>1231347.71</td>
</tr>
<tr>
<td>201</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00484</td>
<td>0.7000483</td>
<td>600099.000</td>
<td>1231350.30</td>
</tr>
<tr>
<td>202</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00484</td>
<td>0.7000483</td>
<td>600099.000</td>
<td>1231349.90</td>
</tr>
<tr>
<td>203</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00484</td>
<td>0.7000483</td>
<td>600099.000</td>
<td>1231349.49</td>
</tr>
<tr>
<td>204</td>
<td>0.10000062</td>
<td>999.9961</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231347.20</td>
</tr>
<tr>
<td>205</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231347.14</td>
</tr>
<tr>
<td>206</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00484</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231350.11</td>
</tr>
<tr>
<td>207</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00484</td>
<td>0.7000386</td>
<td>600099.000</td>
<td>1231349.35</td>
</tr>
<tr>
<td>208</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00484</td>
<td>0.7000581</td>
<td>600099.000</td>
<td>1231347.99</td>
</tr>
<tr>
<td>209</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00484</td>
<td>0.7000483</td>
<td>600091.625</td>
<td>1231350.20</td>
</tr>
<tr>
<td>210</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00488</td>
<td>0.7000483</td>
<td>600106.250</td>
<td>1231350.00</td>
</tr>
<tr>
<td>Iteration Number</td>
<td>Acetone Conversion</td>
<td>Quench Unit Inlet Gas Temperature (deg F)</td>
<td>Quench Unit Exit Gas Temperature (deg F)</td>
<td>Acid/Anhydride Ratio In Recycle</td>
<td>Water Rate to Condenser (LBS/HR)</td>
<td>Yearly Profit (£/year)</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------</td>
<td>------------------------------------------</td>
<td>------------------------------------------</td>
<td>---------------------------------</td>
<td>---------------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>211</td>
<td>0.100000205</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231353.35</td>
</tr>
<tr>
<td>212</td>
<td>0.10000074</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231352.28</td>
</tr>
<tr>
<td>213</td>
<td>0.10000068</td>
<td>999.9973</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231347.19</td>
</tr>
<tr>
<td>214</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231347.14</td>
</tr>
<tr>
<td>215</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231352.13</td>
</tr>
<tr>
<td>216</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231352.25</td>
</tr>
<tr>
<td>217</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231350.07</td>
</tr>
<tr>
<td>218</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00537</td>
<td>0.7000483</td>
<td>600102.625</td>
<td>1231352.17</td>
</tr>
<tr>
<td>219</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00537</td>
<td>0.7000483</td>
<td>600099.000</td>
<td>1231352.08</td>
</tr>
<tr>
<td>220</td>
<td>0.10000139</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231349.86</td>
</tr>
<tr>
<td>221</td>
<td>0.1000014</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231350.57</td>
</tr>
<tr>
<td>222</td>
<td>0.1000068</td>
<td>999.9993</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.23</td>
</tr>
<tr>
<td>223</td>
<td>0.1000062</td>
<td>999.9980</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.16</td>
</tr>
<tr>
<td>224</td>
<td>0.1000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231353.15</td>
</tr>
<tr>
<td>225</td>
<td>0.1000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231352.13</td>
</tr>
<tr>
<td>226</td>
<td>0.1000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231350.17</td>
</tr>
<tr>
<td>227</td>
<td>0.1000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231350.01</td>
</tr>
<tr>
<td>228</td>
<td>0.1000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600097.125</td>
<td>1231352.15</td>
</tr>
<tr>
<td>229</td>
<td>0.1000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000483</td>
<td>600100.750</td>
<td>1231352.11</td>
</tr>
<tr>
<td>230</td>
<td>0.1000062</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231348.63</td>
</tr>
<tr>
<td>231</td>
<td>0.1000038</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231344.04</td>
</tr>
<tr>
<td>232</td>
<td>0.1000062</td>
<td>999.9990</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231347.16</td>
</tr>
<tr>
<td>233</td>
<td>0.1000062</td>
<td>999.9983</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231350.11</td>
</tr>
<tr>
<td>234</td>
<td>0.1000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231353.15</td>
</tr>
<tr>
<td>235</td>
<td>0.1000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231352.13</td>
</tr>
<tr>
<td>236</td>
<td>0.1000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231350.19</td>
</tr>
<tr>
<td>237</td>
<td>0.1000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000495</td>
<td>600098.063</td>
<td>1231352.18</td>
</tr>
<tr>
<td>238</td>
<td>0.1000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000483</td>
<td>600099.875</td>
<td>1231352.12</td>
</tr>
<tr>
<td>239</td>
<td>0.1000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000495</td>
<td>600099.000</td>
<td>1231349.38</td>
</tr>
<tr>
<td>240</td>
<td>0.1000092</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231353.09</td>
</tr>
<tr>
<td>241</td>
<td>0.1000050</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231350.11</td>
</tr>
<tr>
<td>242</td>
<td>0.1000062</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231350.11</td>
</tr>
<tr>
<td>243</td>
<td>0.1000062</td>
<td>999.9983</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231350.11</td>
</tr>
<tr>
<td>244</td>
<td>0.1000062</td>
<td>999.9983</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231350.11</td>
</tr>
<tr>
<td>245</td>
<td>0.1000062</td>
<td>999.9983</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231352.13</td>
</tr>
<tr>
<td>ITERATION NUMBER</td>
<td>ACETONE CONVERSION</td>
<td>QUENCH UNIT INLET GAS TEMPERATURE (DEG F)</td>
<td>QUENCH UNIT EXIT GAS TEMPERATURE (DEG F)</td>
<td>ACID/ANHYDRIDE RATIO IN RECYCLE</td>
<td>WATER RATE TO CONDENSER (LBS/HR)</td>
<td>YEARLY PROFIT (£/YEAR)</td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------</td>
<td>------------------------------------------</td>
<td>------------------------------------------</td>
<td>---------------------------------</td>
<td>---------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>246</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00513</td>
<td>0.7000477</td>
<td>600099.000</td>
<td>1231352.16</td>
</tr>
<tr>
<td>247</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00513</td>
<td>0.7000489</td>
<td>600099.000</td>
<td>1231352.14</td>
</tr>
<tr>
<td>248</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00513</td>
<td>0.7000483</td>
<td>600099.000</td>
<td>1231352.13</td>
</tr>
<tr>
<td>249</td>
<td>0.10000062</td>
<td>999.9983</td>
<td>290.00513</td>
<td>0.7000483</td>
<td>600099.000</td>
<td>1231352.12</td>
</tr>
<tr>
<td>250</td>
<td>0.10000086</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231347.34</td>
</tr>
<tr>
<td>251</td>
<td>0.10000062</td>
<td>999.9988</td>
<td>290.00513</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.17</td>
</tr>
<tr>
<td>252</td>
<td>0.10000062</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.17</td>
</tr>
<tr>
<td>253</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>254</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>255</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>256</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>257</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>258</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>259</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>260</td>
<td>0.10000086</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.37</td>
</tr>
<tr>
<td>261</td>
<td>0.10000068</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.18</td>
</tr>
<tr>
<td>262</td>
<td>0.10000062</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.17</td>
</tr>
<tr>
<td>263</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>264</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>265</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>266</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>267</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>268</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>269</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>270</td>
<td>0.10000086</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.37</td>
</tr>
<tr>
<td>271</td>
<td>0.10000074</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.36</td>
</tr>
<tr>
<td>272</td>
<td>0.10000068</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231347.18</td>
</tr>
<tr>
<td>273</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.17</td>
</tr>
<tr>
<td>274</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>275</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>276</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>277</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>278</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>279</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.15</td>
</tr>
<tr>
<td>280</td>
<td>0.10000086</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231353.37</td>
</tr>
<tr>
<td>ITERATION NUMBER</td>
<td>ACETONE CONVERSION</td>
<td>QUENCH UNIT INLET GAS TEMPERATURE (DEG F)</td>
<td>QUENCH UNIT EXIT GAS TEMPERATURE (DEG F)</td>
<td>ACID/ANHYDRIDE RATIO IN RECYCLE</td>
<td>WATER RATE TO CONDENSER (LBS/HR)</td>
<td>YEARLY PROFIT (£/YEAR)</td>
</tr>
<tr>
<td>------------------</td>
<td>---------------------</td>
<td>-------------------------------------------</td>
<td>------------------------------------------</td>
<td>-------------------------------</td>
<td>---------------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>281</td>
<td>0.10000074</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231353.36</td>
</tr>
<tr>
<td>282</td>
<td>0.10000068</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231347.18</td>
</tr>
<tr>
<td>283</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231345.17</td>
</tr>
<tr>
<td>284</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231353.15</td>
</tr>
<tr>
<td>285</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000483</td>
<td>600099.000</td>
<td>1231353.15</td>
</tr>
<tr>
<td>286</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231353.15</td>
</tr>
<tr>
<td>287</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231353.15</td>
</tr>
<tr>
<td>288</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000483</td>
<td>600098.938</td>
<td>1231353.15</td>
</tr>
<tr>
<td>289</td>
<td>0.10000062</td>
<td>999.9985</td>
<td>290.00537</td>
<td>0.7000483</td>
<td>600098.938</td>
<td>1231353.15</td>
</tr>
</tbody>
</table>

**OPTIMUM IS REACHED**
<table>
<thead>
<tr>
<th>ITERATION NUMBER</th>
<th>ACETONE CONVERSION</th>
<th>QUENCH UNIT INLET GAS TEMPERATURE (DEG F)</th>
<th>QUENCH UNIT EXIT GAS TEMPERATURE (DEG F)</th>
<th>ACID/ANHYDRIDE RATIO IN RECYCLE</th>
<th>WATER RATE TO CONDENSER (LBS/HR)</th>
<th>YEARLY PROFIT (£/YEAR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>289</td>
<td>0.10000086</td>
<td>999.9988</td>
<td>290.00537</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231353.37</td>
</tr>
</tbody>
</table>

VALUES AT OPTIMUM POINT

OPTIMUM REFLUX RATIO FOR ACETONE COLUMN = 0.33
OPTIMUM REFLUX RATIO FOR ANHYDRIDE COLUMN = 1.77
APPENDIX D (Continued)

D. 4

Program output (Continued)

(with I OPHN = 1 and I PRINT = - 1)
<table>
<thead>
<tr>
<th>ITERATION NUMBER</th>
<th>ACETONE CONVERSION</th>
<th>QUENCH UNIT INLET GAS TEMPERATURE (DEG F)</th>
<th>QUENCH UNIT EXIT GAS TEMPERATURE (DEG F)</th>
<th>ACID/ANHYDRIDE RATIO IN RECYCLE</th>
<th>WATER RATE TO CONDENSER (LBS/HR)</th>
<th>YEARLY PROFIT (£/YEAR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.19999981</td>
<td>900.0000</td>
<td>295.0000</td>
<td>1.0999994</td>
<td>750000.000</td>
<td>1151047.97</td>
</tr>
<tr>
<td>0</td>
<td>0.19999981</td>
<td>880.0000</td>
<td>295.0000</td>
<td>1.0999994</td>
<td>720000.000</td>
<td>1148394.35</td>
</tr>
<tr>
<td>0</td>
<td>0.19999981</td>
<td>920.0000</td>
<td>295.0000</td>
<td>1.0999994</td>
<td>780000.000</td>
<td>1152974.87</td>
</tr>
<tr>
<td>0</td>
<td>0.17999983</td>
<td>900.0000</td>
<td>294.0000</td>
<td>1.0199995</td>
<td>750000.000</td>
<td>1162731.28</td>
</tr>
<tr>
<td>0</td>
<td>0.21999979</td>
<td>900.0000</td>
<td>296.0000</td>
<td>1.1799994</td>
<td>750000.000</td>
<td>117526.86</td>
</tr>
<tr>
<td>0</td>
<td>0.19999981</td>
<td>880.0000</td>
<td>296.0000</td>
<td>1.1799994</td>
<td>720000.000</td>
<td>1126801.28</td>
</tr>
<tr>
<td>0</td>
<td>0.17999983</td>
<td>880.0000</td>
<td>294.0000</td>
<td>1.0199995</td>
<td>720000.000</td>
<td>1160658.50</td>
</tr>
<tr>
<td>0</td>
<td>0.17999983</td>
<td>920.0000</td>
<td>294.0000</td>
<td>1.0199995</td>
<td>780000.000</td>
<td>1183567.38</td>
</tr>
<tr>
<td>0</td>
<td>0.21999979</td>
<td>920.0000</td>
<td>296.0000</td>
<td>1.1799994</td>
<td>780000.000</td>
<td>119632.19</td>
</tr>
<tr>
<td>0</td>
<td>0.11999989</td>
<td>950.0000</td>
<td>295.0000</td>
<td>1.000000</td>
<td>700000.000</td>
<td>1199845.38</td>
</tr>
<tr>
<td>0</td>
<td>0.29999983</td>
<td>1000.0000</td>
<td>310.0000</td>
<td>1.500000</td>
<td>900000.000</td>
<td>973749.72</td>
</tr>
<tr>
<td>0</td>
<td>0.29999983</td>
<td>1000.0000</td>
<td>310.0000</td>
<td>0.700000</td>
<td>600000.000</td>
<td>1006964.79</td>
</tr>
<tr>
<td>0</td>
<td>0.25000000</td>
<td>800.0000</td>
<td>300.0000</td>
<td>1.000000</td>
<td>780000.000</td>
<td>963141.11</td>
</tr>
<tr>
<td>0</td>
<td>0.25000000</td>
<td>800.0000</td>
<td>310.0000</td>
<td>1.500000</td>
<td>780000.000</td>
<td>1083208.15</td>
</tr>
<tr>
<td>0</td>
<td>0.25000000</td>
<td>800.0000</td>
<td>310.0000</td>
<td>1.500000</td>
<td>900000.000</td>
<td>1030738.49</td>
</tr>
<tr>
<td>ITERATION NUMBER</td>
<td>ACETONE CONVERSION</td>
<td>QUENCH UNIT INLET GAS TEMPERATURE (DEG F)</td>
<td>QUENCH UNIT EXIT GAS TEMPERATURE (DEG F)</td>
<td>ACID/ANHYDRIDE RATIO IN RECYCLE</td>
<td>WATER RATE TO CONDENSER (LBS/HR)</td>
<td>YEARLY PROFIT (£/YEAR)</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------</td>
<td>------------------------------------------</td>
<td>------------------------------------------</td>
<td>---------------------------------</td>
<td>--------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>0</td>
<td>0.11999989</td>
<td>950.0000</td>
<td>295.0000</td>
<td>1.0000000</td>
<td>700000.000</td>
<td>1199845.38</td>
</tr>
</tbody>
</table>

OPTIMUM IS REACHED
<table>
<thead>
<tr>
<th>Iteration Number</th>
<th>Acetone Conversion</th>
<th>Quench Unit Inlet Gas Temperature (°F)</th>
<th>Quench Unit Exit Gas Temperature (°F)</th>
<th>Acid/Anhydride Ratio in Recycle</th>
<th>Water Rate to Condenser (Lbs/hr)</th>
<th>Yearly Profit (£/Year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.10000086</td>
<td>999.9988</td>
<td>290.00513</td>
<td>0.7000484</td>
<td>600099.000</td>
<td>1231353.37</td>
</tr>
</tbody>
</table>

Optimum reflux ratio for acetone column = 0.33
Optimum reflux ratio for anhydride column = 1.77