THE USE OF A MATHEMATICAL MODEL IN THE COMPUTER CONTROL OF AN INDUSTRIAL DISTILLATION TOWER

By
HENRY RAY WENGROW

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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To Vicki, my precious wife,

"...the trewest and best wyf
That evere yet I knew in al my lyf."
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Abstract of Dissertation Presented to the Graduate Council in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

THE USE OF A MATHEMATICAL MODEL IN THE COMPUTER CONTROL OF AN INDUSTRIAL DISTILLATION TOWER

By

Henry Ray Wengrow

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Chairman: Dr. Frank P. May
Major Department: Chemical Engineering

In this investigation a mathematical model of a continuous stage-wise distillation column was derived. A convergence technique was developed to solve the mathematical model with the use of a digital computer. Experimental data from an industrial column was used to verify the accuracy of the model to simulate plant conditions.

The mathematical model was then modified so that it could be used to predict the steady-state control points to maintain composition quality in one of the product streams of this column. This control model was then used to control a tower in a tall oil production unit.

The mathematical model consists of steady-state material and energy balances around the upper and lower sections of the fractionating column after the method of Sorel. The convergence method uses a ratio
of feed plate compositions, as computed from the top and bottom, raised to a power in order to adjust the top and bottom compositions for the next trial. Convergence is reached when the ratio equals one. The control model convergence technique adjusts overheads flow rate in order to maintain constant composition in the sidestream during the convergence procedure.

An IBM 1620/1070 computer system was programmed with the control model and linked to an industrial tall oil fatty acid fractionating column. Vapor phase chromatograph analyses of the feed stream were entered into the computer at regular intervals and the model then predicted external flow rates necessary to maintain constant product composition in the sidestream. A 1 per cent increase in yield of the main product resulted from this control. This would produce a financial return of $10,000 a month for the average tall oil plant with a throughput of 10,000 tons per month.

On the basis of this work, several conclusions may be made:

It is possible to write a theoretical description of an actual industrial distillation column with sufficient accuracy to allow its control by a digital computer.

It is not always necessary to have all physical data completely defined before a model may be used, but actual operating data may be used to fill the gaps in our knowledge.

The power ratio convergence technique has proved itself to be a useful method in the solution of steady-state distillation calculations and should have applications in other types of trial and error calculations.
CHAPTER I

INTRODUCTION

A. The Process of Distillation and Its Amenability to Control

Distillation is one of the major unit operations in the chemical and related industries. Entire plants consist of distillation towers and their auxiliary equipment. The control of these towers and plants has occupied many working hours of many process chemical engineers.

Before World War II, process control was more of an art than a science. It consisted mainly of measurement and control of various parts of the process independently of each other and with little regard for the overall process involved. Control was regarded as primarily a function of instruments and hardware (1) and not of the process. With the development of an adequate theory of control, the possibility of integrating the process and its controllers into one overall system for analysis and design became a practical goal, and much effort in recent years has been in this direction. This approach made necessary consideration of the process dynamics and the realization of the need of rapid and reliable continuous composition analyzers. Though much work is still to be done in this area, considerable progress is evident from the results being reported in the literature.

One of the first things one realizes when trying to effect control of a unit operation is that the two concepts of design and control have in the past been thought of as separate entities, whereas good design should include consideration of dynamics and control. Classical design equations have limited utility in predicting how a plant will operate (1). Design is always concerned with size and operating conditions
are assumed to be fixed. But once the design is implemented, process people want and have to know how the plant operates under a variety of conditions, regardless of what it was designed to do. Design equations and procedures for the sizing of equipment do not lend themselves readily to the prediction of operating conditions without the use of trial and error procedures. However, it is reasonable to assume that the control problem can always be formulated in a way which will yield answers to the questions of how the plant operates.

The study of an operating system can be thought of in two ways, which while related, may be treated as separate topics. The process may be described as a time-invariant operation, or in a steady state, or a more complete description of the process can be formulated in which time varying conditions are included. The latter is the dynamic model approach and of course includes the steady-state information as a special case.

1. Steady State

Most design is carried out on a steady-state basis. That is, the equipment is sized to produce certain results when operating at constant conditions. Moreover, most industrial operations are geared for operation at steady-state conditions because the process engineers and operators want to "line out" their column and hold the product on grade to meet sales specifications. Thus, it is not surprising to find many applications for control of a distillation tower on a steady-state basis. In addition, the added time and expense to describe the system dynamically may be difficult to justify from an economic point of view, even though it would appear obvious that a thorough dynamic analysis may yield
dividends in processing knowledge that would not be obtainable from a steady state consideration.

The steady-state problem can be stated in this fashion: Given a feed rate and composition, at what values must the controlled variables be set so as to achieve "best operation" (i.e., on-grade product) when the column reaches a steady state?

2. Dynamic

Dynamic distillation models have been formulated by several investigators. Huckaba, Franke, and May (2) described a model for binary distillation and Distefano (3) used this model in an open loop predictive control scheme on a pilot plant size laboratory column with good success. Other dynamic models have appeared in the literature (4,5,6), but their application to control has been limited. It is reasonable to assume that some operating advantage could be obtained by using transient conditions to operate a better column; however, no published description of such an operation has come to the attention of the author. Some systems, such as batch distillation, are inherently dynamic and the dynamic approach is necessary to describe and understand them.

In order to use a dynamic model in an industrial control problem, and not in the study of the system for design of the control, several conditions must be present. Perhaps the first one, which is basic to all engineering problems, is that the financial return for the more complex dynamic study must be great enough to pay out the additional expense. There is no general answer to this problem either one way or the other, but the largest drawback to a dynamic analysis at the present time is the
lack of experience in these sorts of techniques. Another consideration is the availability of physical data and the obtaining of experimental verifications of the dynamic model. In the plant project discussed in this work, the difficulty of obtaining samples from the process and the long involved chemical analysis of these samples made the verification of any dynamic model impractical. A third consideration is the estimated response time of the process and the frequency and magnitude of process upsets. If the process has a very fast response time, then the dynamic considerations are perhaps not as important as the more usual slow response that is found in the chemical process industry. Also, if upsets are infrequent, then the dynamic problem is a minor consideration. If the upsets are low in magnitude and slowly changing, rather than abruptly, it would be possible to handle the dynamics by alert operators rather than a computer. One last consideration is the available computer power. Dynamic analysis requires a high speed digital computer to be used in an on-line basis. In addition, even an off-line study requires large core and very fast computational speed to provide answers in a reasonable amount of time. Again, in the plant project, we were restricted to the use of an IBM 1620 with limited access to the University of Florida's IBM 709. The IBM 1620 is a medium speed computer and takes in the range of one to two hours to solve the steady-state analysis of the distillation tower.

B. Previous Work

The literature of chemical engineering is replete with methods to calculate the performance of distillation towers. As pointed out in Part A, most of these techniques are design techniques which give size
and amount of equipment rather than predict the performance of existing equipment.

The complexity of the equations and the large number of variables in any distillation calculation make the job of calculating the conditions within the column a formidable one. However, only a relatively small number of these variables are independent and thus have to be specified before the problem is determinate. The number of specifications and the way these should be picked have been discussed by Gilliland and Reed (7), Kwauk (8), and others (9,10). An analysis of the degrees of freedom for this problem is discussed in Appendix A.

1. Calculation Procedures for the Steady State

a. Short-cut Methods

Short-cut methods which give approximate solutions to the rigorous distillation equations continue to serve a useful purpose even with the availability of high-speed computers which reduce the work necessary to obtain rigorous solutions. Often the data available do not warrant the use of rigorous equations, or perhaps a large number of different design configurations should be examined before attention is focused on the detailed analysis of one column.

Fenske (11) has presented an equation which relates the separation obtained between two components at total reflux to the number of equilibrium stages. Although the equation is derived for a binary, it may be used for a pair of components in a multi-component mixture. Underwood (12,13,14,15) developed equations which are convenient for estimating the minimum reflux corresponding to any specified separation of two key components in a multicomponent feed.
Gilliland (16) has presented a useful correlation which relates minimum stages (calculated with Fenske equations) and minimum reflux (calculated with Underwood equations) to the actual number of equilibrium stages and the actual reflux ratio.

Sauer (17) has presented a computer program which uses the Fenske and Underwood equations and makes use of the Gilliland correlations to calculate theoretical stages and reflux ratio.

Smith (9) presents a general short-cut method which is applicable to all equilibrium stage processes and he recommends its use.

It should be pointed out that there are many simplifying assumptions with any of the short-cut methods. The assumption of optimum feed location is inherent in the Underwood equations; the assumption of saturated reflux is inherent in both the Fenske and Underwood equations. Constant molal overflow is assumed in all these short-cut methods. To use the Fenske equations, it is necessary to estimate an average relative volatility for each component. For very small volatility differences, the Fenske equations can be widely in error (9).

Harbert (18) also presented equations for the case of constant molal overflow and constant relative volatilities.

b. Rigorous Methods

Sorel (19) developed and applied the mathematical theory of the rectifying column for binary mixtures. By making energy and material balances around each plate and assuming that equilibrium was attained between the vapor and liquid leaving the plate, he was able to calculate stepwise through the column. All of the more modern methods have been built upon Sorel's foundation.
Lewis and Matheson (20) applied Sorel's method to multicomponent mixtures. As originally presented, their method was concerned with picking the number of ideal stages, feed location and operating pressure for the column. Robinson and Gilliland (21) present a discussion of this method, and Bonner (22) has modified the Lewis and Matheson method and made it useful for machine computation. Smith (9) gives a detailed discussion of Bonner's use of the method.

The other most common technique for solving multicomponent distillation problems is the Thiele-Geddes (23) method. This method differs from the Lewis and Matheson method in that rather than assuming top and bottom compositions, a complete temperature profile for the column is assumed. These two methods differ only in computational technique; the final results of the calculations are the same. Some authors have shown distinct preference for one technique or the other. Holland (24) states that his convergence method works best with the Thiele-Geddes method. The choice of which method should be used depends to a large extent on the particular problem being solved. The convergence method presented in this work is independent of the distillation calculations and works equally well with both Lewis-Matheson and Thiele-Geddes techniques.

Other multicomponent distillation calculation procedures include that of Amundson-Pontinen (25,26), in which the equations are written as a system of simultaneous algebraic equations and solved by matrix techniques. Rose, et al. (27) have applied a relaxation technique to carry the solutions of the differential-difference equations to steady state. This is slower than most other methods for obtaining the steady-
state solution, but has the advantage of allowing one to follow the transient response from the disturbance to steady state if realistic initial conditions are specified. Ball (28) has modified the Rose relaxation method and speeded it up to make it competitive with other methods for obtaining steady-state solutions at the expense of correct dynamic results. Rosenbrock (29) has also presented a method for obtaining rapid steady-state solutions from a dynamic model. With the advent of better and more efficient numerical methods, steady-state solutions to a system of differential-difference equations may well prove the most practical method to make multicomponent distillation calculations. This will undoubtedly be tested as the transient response becomes more common in its use by design and operating personnel.

2. Control Applications

Many articles have been written on the control of distillation towers; however few take the view that it is necessary to have a rigorous mathematical model to describe the process. Most attempts at control have focused on a particular problem (30) and the development of hardware to handle a particular job. Buckley (1) in his book, *Techniques of Process Control*, devotes four chapters exclusively to control of distillation towers. The reader is referred to this work as a scholarly exposition of the state of the art.

Horn and Miller (31) have described the fitting of "an available complex, plate-to-plate engineering-calculation computer program" to actual plant data. They use this model to generate data for a regression analysis to obtain simple approximate relations among the control variables.
MacMullan and Shinsky (32) report the feedforward control of a super fractionator using a pneumatic analog controller. They use a material balance equation over the entire column for steady state and postulate a second-order model with one lead and two lag terms to simulate the dynamics of the system. They report substantial improvement over the more conventional feedback control techniques, reducing the distillation composition variation from 5 per cent to 1 per cent.

C. Statement of the Problem

The problem of digital computer control of distillation processes is a general one but its realistic application has to be directed at a particular process. The author has been employed during the past year and a half by the Organic Chemicals Division of The Glidden Company and it was a happy circumstance that they were interested in using computer control of a crude tall oil distillation process at their Port St. Joe, Florida plant. The work undertaken was primarily of interest for its theoretical aspect but it was most gratifying to be able to actually test the theory in a real world situation.

Specifically, the problem discussed in this work is:

1. To describe in mathematical terms the multicomponent distillation process as it applies to the tower designated A-30.

2. To develop a calculation procedure which will allow the mathematical model to be solved.

3. To fit the mathematical model's predicted composition profiles to those obtained experimentally from the distillation column.

4. To use the mathematical model to develop insight into the problem of digital computer control of the process.
5. To develop and implement the mathematical model to provide predictive control of the actual process located at a distance of about 300 miles from the digital computer.
CHAPTER II

MATHEMATICAL PROCEDURES

A schematic diagram of the column (designated A-30) is shown in Figure 1. The operation taking place in A-30 consists of the low pressure distillation of a mixture of fatty acids and organic impurities known as unsaponifiables (unsaps). The feed to A-30 is the fatty acid cut of crude tall oil consisting in the most part (80%) of oleic and linoleic (C-18) acids. There is also an appreciable amount of palmitic (C-16) acid together with higher and lower straight chain acids and the unsaps. The commercial object of the process is to produce a fatty acid with low unsaps (approx. 1%) concentration which is essentially free of palmitic acid. Steam is introduced in the reboiler to allow the distillation to take place at a low temperature by reducing the partial pressure of the organics and thereby saving the product from thermal degradation. The feed is heated by a feed preheater before entering the column and the overhead vapors are condensed in an internal type condenser.

A. The Mathematical Model

The mathematical model is derived by using the method of Sorel (19) in applying energy and material balances around separate sections of the column.

1. Assumptions

The following assumptions are made in the basic model:

1. Steam is always a superheated vapor.
2. The liquid phase and the vapor phase form ideal solutions
Figure 1. Schematic Diagram of A-30 Distillation Column
(i.e. no heat of mixing) so that the total enthalpy of a liquid or vapor stream may be treated as an additive function of pure component enthalpies.

3. The equilibrium may be represented by Raoult's law.

4. The heat capacity and heat of vaporization for each component are functions of temperature only.

5. The efficiency of each component is equal and constant.

6. There is no heat loss to the atmosphere.

7. The feed is a saturated liquid.

8. The liquid and vapor streams within the column are at their bubble and dew points, respectively.

2. Derivation of the Basic Equations

Taking a total material balance around the reboiler (envelope 1 of Figure 1) we obtain

\[ L_2 + S_0 = B + V_1 \]  

(1)

The individual component balances for the organics can be written as

\[ x_{i2}L_2 = Bx_{i1} + V_1y_{i1} \]

(2)

and for water vapor

\[ S_0 = y_{w1}V_1 = S_1 \]

(3)

The energy balance for the reboiler is

\[ Q_S + h_2L_2 + h_{so}S_0 = h_1B + h_1V_1 \]

(4)

The total enthalpy of any liquid stream may be represented by

\[ h_n = \sum_{i=1}^{c} h_{in}x_{in} \]  

(5)
and for any vapor stream as

\[ H_n = \sum_{i=1}^{c} \frac{H_n}{H_n} y_{in} + H_{sn} y_{wn} \]  

(6)

where \( c \) is the total number of organic components.

Combining Equations 4, 5, and 6, we obtain

\[ Q_S + \sum_{i=1}^{c} \frac{H_{12}}{h_{12}} x_{12} L + H_{so} S = \sum_{i=1}^{c} \frac{H_{ii}}{h_{ii}} x_{ii} B + \sum_{i=1}^{c} H_{ii} h_{ii} V_l \]

\[ + H_{sl} y_{wl} V_l \]

(7)

Substituting the \( c \) equations represented by 2 into 7 and rearranging gives

\[ V_1 = \frac{Q_S + S_o (H_{so} - H_{sl}) - B \sum_{i=1}^{c} (h_{ii} - h_{12}) x_{ii}}{\sum_{i=1}^{c} (H_{ii} - h_{12}) y_{ii}} \]

(8)

If the temperature in the reboiler is known, we may calculate the composition of the vapor leaving the reboiler

\[ y_{il} = \frac{p_{il} x_{il}}{\pi_l} \]

(9)

The pressure in the reboiler may be calculated by summing Equation 9 over \( c \) and using Equation 3

\[ \sum_{i=1}^{c} y_{il} = \frac{p_{il} x_{il}}{\pi_l} = 1 - y_{wl} \]

(10)

\[ \sum_{i=1}^{c} \frac{p_{il} x_{il}}{\pi_l} = 1 - \frac{S_o}{V_1} \]

(11)
The vapor rate, \( V_1 \), in Equation 11 must be equal to that calculated from Equation 8

\[
\frac{\sum_{i=1}^{c} p^* x_{i1}}{\pi} = 1 - \frac{\sum_{i=1}^{c} S \left( h_{i1} - h_{i2} \right)}{\pi_1} + B \sum_{i=1}^{c} (h_{i1} - h_{i2}) x_{i1}
\]

(12)

Solving for \( \pi_1 \), in Equation 12, we get

\[
\pi_1 = \sum_{i=1}^{c} p^* x_{i1} + \frac{\sum_{i=1}^{c} S \left( h_{i1} - h_{i2} \right) p^* x_{i1}}{\sum_{i=1}^{c} S \left( h_{i1} - h_{i2} \right) - B \sum_{i=1}^{c} (h_{i1} - h_{i2}) x_{i1}}
\]

(13)

All the quantities on the right hand side of Equation 13 are known or assumed so we may calculate the reboiler pressure.

The order of solution for these equations is:

1. Obtain \( \pi_1 \) from Equation 13
2. Obtain \( y_{i1} \) from Equation 9
3. Obtain \( V_1 \) from Equation 8
4. Obtain \( L_2 \) from Equation 1
5. Obtain \( x_{12} \) from Equation 2.

Taking energy and material balances around the bottom of the column, below the side stream (envelope II in Figure 1) and making use of the equilibrium and Murphree efficiency relationships,

\[
y_{in}^* = \frac{p_{in}^* x_{in}}{\pi_n}
\]

(9)

\[
y_{in} = y_{in-1} + E_{vin} (y_{in}^* - y_{in-1})
\]

(14)

we may derive exactly the same sort of relationships as for the reboiler.

Defining some intermediate quantities as:
\[
C_1 = \sum_{i=1}^{c} E_{Vin}^p x_{in}^* \quad \text{(15)}
\]

\[
C_2 = \sum_{i=1}^{c} (\bar{H}_{in} - \bar{h}_{in+1}) E_{Vin}^p x_{in}^* \quad \text{(16)}
\]

\[
C_3 = \sum_{i=1}^{c} (\bar{h}_{in+1} - \bar{h}_{11}) x_{11} \quad \text{(17)}
\]

\[
C_4 = \sum_{i=1}^{c} (1 - E_{Vin}) y_{in-1} \quad \text{(18)}
\]

\[
C_5 = \sum_{i=1}^{c} (\bar{H}_{in} - \bar{h}_{in+1})(1 - E_{Vin}) y_{in-1} \quad \text{(19)}
\]

\[
D_1 = Q_S + (H_{so} - H_{sn}) S + B \cdot C_3 \quad \text{(20)}
\]

We may write:

\[
\pi_n = (C_1 + SC_2/D_1)/(1 - C_4 - S \cdot C_5/D_1) \quad \text{(21)}
\]

\[
V_n = D_1 / \sum_{i=1}^{c} (\bar{H}_{in} - \bar{h}_{in+1}) y_{in} \quad \text{(22)}
\]

\[
L_{n+1} = B + V_n - S \quad \text{(23)}
\]

\[
x_{in+1} = (Bx_{11} + V_n y_{in})/L_{n+1} \quad \text{(24)}
\]

In the same manner as above, we can derive the equations which apply between the sidestream and the feed plate.

Defining

\[
C_6 = \sum_{i=1}^{c} (\bar{H}_{in+1} - \bar{h}_{ic}) x_{ic} \quad \text{(25)}
\]

\[
D_2 = Q_S + (H_{so} - H_{sn}) S + BC_3 + CFA - C_6 \quad \text{(26)}
\]
We may write:

\[ \pi_n = \frac{(C_1 + SC_2/D_2)}{(1 - C_4 - SC_5/D_2)} \]  
(27)

\[ V_n = D_2 / \sum_{i=1}^{c} (\bar{H}_{in} - \bar{h}_{in+1})y_{in} \]  
(28)

\[ L_{n+1} = B + V_n + CFA - S_o \]  
(29)

\[ x_{in+1} = \frac{(Bx_{i1} + CFAx_{iCFA} + V_n y_{in})}{L_{n+1}} \]  
(30)

The above equations (27-30) are used for \( n < f \).

Taking energy and material balances around the entire column, we can calculate a value for the condenser heat duty.

\[ \phi_c = F \sum_{i=1}^{c} \bar{h}_{iF}x_{iF} - (B \sum_{i=1}^{c} \bar{h}_{i1}x_{i1} + CFA \sum_{i=1}^{c} \bar{h}_{iCFA}x_{iCFA} \]

\[ + D \sum_{i=1}^{c} \bar{h}_{iD}x_{iD} + Q_S + (H_{so} - H_{sD})S_o \]  
(31)

By taking balances around the condenser system, the vapor composition leaving the top plate may be calculated:

\[ L_R = \left[ \left( H_{sD} - H_{sD-1} \right) S_o + \phi_c \right] / \sum_{i=1}^{c} (\bar{H}_{iD-1} - \bar{h}_{iD})x_{iD} - D \]  
(32)

\[ V_{D-1} = L_R + D + S \]  
(33)

\[ y_{iD-1} = \frac{(L_R + D)x_{iD}}{V_{D-1}} \]  
(34)

The pressure at the plate can be calculated by

\[ \pi_{D-1} = \frac{1}{\sum_{i=1}^{c} \frac{y_{iD-1}}{P_{iD-1}}} \]  
(35)
The following equations are used to calculate conditions in the top of the column:

\[ x_{in}^* = \pi_n y_{in}^*/\overline{p}_{in} \]  
(36)

\[ x_{in} = x_{in+1} - E_{Lin}(x_{in+1} - x_{in}^*) \]  
(37)

\[ L_n = \left[ \frac{c + (H_{so} - H_{n-1})S + D}{\sum_{i=1}^{c} (H_{iD} - \overline{H}_{n-1})x_{iD}} \right] \]  
\[ \sum_{i=1}^{c} (H_{iD} - \overline{H}_{in})x_{in} \]  
(38)

\[ V_{n-1} = L_n + D + S \]  
(39)

\[ y_{in-1} = \frac{(L_n x_{in} + Dx_{iD})}{V_{n-1}} \]  
(40)

\[ \pi_{n-1} = \frac{1}{\sum_{i=1}^{c} \frac{y_{in-1}}{x_{in}^*}} \]  
(41)

Equations 36 and 37 are repeated by incrementing \( n \) and 38-41 are repeated until \( n = f + 1 \). At the feed plate, an average composition of the liquid entering the feed plate is calculated by Equation 42.

\[ x_{imix} = (F x_{iF} + L_{f+1} x_{if+1}) \left( \frac{F + L_{f+1}}{F_{f+1}} \right) \]  
(42)

The liquid which would be in equilibrium with the vapor leaving the feed plate is calculated by Equation 36 with \( n = f \) and the liquid leaving the feed plate as calculated from the top is

\[ x_{if} = x_{imix} - E_{Lif}(x_{imix} - x_{if}^*) \]  
(43)
When the compositions calculated from Equation 43 and Equation 30 are equal, the correct top and bottom compositions have been selected and the solution has converged.

**B. Calculation and Convergence Techniques**

One of the basic problems in any multicomponent distillation calculation is that of convergence to the proper solution. This problem is especially acute if a modern digital computer is used, since manual intervention is for all practical purposes impossible without great losses in time and money. In any hand-calculated solution, much subconscious judgment comes into play allowing the calculator to abandon fruitless paths without carrying the solution very far. However, a computer, no matter how fast or sophisticated, cannot exercise the engineering judgment of the most unskilled practitioner and therefore must be programmed in a foolproof method which assures convergence to a proper solution. By convergence, it is meant that by taking sufficient trials, the error may be reduced to within any predetermined limits.

1. **Previous Work**

Smith (9) has an excellent summary of the various methods of choosing new variables for the distillation calculations and two books (10, 24) have recently been written on this subject alone.

Perhaps the oldest method in use is that of direct-iteration which uses the results of the previous trial without any manipulation to start the next trial. Lewis and Matheson (20) in their original paper illustrate the direct iteration technique as do Thiele and Geddes (23).

Bonner (22) was one of the first to present a computer program
for the solution of multicomponent distillation problems. He programmed
the basic Lewis-Matheson procedure with slight adjustment for machine
computation. However, his technique for convergence was direct-
iteration.

Lyster, et al. (33) and Holland (24) have presented the Theta
method of convergence and used it with the Thiele-Geddes method of
calculation. Since many articles have appeared on this technique, a
brief description of it seems appropriate.

Let us relate the assumed (trial) and correct values of product
ratios as follows: For any component,

\[ \left( \frac{b_i}{d_i} \right)_{\text{correct}} = \theta_i \left( \frac{b_i}{d_i} \right)_{\text{calculated}} \]  \hspace{1cm} (44)

From the individual component material balances and the require-
ment that the overhead flow rate is fixed, we may write

\[ Fx_iF = (d_i)_{\text{correct}} + (b_i)_{\text{correct}} \]  \hspace{1cm} (45)

\[ D = \sum_{i=1}^{c} (d_i)_{\text{correct}} \]  \hspace{1cm} (46)

If the final and assumed values were known, we could calculate
the set of \( \theta_i \)'s which satisfy Equation 44; however, this is not the
case. We can find a single \( \theta \) which will satisfy Equations 45 and 46,
if the subscript \( i \) is dropped from the \( \theta \) in Equation 44. This single
\( \theta \) can be considered an approximation of each value in the set of \( \theta_i \)'s.
It is argued that this is a reasonable approach because all the \( \theta_i \)'s must
equal one when the assumed value is the correct value.
Solving Equations 44-46 and eliminating the correct values of products (the unknowns), we can obtain Equation 47.

\[ g(\theta) = \sum_{i=1}^{c} \frac{F_{xi}F}{1 + \theta \left( \frac{b_i}{d_i} \right) \text{calculated}} - D = 0 \]  

The desired value of \( \theta \) is the positive root which makes \( g(\theta) = 0 \). Once this \( \theta \) is found (Holland gives several standard methods for finding the roots of algebraic equations) the corrected values of \( d_i \) and \( b_i \) may be calculated from Equations 48 and 49.

\[ (d_i)_{\text{corrected}} = \frac{F_{xi}F}{1 + \theta \left( \frac{b_i}{d_i} \right) \text{calculated}} \]  

\[ (b_i)_{\text{corrected}} = \theta \left( \frac{b_i}{d_i} \right) \text{calculated} \]  

\[ (d_i)_{\text{corrected}} \]  

The Thiele-Geddes iteration is then repeated until convergence is obtained. For a more complete discussion of this method and its usefulness, the reader is referred to the original papers or Holland's book (24) which deals with the Theta method in great detail.

Greenstadt, Bard and Morse (34) developed a very complex IBM 704 computer program to solve the multicomponent distillation problem. Conditions at the top and bottom of the column are assumed. Calculations are carried out until the "feed" or "match" plate is reached. If compositions are not the same, as calculated from the top and bottom, an "appropriately framed form of Newton's method" is used to make this connection. The calculations are then repeated until matching conditions are satisfied. This program, while very sophisticated from a machine
point of view, is rather obscure for the average chemical engineer. It uses a machine type language rather than the more readily understood programming languages, such as FORTRAN, and hence the chemical engineering clarity is sacrificed for the sake of machine considerations.

Deland and Wolf (35) present a procedure for solving distillation problems on an electronic analog computer by replacing the normal algebraic equations with differential equations and obtaining the steady-state solution. A direct-iteration procedure is used to correct the calculated compositions by varying feed rates and number of plates in the column.

Peiser (36) presents a convergence technique which he claims is rapid, with only the most difficult problems taking seven or eight iterations. He considers the distillation column to be made up of two lumped units, rectifying and stripping sections. Consider Figure 2

![Figure 2. Block Diagram of a Distillation Tower](image)
The individual component material balances which must be satisfied are shown in Equations 50 and 51.

\[ L_T x_{iT} + D x_{iD} = V_B y_{iB} + G x_{iG} \]  
\[ L_T x_{iT} + M x_{iM} = V_B y_{iB} + B x_{iB} \]  

If these equations are not satisfied, then new trial values of \( B, x_{iB}, D \) and \( x_{iD} \) must be picked. This is done by treating the feed as if it was flashed and we seek a relationship of the form

\[ \alpha_i = \left( \frac{x_{iD}}{x_{iB}} \right) \gamma_i \]  

where the \( \gamma_i \)'s are so defined as to equal one when Equations 50 and 51 are satisfied. Alpha is the relative volatility of component \( i \). After a certain amount of admitted heuristic argument, Peiser defines the \( \gamma_i \) to be

\[ \gamma_i = \left[ \frac{V_B y_{iB} + G x_{iG}}{L_T x_{ir} + D x_{iD}} \cdot \frac{V_B y_{iB} + B x_{iB}}{L_T x_{ir} + M x_{iM}} \right]^{1/2} \]  

While this form is quite arbitrary, Peiser claims rapid convergence in all cases.

Hansen (10) presents two methods of convergence in his book of computer programs. His Method I is the same as Holland's (24) Theta method and his Method II is derived from the basic differential equations of the dynamic system.

Hansen uses the following equation

\[ (x_n)^{n+1} = \frac{V n^{-1} K n^{-1} x_{n-1} + L n^{+1} x_{n+1}}{V K n + L n} \]
to calculate the value of \( x_n \) for the \( r+1 \)th trial. An additional assumption must be made to start this solution and that is the composition at every stage. Hansen has found it satisfactory to use feed liquid at its bubble point on each plate as a first assumption. Equation 54 has the exact form of the well-known flash equation, so Hansen has termed this method as the "Method of Successive Flashes."

Other convergence techniques include those of Bonner (22) and Ball (28).

2. The Power Ratio Convergence Technique

A method developed in this work which is presented here makes use of a ratio of compositions at the feed plate as calculated from the top and bottom by a plate-to-plate calculation. This ratio raised to a power which acts as a "gain factor" in eliminating the error between top and bottom calculations has been found to be particularly useful in this work and appears to have a considerable potential for wide-spread application in multicomponent distillation work. This method was developed because of difficulties which were encountered in trying to use Holland's Theta method on A-30 tower. The difficulties hinged on the fact that A-30 is a complex tower having restrictions on the sidestream composition and having an inert component (steam) passing through the whole tower. Insufficient work was done to prove that Holland's method fails or must be modified for this tower, but it was clearly very difficult to implement. It is also clear from Holland's writings (24) that complex columns require special arrangements of his equations that often depend on the particular column being considered.
Only one reference has been found (37) in which the use of a ratio as the basis for a convergence technique is mentioned. The ratio is used without the gain factor and in an entirely different fashion from that proposed here. There is no report of its use except with a single simple tower.

In the Power Ratio Convergence Technique, the form of the distillation equations is unimportant; all that is necessary is that one be able to calculate compositions from both directions, starting with composition values in the top and bottom streams. The choice of the particular stream on which the convergence is made is unrestricted, as the method works equally well on vapor streams or other liquid streams. The feed plate is a convenient choice because this avoids the possibility of computing negative values from the material balance equations. When we compute negative flow rates or composition, we move mathematically into a physically unattainable region which violates the implied assumption in all distillation problems of a real-world situation with positive flow rates and compositions.

If we designate the liquid leaving the feed plate as \( x_{\text{rifT}} \) when calculated from the top and as \( x_{\text{rifB}} \) when calculated from the bottom we can compute a ratio for each component \( i \),

\[
\gamma_i = \frac{x_{\text{rifT}}}{x_{\text{rifB}}} \tag{55}
\]

This ratio is equal to 1 when both computed compositions are the same. If we examine the ratio relative to calculated composition profiles, we find that it is greater than 1 when the profiles do not meet, as shown
in Figure 3, and less than 1 when the profiles overlap one another, as shown in Figure 4. A ratio greater than 1 indicates that the guess of $x_{1B}$ (bottom composition) was too small and $x_{1T}$ (top composition) was too large, while a ratio less than 1 indicates the exact opposite.

The correction to make these profiles meet at the feed plate can be shown if we consider the bottom half of the column alone. When the column profile is plotted with composition on a logarithmic scale and stage number on an arithmetic scale, for different trial values of $x_{1B}$, an important property of the composition-position function is observed. The second profile appears to be a linear displacement of the first with respect to the log axis. As shown in Figure 5, a change in $x_{1B}$ produces an approximately equal change in $x_{1fB}$.

We can express the column profile for any trial as a function of $\log x_i$

$$N = \phi(\log x_i)$$

(56)

and transform this function into the profile for any other trial by the linear translation

$$\log x_i^1 = \log x_i + \log a = \log a x_i$$

(57)

The factor $a$ is a function of the ratio term defined by Equation 55 since the ratio is the percentage on the log axis by which we want to displace the profile. The ratio is the factor by which all points in the bottom profile must be multiplied in order to displace the feed plate composition to meet the previous value of the feed plate composition which was calculated for the top profile.

The top and bottom compositions are directly related by the
Figure 3. Column Profile: Ratio Greater Than One
Figure 4. Column Profile: Ratio Less Than One
Figure 5. Column Profile: Linear Translation of Profile
overall material balance so any change in one effects the other.
Therefore, if we shift the bottom profile to meet the top profile, the
top profile also moves and the profiles could possibly pass one another
on the next trial, especially if the top and bottom compositions are
of the same order of magnitude. To allow for this problem, each ratio
is raised to a power, the value of which is selected based on past
history of the ratio, that is on whether the ratio is oscillatory about
1 or not. We, therefore, define a gain factor \( g_i \) by the equation

\[
k_i = \gamma_i^g
\]

(58)
in order to control the corrective action.

Since \( x_{iB} \) and \( x_{iT} \) are related by the material balance equations,
some method must be devised to allow both the restrictions of match and
component material balance to be satisfied. One obvious method is to
apply all the ratio corrections to either the top or bottom stream and
calculate the other stream composition using the overall component
material balance. Using this technique has the disadvantage that a
component whose concentration is high in the stream corrected by the
ratio may be changed so that the material balance gives a negative
concentration in the other stream. This difficulty is avoided by
correcting those components which concentrate in the top (lights) in
the bottom and those components which concentrate in the bottom (heavies)
in the top. In addition, some consideration should be made of the side-
stream concentrations. For a sidestream which is located in the bottom
section of the tower, it appears logical to apply the same correction
as we have made to the bottom stream, while if the sidestream is
located in the top section of the tower, we should make the same correction as we have made in the top stream.

Based on these considerations, the following equations were used to correct the assumed top and bottom compositions for A-30 column which had one sidestream located in the bottom section of the column.

For the light components

$$x_{iB}^N = x_{iB}^0 k_1$$  \hspace{1cm} (59)

and by material balance,

$$x_{iD}^N = \frac{Fx_{iF}^N - (CPA_{iCFA}^0/x_{iB}^0 + B)x_{iB}^N}{D}$$  \hspace{1cm} (60)

For the heavy components

$$x_{iT}^N = x_{iT}^0 / k_1$$  \hspace{1cm} (61)

and by material balance,

$$x_{iB}^N = \frac{Fx_{iF}^N - Dx_{iD}^N}{(CPA_{iCFA}^0/x_{iB}^0 + B)}$$  \hspace{1cm} (62)

In the event that Equations 60 or 62 give a negative number, the previous value of that variable is used in the next trial.

It has been found that the rate of convergence of this technique is a function of the gain factor. At a fixed gain of 1 for all components (applying the entire ratio correction) the method is oscillatory; therefore, to begin the solution, gains of less than one are used with the ratio terms being monitored in the computer program. Any repeated
change in ratio from greater than 1 to less than 1 (which indicates oscillation) causes a reduction in the size of the gain factor. However, it is desirable to keep the gain as high as possible in order to reduce the number of column calculations necessary for convergence; therefore, the gain is increased on those components which are not oscillatory.

Figures 6 through 8 show the effect of this gain factor upon convergence time. These plots are of the ratio for same three components vs. iteration number. Figure 6 shows a gain of 0.5, while Figure 7 illustrates the oscillatory behavior with a constant gain on each component of unity. The data which are plotted in Figure 8 was made with a constant gain equal to 0.9. It is interesting to note that the reduction in error is almost twice as much per iteration in this case as it is with a gain of 0.5.
Figure 6. Ratio with Constant Gain of 0.5
Figure 7. Ratio with Constant Gain of 1.0
Figure 8. Ratio with Constant Gain of 0.9
CHAPTER III

MODEL FITTING AND EXPERIMENTAL RESULTS

To be of practical use, a theoretical model must describe the process with reasonable accuracy. One of the identifying attributes of most industrial operations is the lack of accurate and reliable physical data. This lack of data must be overcome, at least to the extent of having the model duplicate the actual plant process within acceptable limits. This was done in this work by varying the constants in the vapor pressure relationships until a good fit of the experimental plant data was obtained. These constants were then verified by an independent set of plant data.

A. Physical Data

An examination of the model as derived in Chapter II will show that there are several parameters which can be changed to obtain a good fit for the model. The two most important parameters used in the model are the vapor pressure of each component and the plate efficiencies. Therefore, it became necessary to define the components in the tall oil fatty acid and determine or assign vapor pressures to each of them.

The feed to A-30 column consists of the fatty acid (FA) portion of crude tall oil (CTO). The FA is composed of the straight chain fatty acids, both saturated and unsaturated, with carbon numbers of 14 and higher and certain structurally unknown substances designated as unsaps. From vapor phase chromatography (VPC) the feed stock to A-30 was split into 4 acids and 5 unsaps. The acids are designated as C-14 (Myristic), C-16 (Palmitic), C-18 (Oleic), and C-20 (Sterric) and the unsaps as L-1 through L-5 with molecular weights assigned as 239, 290, 312,
318, and 332, respectively. The VPC method, of determining the composition of FA presented in Appendix D, was developed in the Port St. Joe Laboratory and is faster and more detailed than the standard method (38).

Vapor pressure data on pure components were collected from as many sources as possible and are shown in Appendix B. These data were fit to an Antoine type equation:

$$\log p_i^* = \frac{A_i}{t + C_i} + B_i$$  \hspace{1cm} (63)

By the use of the Clausius-Clapeyron equations, a relationship was derived to give the latent heat of vaporization on a function of temperature (39).

$$\lambda_i = -\frac{R}{\log c} \frac{A_i}{10} \left[ \frac{t + 273}{t + C_i} \right]^2$$  \hspace{1cm} (64)

Liquid heat capacity data were obtained from the literature for those substances which were known (straight chain acids) and an average $c_{pi}$ based on the fatty acids were used for the unsaps. All of the data obtained on these substances could be reasonably related to temperatures by a linear relationship.

$$c_{pi} = a_i + b_i t$$  \hspace{1cm} (65)

Saturated liquid enthalpies were calculated by Equation 66 and vapor enthalpies were calculated by Equation 67.

$$\bar{h}_{in} = \int_{t_R}^{t_n} (a_i + b_i t) dt$$  \hspace{1cm} (66)

$$\bar{H}_{in} = \bar{h}_{in} + \lambda_{itn}$$  \hspace{1cm} (67)

Using the available literature values for vapor pressure and
assuming 100 per cent efficiency, a steady-state calculation on the computer was made with flow rates, feed composition, and reboiler heat duty corresponding to an actual experimental run on the column. The efficiencies were lowered until the trends of the computed profiles tended to be the same as the observed profiles. The constants in the vapor pressure curves were then varied until a reasonable fit of the experimental data was made. The final physical constants used in this work are also shown in Appendix B.

B. Experimental Work

Two complete sets of data were taken on the tower. A complete set of data consists of samples of the feed, top, side, and bottom streams of the column, 8 samples from trays within the tower, of flow rates of all streams, temperatures at selected plates in the column, and the reboiler heat duty. One set of data (040165) was used to obtain the proper physical constants for the vapor pressures of each component as described in Part A of this chapter. The other set of data (050665) was used to verify the model's fit to the actual process. In addition, a partial set of data (i.e., everything but internal plate samples) was obtained at rates which differed drastically from the normal operating conditions.

Table 1 shows the experimental analysis of the samples collected for Run 040165. Table 2 shows the operating conditions for Run 040165. Figure 9 shows the total unsaps concentration as calculated by the model and as obtained experimentally for Run 040165. Figures 10-18 show each individual component profile for Run 040165 as obtained experimentally and as calculated with the mathematical model.

The disagreement between the experimental points and the calculated curves for L-1 (Figure 11) and L-2 (Figure 13) is probably
## TABLE 1

**Composition Data**

Run 040165

<table>
<thead>
<tr>
<th>Location</th>
<th>C-14</th>
<th>C-16</th>
<th>C-18</th>
<th>C-20</th>
<th>L-1</th>
<th>L-2</th>
<th>L-3</th>
<th>L-4</th>
<th>L-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heads</td>
<td>5.00</td>
<td>36.99</td>
<td>36.72</td>
<td>1.03</td>
<td>2.17</td>
<td>9.12</td>
<td>2.08</td>
<td>5.61</td>
<td>1.27</td>
</tr>
<tr>
<td>Tray 24</td>
<td>0.54</td>
<td>13.04</td>
<td>80.04</td>
<td>0.77</td>
<td>0.21</td>
<td>0.83</td>
<td>0.41</td>
<td>3.28</td>
<td>0.86</td>
</tr>
<tr>
<td>Tray 22</td>
<td>0.37</td>
<td>8.60</td>
<td>85.44</td>
<td>1.50</td>
<td>0.14</td>
<td>0.58</td>
<td>0.28</td>
<td>2.10</td>
<td>1.00</td>
</tr>
<tr>
<td>Feed</td>
<td>1.03</td>
<td>8.35</td>
<td>81.20</td>
<td>3.56</td>
<td>0.69</td>
<td>2.05</td>
<td>0.42</td>
<td>1.87</td>
<td>0.83</td>
</tr>
<tr>
<td>Tray 14</td>
<td>0.10</td>
<td>6.00</td>
<td>87.61</td>
<td>3.31</td>
<td>0.07</td>
<td>0.38</td>
<td>0.22</td>
<td>1.67</td>
<td>0.64</td>
</tr>
<tr>
<td>Tray 12</td>
<td>0.09</td>
<td>4.43</td>
<td>89.50</td>
<td>3.40</td>
<td>0.02</td>
<td>0.14</td>
<td>0.14</td>
<td>1.48</td>
<td>0.80</td>
</tr>
<tr>
<td>Tray 10</td>
<td>0.33</td>
<td>3.56</td>
<td>90.84</td>
<td>3.31</td>
<td>0.04</td>
<td>0.03</td>
<td>0.10</td>
<td>1.19</td>
<td>0.60</td>
</tr>
<tr>
<td>Tray 8</td>
<td>0.20</td>
<td>2.57</td>
<td>91.98</td>
<td>3.42</td>
<td>0.02</td>
<td>0.04</td>
<td>0.06</td>
<td>1.06</td>
<td>0.64</td>
</tr>
<tr>
<td>Tray 6</td>
<td>0.22</td>
<td>1.53</td>
<td>92.88</td>
<td>3.52</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
<td>1.03</td>
<td>0.71</td>
</tr>
<tr>
<td>Tray 3*</td>
<td>0.36</td>
<td>1.08</td>
<td>91.69</td>
<td>5.63</td>
<td>0.02</td>
<td>0.04</td>
<td>0.03</td>
<td>0.64</td>
<td>0.51</td>
</tr>
<tr>
<td>Tray 2</td>
<td>0.13</td>
<td>0.60</td>
<td>91.40</td>
<td>6.72</td>
<td>0.04</td>
<td>0.05</td>
<td>0.02</td>
<td>0.52</td>
<td>0.53</td>
</tr>
<tr>
<td>Bottoms</td>
<td>0.34</td>
<td>0.14</td>
<td>84.38</td>
<td>13.40</td>
<td>0.12</td>
<td>0.11</td>
<td>0.04</td>
<td>0.59</td>
<td>0.87</td>
</tr>
</tbody>
</table>

*Sidestream*
TABLE 2

Operating Conditions:

Run 040165

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed rate</td>
<td>100 units/hr.</td>
</tr>
<tr>
<td>Bottoms</td>
<td>5.2 units/hr.</td>
</tr>
<tr>
<td>Sidestream</td>
<td>70.8 units/hr.</td>
</tr>
<tr>
<td>Heads **</td>
<td>21.8 units/hr.</td>
</tr>
<tr>
<td>Steam</td>
<td>39.4 units/hr.</td>
</tr>
<tr>
<td>Reboiler Heat Duty</td>
<td>$8.67 \times 10^5$ Btu/hr.</td>
</tr>
<tr>
<td>Reflux Temperature</td>
<td>85°C</td>
</tr>
</tbody>
</table>

* Flow rates are based on 100 units/hr. of feed

** Overhead product is designated as Heads throughout this work.
Figure 9. Total Unsaps Profile Run 040165
Figure 14. C-18 Profile Run 040165
Figure 15. L-3 Profile Run 040165
Figure 16. L-4 Profile Run 040165
Figure 17. L-5 Profile Run 040165
due to the analysis technique. The feed to the tower actually contains a very small amount rosin acid (1-2%) which is left after the split between rosin acid and FA is made on the CTO in a tower immediately upstream of A-30 tower. A rosin acid determination on the bottoms of the column shows that almost all of these acids go out of the bottom of the tower and that none can be determined above plate 8 (40). In addition, the retention position occupied by these unsaps on a VPC is the same as that occupied by the rosin acids present in CTO. Therefore, the reported unsaps concentrations in the bottom of the tower for the light unsaps is most likely in error and what really are present are rosin acids. The disagreement shown in the C-14 profile (Figure 10) in the bottom of the column probably comes from polymerizations of the C-14's in the bottom due to high temperature and long holding times and a cracking which occurs during the VPC analysis.

The agreement between experimental points and calculated curves for the other components is within the experimental error of the analysis technique and is rather good for actual plant process data.

Table 3 gives the experimental compositions data for Run 050665 and Table 4 gives the operating conditions for this same run. Figure 19 shows the total unsap profile and Figures 20-28 show the individual component profiles for Run 050665.

The agreement between calculated and experimental points is better for this run for L-1 (Figure 21) and L-2 (Figure 23) than for the previous run. Except for the bottom stream, no L-1 is detected below tray 8 and the probable reason is that the feed stock in this case was exceptionally low in rosin acids (40).
## TABLE 3

**Composition Data**

Run 050665

<table>
<thead>
<tr>
<th>Location</th>
<th>C-14</th>
<th>C-16</th>
<th>C-18</th>
<th>C-20</th>
<th>L-1</th>
<th>L-2</th>
<th>L-3</th>
<th>L-4</th>
<th>L-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heads</td>
<td>5.39</td>
<td>34.13</td>
<td>37.37</td>
<td>1.00</td>
<td>2.19</td>
<td>10.08</td>
<td>2.39</td>
<td>6.18</td>
<td>1.28</td>
</tr>
<tr>
<td>Tray 24</td>
<td>0.82</td>
<td>14.01</td>
<td>77.81</td>
<td>1.38</td>
<td>0.14</td>
<td>0.71</td>
<td>0.60</td>
<td>3.43</td>
<td>1.09</td>
</tr>
<tr>
<td>Tray 22</td>
<td>0.45</td>
<td>8.30</td>
<td>85.87</td>
<td>0.64</td>
<td>0.05</td>
<td>0.62</td>
<td>0.39</td>
<td>2.50</td>
<td>0.98</td>
</tr>
<tr>
<td>Feed</td>
<td>1.15</td>
<td>8.38</td>
<td>80.71</td>
<td>3.60</td>
<td>0.56</td>
<td>2.29</td>
<td>0.57</td>
<td>2.02</td>
<td>0.72</td>
</tr>
<tr>
<td>Tray 14</td>
<td>0.35</td>
<td>7.19</td>
<td>85.64</td>
<td>3.51</td>
<td>0.01</td>
<td>0.40</td>
<td>0.32</td>
<td>1.85</td>
<td>0.73</td>
</tr>
<tr>
<td>Tray 12</td>
<td>0.42</td>
<td>4.75</td>
<td>89.45</td>
<td>3.04</td>
<td>0.02</td>
<td>0.14</td>
<td>0.19</td>
<td>1.40</td>
<td>0.58</td>
</tr>
<tr>
<td>Tray 10</td>
<td>0.36</td>
<td>3.69</td>
<td>90.54</td>
<td>3.25</td>
<td>0.0</td>
<td>0.07</td>
<td>0.10</td>
<td>1.37</td>
<td>0.62</td>
</tr>
<tr>
<td>Tray 8</td>
<td>0.18</td>
<td>2.68</td>
<td>92.57</td>
<td>2.53</td>
<td>0.01</td>
<td>0.08</td>
<td>0.08</td>
<td>1.25</td>
<td>0.61</td>
</tr>
<tr>
<td>Tray 6</td>
<td>0.28</td>
<td>1.86</td>
<td>93.02</td>
<td>3.36</td>
<td>0.0</td>
<td>0.08</td>
<td>0.05</td>
<td>0.87</td>
<td>0.48</td>
</tr>
<tr>
<td>Tray 3*</td>
<td>0.44</td>
<td>1.11</td>
<td>92.54</td>
<td>4.63</td>
<td>0.0</td>
<td>0.02</td>
<td>0.03</td>
<td>0.72</td>
<td>0.51</td>
</tr>
<tr>
<td>Tray 2</td>
<td>0.36</td>
<td>0.63</td>
<td>92.34</td>
<td>5.56</td>
<td>0.0</td>
<td>0.03</td>
<td>0.03</td>
<td>0.59</td>
<td>0.46</td>
</tr>
<tr>
<td>Bottoms</td>
<td>0.45</td>
<td>0.28</td>
<td>85.54</td>
<td>12.04</td>
<td>0.11</td>
<td>0.07</td>
<td>0.04</td>
<td>0.72</td>
<td>0.75</td>
</tr>
</tbody>
</table>

\* Sidestream
### TABLE 4

**Operating Conditions***

Run 050665

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed rate</td>
<td>100 units/hr.</td>
</tr>
<tr>
<td>Bottoms</td>
<td>4.7 units/hr.</td>
</tr>
<tr>
<td>Sidestream</td>
<td>75.0 units/hr.</td>
</tr>
<tr>
<td>Heads</td>
<td>20.2 units/hr.</td>
</tr>
<tr>
<td>Steam</td>
<td>39.6 units/hr.</td>
</tr>
<tr>
<td>Reboiler Heat Duty</td>
<td>$7.16 \times 10^5$ Btu/hr.</td>
</tr>
<tr>
<td>Reflux Temperature</td>
<td>81°C</td>
</tr>
</tbody>
</table>

*Flow rates are based on 100 units/hr. of feed*
Figure 19. Total Unsaps Profile Run 050665
Figure 22. C-16 Profile Run 050665
Figure 24. C-18 Profile Run 050665
Run 060365 was made at one-half the rates normally used on the column. Table 5 shows the operating conditions for this run. The mathematical model predicted an unsaps concentration in the sidestream of 0.72 mole per cent while the actual experimental value of unsaps was 0.67 mole per cent. This was a rather drastic test for the model, since the flow rates for this run were 50 per cent of those in the run used to fit the model. In addition, the control model, as will be discussed in Chapter IV, predicted a heads rate of 17.8 units/hour to bring the unsaps concentration to 1.4 per cent. At the time of this run, the computer and the associated equipment necessary for routine transmission of data between Port St. Joe and Jacksonville were not installed and, therefore, this control model was run after the fact. However, the operator, on the basis of laboratory reports of unsaps concentrations, brought the sidestream on specifications at 1.4 per cent by using a heads rate of 18.5 units/hour.

C. Evaluation of Operating Variable Accuracy

One interesting result from this work was an investigation of the effect of accurate values for the various operating variables used in this particular model. Most of the pertinent parameters were varied to determine their individual effects. Since one of the important computed variables is total unsaps in the sidestream, the following discussion is on the effect of the varied parameters on this concentration.

The concentrations of unsaps in the sidestream was 1.40 mole per cent at an arbitrary set of standard operating conditions. A change in reboiler heat duty of ±10 per cent gave a change in this concentration
TABLE 5

Operating Conditions*

Run 060365

<table>
<thead>
<tr>
<th>Feed rate</th>
<th>100 units/hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottoms</td>
<td>6.5 units/hr.</td>
</tr>
<tr>
<td>Sidestream</td>
<td>60.5 units/hr.</td>
</tr>
<tr>
<td>Heads</td>
<td>33.0 units/hr.</td>
</tr>
<tr>
<td>Steam</td>
<td>43.0 units/hr.</td>
</tr>
<tr>
<td>Reboiler Heat Duty</td>
<td>$8.05 \times 10^5$ Btu/hr.</td>
</tr>
<tr>
<td>Reflux temperature</td>
<td>$87^\circ C$</td>
</tr>
</tbody>
</table>

* Flow rates based on 100 units/hr. of feed.
of ±0.08 mole per cent while a change in steam flow rate of ± 10 per cent made a change of ±0.02 mole per cent. A change in feed plate from plate 16 to plate 20 increased the unsaps concentration by 0.08 mole per cent. None of these parameters affected the distribution of the individual components to any large degree. The individual component profiles were well within the experimental error of the composition analysis.

Although it was not done for the control project described here, such simulations as those described above should be done before completely specifying the hardware for a computer control system. The results of these types of simulation would indicate which process variables are critical and should be measured with a high degree of accuracy, which variables should be monitored only on a routine or demand basis, and which variables are unimportant to the overall process and do not need to be monitored by the computer system.
CHAPTER IV

THE CONTROL PROBLEM

A. Mathematical Procedures

The mathematical model developed for A-30 Column was modified so that it could be used in a feedforward fashion to predict the overheads rate necessary to keep the unsaps concentrations in the sidestream within desired specifications. This modification consisted of replacing one degree of freedom (heads rate) with another degree of freedom (unsaps concentration) and obtaining the steady-state solution.

Other authors (10,24) have suggested that this problem be handled by repeated solutions of design distillation models similar to the simulation model presented in Chapter II. Since this technique would involve a multiplicity of steady-state solutions before obtaining the desired operating information, it seems that less time would be required if the calculations converged to the operating point and the final steady state simultaneously. Therefore, the method presented below was developed to provide this type solution.

The ratio technique, in addition to calculating new top and bottom compositions for the next trial, also provides estimates for the concentration of any exit streams. The estimated unsaps concentrations in the sidestream is calculated and checked to see if it is within the desired limits. If it isn't, the heads rate is changed proportional to the estimated concentrations.

\[ D_N = D_0 \frac{\sum x_{1c}}{\text{specification}} \quad (68) \]
When this technique is applied every iteration, the solution is very sensitive to these changes and the convergence rate is slowed down. Figures 29 and 30 show the change in unsaps concentrations and the heads rate change for a calculation using this technique.

To damp out the oscillation, the heads rate correction was applied every other iteration and the top and bottom compositions were recalculated using the new flow rates so that the material balance restrictions were satisfied. Figures 31 and 32 show the unsaps concentrations and heads rate as calculated in this fashion.

The computer listing for the control model convergence subroutine is shown in Appendix C.

**B. Experimental Verification**

Once the simulation of A-30 was made and the model described the actual column within experimental limits, the control model as described above was programmed for the IBM 1620/1070 System. There are several limitations on the programming which are a result of the choice of this particular computer system. In effect, the program had to be "stream-lined" in such a fashion as to make it as fast and as efficient as possible. The first effort to reduce the computation time of the model was to replace the simulation of "real trays" having Murphree efficiencies less than 100 per cent by an equivalent number of "ideal trays" at 100 per cent efficiency. The main problem here was to maintain a 1 to 1 correspondence between the various external streams. The model was reduced to 15 ideal plates (vs. 29 in the actual column) with the sidestream at plate 2 (vs. 3 in the actual column). Several tests were run on this model with the unsaps concentration and external flow rates
Figure 31. Unsaps Concentration
Figure 32. Heads Rate

Heads Rate x 10^-1 moles/hr.
identical to the full scale model. The second simplification of the model was to assume a constant temperature profile for this reduced model. This assumption removed the necessity of monitoring the actual tray temperatures from the real column averaging them in some fashion for use on the reduced column and then computing the vapor pressures, and vapor and liquid enthalpies for each component at each plate. Computer calculations indicated that slight differences in temperatures, as would occur in normal day to day operation, did not effect the concentration profile of the model. These simplifications of the model reduced the computer running time by about 40 per cent.

The control of A-30 tower is initiated in the following fashion. A sample of the feed stream and the sidestream is collected every 4 hours by operating personnel. These samples are then taken to the laboratory where they are prepared and run on the VPC (see Appendix D). The results from the VPC are entered into the IBM 1070 at Port St. Joe. The computer accepts these results, calculates the weight per cent of each component and sends this information back to the Port St. Joe Plant. The computer then collects data from the column at Port St. Joe and makes a series of mechanical checks on key variables. These variables are top column pressure and temperature, base column pressure and temperature, and steam flow rate. If these variables are within predetermined limits, the first program for the control calculations is then loaded into the core of the computer (see Figure 33 for the flow chart of the A-30 control programs). This first program converts the weight per cent from the preceding program to mole per cent, compares the feed analysis and rate to the last
Enter VPC Analysis at Port St. Joe

Calculate Weight Per Cent of Components

Report to PSJ

Calculate Mole Per Cent of Components

Has Feed Changed?

Y

A-30 Control

N

Return to PSJ "No Control"

Y

Return to PSJ "Heads Rate"

N

Figure 33. A-30 Control Programs
available feed analysis and rate and makes the decision to run the control model. If control is to be exercised, the results are reported back to Port St. Joe as heads rate calculated in per cent of chart reading for the use of the operators. The heads to feed ratio is also calculated and this ratio is maintained by the operators until the next time the control model is run. This is necessary because of changes made in the A-30 feed rate to control another column which produces the feed to A-30 Column.

Data for evaluation of the model and the control scheme were obtained during a test period from December 15 to 19, 1965. In order to provide a basis for comparison, data were taken under operator control conditions for the four days preceding the actual test. Table 6 shows the yields for both of these periods. These yields are based on flow rates which are monitored every 40 seconds by the IBM 1620/1070 and the average rate is computed in engineering units (pounds per hour) approximately every 2 hours. During the test period, there was a 1 per cent increase in crude fatty acid production and a 1 per cent decrease in heads production. Based on current price differential between the value of crude fatty acid and heads, this represents a savings of approximately $10,000 per month for the average crude tall oil plant where throughput is 10,000 tons per month (i.e. savings of $1 per ton of CTO).

The fatty acid produced during this test period was below the maximum unsaps allowable for sale of this material and a further increase in yield could be obtained by adjusting the unsaps specifications in the model closer to the upper limit. This control point in
TABLE 6

Operating Yields for Test Periods

<table>
<thead>
<tr>
<th>Dates</th>
<th>Units of A-30 Feed*</th>
<th>Units of CFA*</th>
<th>Units of Heads*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dec. 11-15</td>
<td>36.69</td>
<td>24.24</td>
<td>8.59</td>
</tr>
<tr>
<td>15-19</td>
<td>36.51</td>
<td>25.23</td>
<td>7.51</td>
</tr>
</tbody>
</table>

*Based on total CTO throughput to plant as 100 units
the model was kept low purposely during the test so as to minimize
the risk of producing off-grade material.

Table 7 gives the unsaps concentrations as determined by the
VPC during the duration of the test. The average unsaps concentrations
was 1.43 per cent with a sample variance of 0.04. The control point
in the model was 1.40 per cent and a "t" test showed that the average
was not significantly different from the control point.

The control model was put on line successfully at the Port St. Joe
plant on a continuing basis after a plant shutdown which occurred at
the end of December, 1965. In general the results of the test period
have been confirmed during continuous operation. Improved economic
operation has been maintained and operator confidence has continually
increased. An interesting by-product of the industrial implementation
of this work became apparent when due to equipment difficulties (i.e. the
VPC) the control of the column was returned to the operators. The
method of control of the column (without the computer) is to make
adjustments on the heads rate on the basis of one unsaps determination
made on a 24 hour composite of material. The operators began to make
much smaller changes in the heads rate for the same analysis after
using the computer than before. In other words, the operators went
through a learning process and became better operators. During the
period when the computer control was not in operation, the plant was
able to maintain about one half of the gains obtained with the computer.

Other advantages were also apparent after the installation of
the computer control system in the plant. Some of these were:

1. An increased reliability in instrumentations due to the
TABLE 7

Total Unsaps Concentration in Crude Fatty Acid

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>Unsaps</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-15-65</td>
<td>18:45</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>22:30</td>
<td>1.46</td>
</tr>
<tr>
<td>12-16-65</td>
<td>2:00</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>6:15</td>
<td>1.72</td>
</tr>
<tr>
<td></td>
<td>9:45</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>14:15</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td>18:00</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>23:15</td>
<td>1.58</td>
</tr>
<tr>
<td>12-17-65</td>
<td>0:00</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td>1:45</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>6:45</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>8:15</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>10:45</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>15:30</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>18:00</td>
<td>1.32</td>
</tr>
<tr>
<td>12-18-65</td>
<td>4:15</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>7:30</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>11:30</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>14:15</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>19:00</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td>22:15</td>
<td>1.46</td>
</tr>
<tr>
<td>12-19-65</td>
<td>2:45</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>12:45</td>
<td>1.38</td>
</tr>
</tbody>
</table>
demand of the computer and the rapid knowledge of instrument mal-
functions

2. Faster knowledge of yields and throughput

3. The ability to spot differences between shifts in the operating of the equipment

4. The ability to provide engineering assistance from the main plant in Jacksonville in case of processing problems.
CHAPTER V

CONCLUSIONS

Several specific conclusions may be made on the basis of this work.

1. It is possible to write a theoretical description of an actual industrial distillation column with sufficient accuracy to allow its control by a digital computer.

2. The technique of fitting a rigorous mathematical model to actual plant data can be used to obtain estimates of physical data which might otherwise be unknown. In other words, it is not always necessary to have all physical data completely defined before a model may be used, but actual operating data may be used to fill the gaps in our knowledge.

3. As pointed out in Chapter III, if a rigorous model is developed, its utility in situations which vary widely from the actual conditions used to estimate physical data will be greatly enhanced. However, if plant operating data had been collected and curve fitting techniques used to force a relationship among variables thought to be important, extrapolation of these relationships would be a risky business.

4. The computer control of the Port St. Joe Crude Tall Oil plant is economically feasible, based on economic data prevailing at the time of the test.

5. The power ratio convergence technique has proved itself to be a useful method in the solution of steady-state distillation calculations and should have applications in other types of trial and
error calculations.

Because of the author's participation in a pioneering computer control project on a commercial scale, several general conclusions should be mentioned which derive from the overall effort but are not primary to the work discussed in this dissertation.

1. There is a necessity for confidence-building interaction between man and machine. It is important for computer experts to realize that some sacrifice of machine efficiency may be necessary in order for the operating people to have a clear understanding of the reasons behind the computer's control strategy.

2. In any project involving computer control, engineering analysis and computer simulations should be completed before computer hardware and additional plant instrumentation are specified.

3. The process industry has to learn to rely more on its own people and less on the computer vendor and manufacturer. This is not due to any overt failure on the vendor's part, but rather, the fact that a company's problems are usually unique to the point that they are best defined by its own people.

4. The reliability of computers for process control should be one of the first considerations in specifying the computer hardware. Control applications are much more critical than traditional data processing to machine failure, and downtime due to computer hardware must be held as low as possible.

5. The installation of a computer on an industrial process returns many benefits that are difficult to justify economically. Such intangible items as the better understanding of the phenomena taking
place resulting from the initial study of the process, the reliable and up-to-date information available once the computer is installed, and the ability to recognize deviations from normal operation are items which cannot be given a specific money value, but are nevertheless important results of such a project.
LIST OF SYMBOLS

Upper Case Letters

\( A_i \)  Antoine Equation Constant (See Equation 63)
\( AN \)  Acid Number
\( B \)  Bottoms Stream Flow Rate
\( B_i \)  Antoine Equation Constant (See Equation 63)
\( C_i \)  Antoine Equation Constant (See Equation 63)
\( CFA \)  Sidestream Flow Rate
\( D \)  Overheads Flow Rate
\( E_L \)  Murphree Liquid Efficiency (See Equation 37)
\( E_V \)  Murphree Vapor Efficiency (See Equation 14)
\( F \)  Feed Rate
\( H_n \)  Total Enthalpy of Organic Vapor Leaving Stage N
\( H_{sn} \)  Enthalpy of Steam Leaving Stage N
\( H_{in} \)  Enthalpy of Vapor of Component i
\( K_n \)  Equilibrium Constant Defined \( y = K x \)
\( L_n \)  Liquid Rate Leaving Stage N
\( N \)  Stage Number
\( Q \)  Rate of Heat Gain or Loss
\( R \)  Ideal Gas Constant
\( RA \)  Rosin Acid Per Cent
\( RAN \)  \( RA \times 1.855 \)
\( S_o \)  Steam Rate Entering Reboiler
\( V_n \)  Vapor Rate Leaving Stage N
\( XAN \)  Empirical Acid Number
Lower Case Letters

\( a_i \)  Constant in Heat Capacity Equation (See Equation 65).

\( b_i \)  Moles Flow Rate of Component \( i \) in the Bottom Defined

\[ b_i = Bx_i \]

\( b \)  Constant in Heat Capacity Equation (See Equation 65)

\( c \)  Total Number of Organic Components

\( c_p \)  Heat Capacity

\( d_i \)  Moles Flow Rate of Component \( i \) in Overhead Defined

\[ d_i = Dx_i \]

\( e \)  Base of Natural Logarithm

\( f \)  Number of Feed Stage

\( g_i \)  Gain Factor as Defined by Equation 58

\( h_{\text{n}} \)  Total Enthalpy of Liquid Leaving Stage \( n \)

\( h_{\text{in}} \)  Enthalpy of Liquid Component \( i \)

\( k_i \)  Ratio Raised to a Power

\( p_{\text{in}} \)  Pure Component Vapor Pressure of Component \( i \) at Temperature of Stage \( n \)

\( t \)  Temperature

\( x_{\text{in}} \)  Concentration of Component \( i \) in Liquid Leaving Stage \( n \)

\( x_{\text{in}}^* \)  Concentration of Liquid Which Would be in Equilibrium with Vapor of Concentration \( y_{\text{in}} \)

\( y_{\text{in}} \)  Concentration of Component \( i \) in Vapor Leaving Stage \( n \)

\( y_{\text{wn}} \)  Concentration of Water in Vapor Leaving Stage \( n \)

\( y_{\text{in}}^* \)  Concentration of Vapor Which Would be in Equilibrium with Liquid of Concentration \( x_{\text{in}} \)
Greek Letters

$\alpha_i$ Relative Volatility
$\theta_i$ Factor Defined by Equation 44
$\lambda_i$ Latent Heat of Vaporization
$\pi_n$ Total Pressure at Stage n
$\phi$ Arbitrary Function
$\gamma_i$ Ratio of Composition as Defined by Equation 55

Superscripts

N Refers to New Trial Value
O Refers to Previous Trial Value

Subscripts

B Refers to Bottom of Tower
C Refers to Condenser
c Refers to Sidestream
D Refers to Overhead of Tower
F Refers to Feed Stream
f Refers to Feed Stage
R Refers to Re flux
S Refers to Re boiler
s Refers to Steam
T Refers to Top of Tower
w Refers to Water Vapor in Organic


APPENDICES
APPENDIX A

EXAMINATION OF THE DEGREES OF FREEDOM FOR A 30 COLUMN

An actual distillation tower is a determinate system. Under a set of fixed conditions the tower produces a unique set of stream compositions, temperatures, pressures, and flow rates.

The purpose of any mathematical model is to give the same solution as the operating unit when subjected to the same set of fixed conditions. The problem of which variables and how many variables may be fixed before the model yields a unique solution has been considered by many authors and this development follows closely the one used by Smith, *Design of Equilibrium Stage Processes*, Chapter 3.

Essentially, any method to determine the degrees of freedom of a system consists of counting the number of variables and the number of independent equations relating these variables. The difference between these two quantities is the number of variables which must be specified to make the system determinate and can be calculated by the simple equation:

\[ N_{df} = N_v - N_e \] (69)

In a complex tower, it is advantageous to consider each individual type of unit separately and then combine these elements to give the system's degrees of freedom.

A. Partial Reboiler

A single homogeneous stream will contribute \( C + 2 \) variables to any element or unit of which it is a part. If the stream is a mixture of \( C \) components, these variables are the \( C - 1 \) compositions, temperature.
pressure, and rate. (Alternately these variables may be considered the C + 1 degrees of freedom as predicted by the thermodynamic phase rule plus the flow rate.)

For a partial reboiler, as shown in Figure 34, we have C + 2 variables for each stream. C is equal to the number of organic components plus 1 for the steam. A heat stream contributes one variable, its rate. Therefore the total number of variables is:

\[ N_v = 4(C + 2) + 1 = 4C + 9 \]  \hspace{1cm} (70)

The number of independent equations which can be written is C material balances, 1 energy balance, C-1 equations relating the liquid and vapor compositions leaving the reboiler, and 2 equations relating temperature and pressure of the exit streams; the total equations are:

\[ N_e = 2C + 3 \]  \hspace{1cm} (71)

The degrees of freedom are:

\[ N_{df} = 4C + 9 - (2C + 3) = 2C + 6 \]  \hspace{1cm} (72)

A choice of variables might be to define the two entering streams, 2(C + 2), the temperature of the exit stream, and the heat load, q. It should be noted that in specifying the steam composition, the organics (C-1 of the components) are zero.

B. Total Condenser

The condenser system on A-30 distillation column can be described as shown in Figure 35. The number of variables is:

\[ N_v = 3(C + 2) + 1 = 3C + 7 \]  \hspace{1cm} (73)
Figure 34. Schematic of a Partial Reboiler

Figure 35. Schematic of a Total Condenser
The number of independent equations is:

\[ N_c = C + 3 \]  \hspace{1cm} (74)

The number of independent specifications which must be made is:

\[ N_{df} = 2C + 4 \]  \hspace{1cm} (75)

These variables might be picked by defining the entering stream \((C + 2)\) and the temperature and pressure of the condenser. There are \(C\) variables picked to show the lack of organic in the steam and the lack of steam in the liquid organic.

### C. Stream Divider (Reflux and Reboiler)

A stream divider, such as that shown in Figure 36, is used to split one stream \((L_1)\) into 2 streams \((L_2\) and \(L_3)\). The arrow head on both ends of the line for the energy stream is meant to show that there may be either a gain or a loss of energy.

The number of variables for a divider is:

\[ N_v = 3(C + 2) + 1 = 3C + 7 \]  \hspace{1cm} (76)

The equations which may be written are: \(C - 1\) equation expressing the concentration equalities between the entering stream and each of the leaving streams for a total of \(2C - 2\); \(1\) overall material balance; \(1\) energy balance; and \(2\) equations expressing the temperature and pressure equalities between the leaving streams. Therefore:

\[ N_c = 2C + 2 \]  \hspace{1cm} (77)

The number of independent variables which must be specified is:

\[ N_{df} = C + 5 \]  \hspace{1cm} (78)
Figure 36. Schematic of a Stream Divider

Figure 37. Schematic of a Equilibrium Stage
These variables could be the specifications of the feed
(C + 2), the heat loss or gain, the pressure, and the ratio of L_2/L_3.
If the divided stream is liquid it must be specified that the composit-
on of steam is zero, which only leaves C + 1 additional specification
to be made on the feed.

D. Equilibrium Stage (Figure 37)

For an equilibrium stage there are 4 entering material streams
and one energy stream, giving a total variable count of:

\[ N_V = 4C + 9 \]  \hspace{1cm} (79)

As independent equations we can write C material balances,
1 energy balance equation, 2 equations relating the temperature and
pressure of \( V_m \) and \( L_m \), one equation specifying the steam composition
is zero in the liquid phase and C - 1 equilibrium relation between the
organic components in \( L_m \) and \( V_m \). The number of equations is:

\[ N_e = 2C + 3 \]  \hspace{1cm} (80)

This leaves the degrees of freedom at:

\[ N_{df} = 2C + 6 \]  \hspace{1cm} (81)

If the stage is not a perfect stage, this introduces C more
variables, the composition that should be in equilibrium with one of
the exit streams, but it also introduces C additional equations, the
efficiency equations.

E. Feed Stage (Figure 38)

For a feed stage, there are 5 entering streams and one energy
stream which gives a total variable count:
Figure 38. Schematic of a Feed Stage

Figure 39. Schematic of a Sidestream Stage
The number of independent equations which can be written is the same as for an equilibrium stage:

\[ N_e = 2C + 3 \]  \hspace{1cm} (83)

The number of independent variables that have to be specified is:

\[ N_{df} = 3C + 8 \]  \hspace{1cm} (84)

These specifications are generally the same as for an equilibrium stage with the additional \( C + 2 \) variables used to describe the feed.

**F. Side Stream Stage (Figure 39)**

The number of variables for a side stream stage is the same as for a feed stage:

\[ N_v = 5C + 11 \]  \hspace{1cm} (85)

The same equations can be written expressing the total equality between \( S \) and either \( V \) or \( L \):

\[ N_e = 3C + 4 \]  \hspace{1cm} (86)

This gives the number of independent specifications which have to be made as:

\[ N_{df} = 2C + 7 \]  \hspace{1cm} (87)

The additional variable over and above those normally made for an equilibrium stage could be the side stream rate.

**G. Combining the Individual Elements**

The degrees of freedom for the total system may be calculated
by combining the degrees of freedom for the individual elements, taking into account any decision made in this process (such as number of like elements) and subtracting any restrictions which may arise from this process.

When combining $K$ equilibrium stages as shown in Figure 40, the number of variables in this case is $K$ times the number of degrees of freedom from each stage plus 1 to reflect the choice made of $K$ elements:

$$ N_v = K(2C + 6) + 1 = 2KC + 6K + 1 \quad (88) $$

The new restrictions which arise are equations which express the equality between streams leaving one element and entering adjacent elements. There are 2 ($K-1$) such interstreams, as shown in Figure 40. This gives an additional number of equations:

$$ N_e = 2(K - 1)(C + 2) = 2KC + 4K - 2C - 4 \quad (89) $$

The number of independent variables which may be specified is:

$$ N_{df} = 2C + 2K + 5 \quad (90) $$

A-30 distillation column is shown schematically in the Figure 41.

Adding up the degrees of freedom for each element:

<table>
<thead>
<tr>
<th>Element</th>
<th>Degrees of Freedom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reboiler</td>
<td>$2C + 6$</td>
</tr>
<tr>
<td>Bottoms divider</td>
<td>$C + 5$</td>
</tr>
<tr>
<td>Stages below sidestream</td>
<td>$2C + 5 + 2(S-1)$</td>
</tr>
<tr>
<td>Sidestream</td>
<td>$2C + 7$</td>
</tr>
<tr>
<td>Stage below feed</td>
<td>$2C + 5 + 2(M-(S))$</td>
</tr>
<tr>
<td>Feed stage</td>
<td>$3C + 8$</td>
</tr>
<tr>
<td>Stages above feed</td>
<td>$2C + 5 + 2(N-(M+1))$</td>
</tr>
<tr>
<td>Condenser</td>
<td>$2C + 4$</td>
</tr>
<tr>
<td>Reflux splitter</td>
<td>$C + 5$</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>$17C + 46 + 2N$</strong></td>
</tr>
</tbody>
</table>
Figure 40. Schematic of k Equilibrium Stages
Figure 41. Schematic Representation of A-30 Distillation Column
There are 14 interstreams, which leaves as the number of independent variables:

\[ N_{df} = 17C + 2N + 46 = 14C - 28 = 3C + 2N + 18 \]  \hspace{1cm} (91)

Due to the nature of the process in A-30 the following conditions must be met: There is no organic material in the steam entering the reboiler; therefore C - 1 equation may be written specifying zero composition for the organic components in this stream; the assumption is made that no organic material is lost in the exit stream from the top of the column, therefore C - 1 equation reflecting this assumption can be written; and since the steam is assumed to be present only in the vapor phase, a total material balance on steam can be written. This leaves the number of independent variables which must be specified before the solution to the equations is unique as:

\[ N_{df} = C + 2N + 19 \]  \hspace{1cm} (92)

H. Choice of Operating Variables

The choice of these variables on an existing column is usually made as follows:

- Pressure at each stage: \( N \)
- Pressure at condenser: 1
- Pressure at reboiler: 1
- Pressure at 2 splitters: 2
- Heat loss at each stage: \( N \)
- Heat loss at 2 splitters: 2
- Total stages: 1
- Feed location: 1
- Sidestream location: \( 2N + 1 \)

The above considerations leave \( C + 10 \) variables to be fixed before the column or the equations are determinate.
If the feed is specified this takes $C + 2$ of these variables (with consideration that the steam composition is zero). If the steam input to the kettle is specified, 3 more degrees of freedom are removed. This leaves 5 variables which must be fixed. These variables may come from the following list:

<table>
<thead>
<tr>
<th>Variable</th>
<th>Degree of Freedom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflux Temperature</td>
<td>1</td>
</tr>
<tr>
<td>Distillate rate</td>
<td>1</td>
</tr>
<tr>
<td>External Reflux Ratio</td>
<td>1</td>
</tr>
<tr>
<td>Reflux rate</td>
<td>1</td>
</tr>
<tr>
<td>Condenser heat load</td>
<td>1</td>
</tr>
<tr>
<td>Concentration of 1 component in one stream</td>
<td>1</td>
</tr>
<tr>
<td>Sidestream rate</td>
<td>1</td>
</tr>
<tr>
<td>Bottoms rate</td>
<td>1</td>
</tr>
<tr>
<td>Reboiler Heat Load</td>
<td>1</td>
</tr>
<tr>
<td>Rate to Reboiler</td>
<td>1</td>
</tr>
</tbody>
</table>

Some of the above variables cannot be specified indiscriminately. Some are restricted to narrow ranges. For example, the condenser heat load must result in a condensate temperature somewhere between the bubble point and the freezing point of the mixture. Some of the variables are so closely related that it is impossible to specify values for all of them independently. For example, for a given feed rate, the distillate rate, sidestream rate, and bottoms rate must give an overall material balance and therefore only two of them can be specified independently.
APPENDIX B

PHYSICAL DATA FOR THE TALL OIL FATTY ACIDS SYSTEM

A. Vapor Pressure

Vapor pressure data for the various tall oil fatty acids were collected from several sources (41,42,43) and available industrial information (44,45). Figure 42 shows data for oleic acid (C-18) which is the major component of the system. Figure 43 shows data for palmitic acid (C-16). The data for stearic acid (C-20) and myristic acid (C-14) are shown in Figures 44 and 45. An available Glidden Co. report (45) gave vapor pressure curves for three unsaps and these are shown in Figure 46.

Using the vapor pressure data as discussed above, a steady-state calculation was made on the computer and the resulting column profiles were plotted along with the experimental data from Run 040165. The constants in these curves were changed; two additional unsaps were postulated to correspond to current analysis information, and calculations were made until agreement between the calculated profiles and the experimental points were within what was estimated to be the experimental error. The final constants used in this work are shown in Table 8.

B. Specific Heats

The constants used for the specific heat curves are shown in Table 9.
Figure 42. Oleic Acid Vapor Pressure
Figure 43. Palmitic Acid Vapor Pressure

The graph shows the vapor pressure of palmitic acid as a function of the reciprocal of a temperature-related expression. The points represent data from references 41 and 43.
Figure 44. Stearic Acid Vapor Pressure
Figure 45. Myristic Acid Vapor Pressure
These Curves
Reference 45

A  Unsaps 1
B  Unsaps 2
C  Unsaps 3

Figure 46. Unsaps Vapor Pressure
### TABLE 8

**Final Antoine Constants for Tall Oil Fatty Acids**

\[
\log_{p_i}^* = \frac{A_i}{e + C_i} + B_i
\]

<table>
<thead>
<tr>
<th>Component</th>
<th>A&lt;sub&gt;i&lt;/sub&gt;</th>
<th>B&lt;sub&gt;i&lt;/sub&gt;</th>
<th>C&lt;sub&gt;i&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-14</td>
<td>-3333.0</td>
<td>8.833</td>
<td>230.</td>
</tr>
<tr>
<td>C-16</td>
<td>-3247.0</td>
<td>8.444</td>
<td>230.</td>
</tr>
<tr>
<td>C-18</td>
<td>-3802.3</td>
<td>9.384</td>
<td>230.</td>
</tr>
<tr>
<td>C-20</td>
<td>-3590.</td>
<td>8.8</td>
<td>230.</td>
</tr>
<tr>
<td>L-1</td>
<td>-3535</td>
<td>9.42</td>
<td>230.</td>
</tr>
<tr>
<td>L-2</td>
<td>-3558.7</td>
<td>9.319</td>
<td>230.</td>
</tr>
<tr>
<td>L-3</td>
<td>-3755.0</td>
<td>9.591</td>
<td>230.</td>
</tr>
<tr>
<td>L-4</td>
<td>-3831.0</td>
<td>9.610</td>
<td>230.</td>
</tr>
<tr>
<td>L-5</td>
<td>-3852.0</td>
<td>9.592</td>
<td>230.</td>
</tr>
</tbody>
</table>
### TABLE 9

**Specific Heat Constants for Tall Oil Fatty Acids**

\[ C_{pi} = a_i + b_i t \]

<table>
<thead>
<tr>
<th>Component</th>
<th>( a_i )</th>
<th>( b_i )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-16</td>
<td>-122</td>
<td>0.9</td>
<td>46</td>
</tr>
<tr>
<td>C-18</td>
<td>-51</td>
<td>0.9</td>
<td>46</td>
</tr>
<tr>
<td>C-20</td>
<td>-198</td>
<td>1.17</td>
<td>46</td>
</tr>
<tr>
<td>C-14</td>
<td>226</td>
<td>0.2667</td>
<td>45*</td>
</tr>
<tr>
<td>L-1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-3</td>
<td>-36</td>
<td>1.5</td>
<td>45*</td>
</tr>
<tr>
<td>L-4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Mean specific heat. Liquid enthalpy is calculated by equation

\[ \bar{h}_{iC} = a_i + b_i (t_i)(t_i - t_R) \]
APPENDIX C

FORTRAN LISTINGS OF CONVERGENCE COMPUTER PROGRAMS
SUBROUTINE CORRVER (CONT)

SUBROUTINE CORRECTING ON TOP AND BOTTOM BY ERROR RATIO
OF MISMATCH AT FEEDPLATE USING VARIABLE GAIN BASED ON CHANGE
IN ERROR RELATIVE TO ONE

COMMON NC, NSIDE, NFEED, NSTAGE, NSAP1, NSAP2, NSAP3,
F, B, CFA, D, S, QSTIL, QCOND, DENOM, HSIN, UNSAP,
DELTA, GAIN, CONST1, CONST2, CONST3, ER, CONS1, CONS2,
CONS3, TEMPCP, TEMPL, CONCP1, CONCP2, CONCP3, CONCP4,
CONHV1, CONHC2, CONHV3, CONHV4, IDENT, ERROR, XF, A, BB,
HS, V, FL, XFBOT, XFTOP, HF, XMIX, C, PRES, TEMP,
DIMENSION IDENT(12), ERROR(10), XF(10), A(10), BB(10), HS(40),
V(40), FL(40), XFBOT(10), XFTOP(10), HF(10), XMIX(10),
C(10), PRES(40), TEMP(40), X(10,40), Y(10,40),
XSTAR(10,40), YSTAR(10,40), PSTAR(10,40), EV(10,40),
E(10,40), HV(10,40), HL(10,40), GAIN(10), CC(10)
DIMENSION XNEW(10), STOP(10), XC(10), COBPER(10), FACTOR(10)

DIMENSION ITESTO(10), ITEST1(10), ITEST2(10)

DIMENSION JTERM(36)
1 FORMAT(11H COMPONENT, I4, 23H MATERIAL BALANCE ERROR, 4X, 1PE20.8)
3. FORMAT( 26I2)
4. FORMAT(10H0 BOTTOMS, 10X, 10H SIDE STREAM, 10X4H TOP, 16X18H CORRECTION
1 FACTOR, 2X, 24H MATERIAL BALANCE ERROR)
5. FORMAT( 26H0 THIS IS ITERATION NUMBER, I4)
6. FORMAT( 1PE20.8)
1051 FORMAT( 11H COMPONENT, I4, 12H GAIN FACTOR, 1PE20.8)

IF( ITER)8,7,8
7 READ INPUT TAPE 5,3, JTERM
8 ITER = ITER + 1
9 \begin{align*}
&K = 0 \\
&10 \text{ DO } 20 \ I = 1, NC \\
&12 \text{ ERROR(I) } = \text{ XFBDP(I)} / \text{ XFBCT(I)} \\
&14 \text{ IF( ABS(ERROR(I) - 1.) - DELTA) 15, 15, 20} \\
&15 \ K = K + 1 \\
&20 \text{ COMPRI(I) } = \text{ XE(I) - (8*K(I,1) + CFA*K(I,NSIDE) + D*K(I,NSTAGE))} / \text{ IF} \\
&21 \text{ GO TO ( 21, 1024), NSAP2} \\
&22 \text{ WRITE OUTPUT TAPE 6, I, ITER} \\
&23 \text{ WRITE OUTPUT TAPE 6, 1, I, COMPRI(I)} \\
\end{align*}

1024 \text{ DO 1035 I=1, NC} \\
1025 \text{ ITEST2(I) } = \text{ ITEST1(I)} \\
1026 \text{ ITEST1(I) } = \text{ ITESTO(I)} \\
1027 \text{ IF( ERROR(I) - 1.) 1028, 1034, 1030} \\
1028 \text{ ITESTO(I) } = 1 \\
1029 \text{ GO TO 1035} \\
1030 \text{ ITESTO(I) } = 0 \\
1031 \text{ GO TO 1035} \\
1034 \text{ ITESTO(I) } = \text{ ITESTO(I)} \\
1035 \text{ CONTINUE} \\

1039 \text{ IF( ITER/3) 25, 25, 1040} \\
1040 \text{ DO 1060 I = 1, NC} \\
1041 \text{ IF(IEST2(I) +IEST1(I)*2 +IEST2(I)*4 -2) 1042, 1043, 1042} \\
1042 \text{ IF(IESTO(I) +IEST1(I)*2 +IEST2(I)*4 -5)1045, 1043, 1045} \\
1043 \text{ GAIND(I) } = \text{ GAIND(I) / 1.1} \\
1044 \text{ GO TO 1050} \\
1045 \text{ GAIND(I) } = \text{ GAIND(I) * 1.1} \\
1050 \text{ GO TO ( 1055, 1060), NSAP2} \\
1055 \text{ WRITE OUTPUT TAPE 6, 1051, I, GAIND(I)} \\
1060 \text{ CONTINUE} \\

25 \text{ IF(K-NC) 90, 30, 30}
30 CONTINUE
30 RETURN
90 DO 91 I=1,NC
91 FACTOR(I) = ERBL/I**GAITH(I)
92 SUMTOP = 0.0
93 SUMBOT = 0.0
94 SURNSID = 0.0
100 DO 130 I = 1,NC
101 IF( X(I,NSTAG) - X(I,1)) 105,105
105 XNEW(I) = X(I,1)*FACTOR(I)
106 XTOP(I) = (P*XP(I) - (CFA*X(I,NSIDE)/X(I,1)+3)*KNEW(I))/Q
107 IF(XTOP(I)) 108,109,109
108 XTOP(I) = X(I,NSTAG)
109 GO TO 125
110 XTOP(I) = X(I,NSTAGE)/FACTOR(I)
111 XNEW(I) = (F*XP(I) - (CFA*X(I,NSIDE)/X(I,1)+E)
112 IF(XNEW(I)) 113,118,118
113 XNEW(I) = X(I,1)
114 GO TO 125
125 XC(I) = X(I,NSIDE)*XNEW(I)/X(I,1)
126 SUMBOT = SUMBOT + XNEW(I)
127 SURNSID = SURNSID + XC(I)
128 SUMTOP = SUMTOP + XTOP(I)
130 CONTINUE
131 DO 135 I=1,NC
132 XNEW(I) = XNEW(I)/SUMBOT
133 XTOP(I)/SUMTOP
134 XC(I) = XC(I)/SURNSID
135 COMPER(I) = XF(I) - (B*XNEW(I) + CFA*XC(I) + Q*XTOP(I))/F
136 WRITE OUTPUT TAPE 6,J
137 GO TO (136,225),NSAP2
138 WRITE OUTPUT TAPE 6,J,XNEW(I),XC(I),XTOP(I),FACTOR(I),COMPER(I)
225 DO 235 I = 1,NC
230 X(I,1) = XNEW(I)
DIMENSION ITSTO(9), ITSTI(9), ITST2(9)
COMMON ITSTO, ITSTI, ITST2
DIMENSION ERROR(9), FACTR(9), XNEW(9), XTOPT(9), C(9), JSAP(9)
1 FORMAT (I10,5E20.8)
2 FORMAT (I10,5I10)

JSAP(1) = 2
JSAP(2) = 4
JSAP(3) = 6
JSAP(4) = 7
JSAP(5) = 3
UNSA = 0.016
DELTA = .01
3 ITER = ITER + 1
4 LOOP = 0
9 K = 0
10 DO 20 I = 1, 9
12 ERROR(I) = XFTOP(I) / XFBOT(I)
14 IF (ABSF(ERROR(I) - 1.) - DELTA) 15, 15, 20
15 K = K + 1
20 CONTINUE
IF(SENSESWITCH4) 9999, 9998
9999 CONTINUE
PRINT 1, K, ERROR
9998 CONTINUE
C
1024 DO 1035 I = 1, 9
1025 ITST2(I) = ITSTI(I)
1026 ITSTI(I) = ITSTO(I)
1027 IF (ERROR(I) - 1.) 1028, 1034, 1030
1029 ITST0(I) = 1
1030 GO TO 1037
1034 ITST0(I) = 0
1031 GO TO 1037
1035 CONTINUE

1039 IF (ITER/3) 25, 25, 1045
1040 DO 1050 I = 1, 9
1041 IF (ITSTO(I) + ITST1(I)*2 + ITST2(I) *4 -2) 1042, 1043, 1044
1042 IF (ITST0(I) +ITST1(I)*2 + ITST2(I)*4 - 5) 1045, 1043, 1044
1043 GAIND(I) = GAIND(I) / 1.1
1044 GO TO 1050
10-5 GAIND(I) = 1.1 * GAIND(I)
1050 CONTINUE
25 IF (K = 9) 90, 30, 30
30 IF (ITER = 1) 1050
50 IF (K = 1) 90, 30, 30
35 CALL LINK(DOUT)
90 DO 91 I = 1, 9
91 FACTR(I) = ERROR(I) ** GAIND(I)
92 SMTOP = 0.0
93 SMBOT = 0.0
94 SMSID = 0.0
95 LOOP = LOOP + 1
100 DO 130 I = 1, 9
101 IF (XTOP(I) - XBOT(I)) 115, 105, 105
105 XNEW(I) = XBOT(I) * FACTR(I)
106 XTOPT(I) = (F*XF(I) - (CFA*XSID(I)/XBOT(I) + B)*XNEW(I))/D
107 IF (XTOPT(I)) 108, 108, 125
108 XTOPT(I) = XTOP(I)
GO TO 125
115 XTOPT(I) = XTOP(I) / FACTR(I)
116 XNEW(I) = (F*XF(I) - D*XTOPT(I))/(CFA*XSID(I)/XBOT(I) + B)
117 IF (XNEW(I)) 118, 118, 125
118 XNEW(I) = XBOT(I)
125 XSI(I) = XSID(I) * XNEW(I)/XBOT(I)
126 SNEWT = SMBOT + XNEW(I)
127 SMSID = SMSID + C(I)
128 SMTUP = SMTUP + XTOPT(I)
130 CONTINUE
131 DO 135 I = 1, 9
132 XNEW(I) = XNEW(I)/SMBOT
133 XTOPT(I) = XTOPT(I)/SMTUP
134 XC(I) = XC(I)/SMSID
135 CONTINUE
   CALL MOD (ITER, JIT)
   GO TO (225,1141), JIT
1141 IF (LOOP - 2) 140, 152, 152
140 ANSWR = 0.0
141 DO 143 I = 1, 5
142 JJ = JSAP(I)
143 ANSWR = ANSWR + XC(JJ)
   IF (SENSE SWITCH4) 9997, 9996
9997 CONTINUE
   PRINT L, ITER, ANSWR, D, CFA
9996 CONTINUE
144 IF (ANSWR - 1.1*UNSAP) 145, 145, 150
145 IF (ANSWR - 0.9*UNSAP) 150, 225, 225
150 D = D*ANSWR/UNSAP
151 CFA = F-3-D
152 CONTINUE
   IF (SENSE SWITCH4) 9995, 9994
9995 CONTINUE
   PRINT L, ITER, D, CFA
9994 CONTINUE
C
   IF (D - 0.16*F) 1152, 1155, 1155
1152 D = 0.16*F
   GO TO 1160
1155 IF (D-0.3*F) 1170, 1170, 1156
1156 D = 0.3*F
1150 CFA = C - B - D
SUM TO 152
1170 CONTINUE

CC

155 IF (LOOP = 2) 92, 225, 225
225 OR 235 I = 1, 9
230 XADT(I) = XNEW(I)
235 XTOP(I) = XTOPT(I)
   IF (ITER = 38) 243, 250, 250
243 CALL LINK (STRPL)
250 CALL LINK (OUTPT)
END
APPENDIX D*

GAS CHROMATOGRAPHIC ANALYSIS OF TALL OIL FATTY ACIDS

The following are the specifications for the VPC analysis of Tall Oil Fatty Acids.

INSTRUMENTS:

   (1) Thermal Conductivity Detector
   (2)Isothermal Operation

2. Recorder (E. H. Sargent and Co.) Model SR
   (1) Range 1.0 mv.
   (2) Sensitivity - maximum obtainable while maintaining satisfactory stability.

3. Integrator (Disc. Chart Integrator)
   Disc. Instrument, Inc. Model K4-1, for Sargent SR and MR Recorders.

   (1) Scale -5 to 100
   (2) Zero Right, Integrator scale
   (3) Range Plug S-72181-30

OPERATING CONDITIONS:

Carrier Gas - Helium 100/140 ml/min.

Temperatures:

*The work discussed here was done by Mr. G. Watkins of the Port St. Joe Lab., The Glidden Company.
Column 270°C
Detector 280 - 290°C
Injector 290°C
Collector 220 - 230°C (approx.)
Filament Current - 200 ma.

Attenuator
S96C (Methyl Esters) - Initial Setting 1, Att. C18 peak to 8, return to 1 for remaining peaks.
A30 Feed (Methyl Esters) - Initial Setting 2, Att. C18 peak to 8, thence to 1 for remaining peaks.
S96C Unsaps. (Extracted) - Initial Setting 1 (No Attenuation)
A30 Feed Unsaps. (Extracted) - Initial Setting 1 (No Attenuation)

Chart Speed - 18"/hr.

Sample Size -
S96C (Methyl Esters) 8.0 Microliters
A30 Feed (Methyl Esters) 7.5 Microliters
A30 Feed Unsaps. (Extracted) 4.0 Microliters
S96C Unsaps. (Extracted) 3.0 Microliters

COLUMN:
Length - 4 Ft. (copper or S.S.)
ID - 4mm
Liquid Phase - Apiezon "L" (13.7% loading)
Support - Chromosorb "W" (80 - 100 mesh - acid washed)

PROCEDURE FOR PREPARATION OF APIEZON "L" COLUMN:
Weigh 1.4 grams of Apiezon "L" in 50 ml. beaker. Dissolve in 15 ml. of
chloroform stock solution. Pour solution over 33 ml. (packed) of chromosorb W (acid washed). Rotate the damp mass (don’t grind or stir). Remove excess chloroform with water aspirator at room temperature until dry (to smell). Pack in 4 ft. length of quarter inch copper tubing. Plug ends with glass wool. Flow helium through column while heating for first time, but do not connect to detector until after heating at 250° for 30 minutes.

PROCEDURE FOR PREPARATION OF CHLOROFORM STOCK SOLUTION:
Dissolve 1 gram Alkaterge T, 1 gram Tergitol N. P. 35, and 1 gram Span 80 in 300 ml. of Chloroform.

PROCEDURE FOR PREPARATION OF SAMPLES FOR G.C. ANALYSIS:
Fatty Acids - Measure approximately 10 - 12 drops of fatty acid sample into a 50 ml. beaker. Add 5 to 10 ml. of Diazomethane and evaporate on steam bath under safety fume hood. ASTM D-1983-64T BF₃ Methanol method for esterification may also be used as an alternate.

Unsaponifiables - This method is applicable to all products derived from Crude Tall Oil. The purpose of the method is to obtain a representative sample of unsaps. for gas chromatography analysis as rapidly as possible, therefore all measurements are performed volumetrically.

Procedure: Pour 20 ml. of sample into 250 ml. erlenmeyer flask. Add 40 ml. of alcoholic K.O.H. and boiling stone. Reflux on hot plate with condenser attached. At the end of 30 mins. cool flask with cold water from tap.
Transfer to 500 ml. separatory funnel using 100 ml. distilled water to facilitate transfer. Extract with 125 ml. ether. Add ether extract to second 500 ml. separatory funnel. Extract again with 30 ml. ether. Add second ether extract to second funnel. Wash combined ether extracts with 15 ml. distilled water. Evaporate ether extract on steam bath in 100 ml. beaker containing boiling stone. Dry unsaps. in oven for 5 - 15 mins. as time permits.

GENERAL PROCEDURE FOR CALCULATION OF ALL PEAK AREAS:

The area per cent of each peak is calculated by dividing the number of integrator strokes under each peak by the total number of integrator strokes for the entire chromatogram.

Area per cent of each peak is converted to relative weight per cent by multiplying each area per cent by its assigned molecular weight. The total molecular weight is determined by the summation. Each molecular contribution is divided by the total molecular weight to obtain values quite close to true weight per cent.

PROCEDURE FOR CALCULATION OF G. C. ANALYSIS FOR COMPUTER:

A-30 TOWER FATTY ACIDS

SYLFAT 96C  See Figure 47.

| Peak Area #1 | C14 | 195 |
| Peak Area #2 | C14 | 234 |
| Peak Area #3 | C16 | 256 |
| Peak Area #4 | C16 | 266 |
### M. W. Assignments

| Peak Area #5 | C18  | 284 |
| Peak Area #6 | C20  | 297 |
| Peak Area #7 | Unsaps | 315 |

**A-30 Feed** See Figure 48.

| Peak Area #1 | C14  | 195 |
| Peak Area #2 | C14  | 234 |
| Peak Area #3 | C16  | 256 |
| Peak Area #4 | C16  | 266 |
| Peak Area #5 | C18  | 284 |
| Peak Area #6 | C20  | 297 |
| Peak Area #7 | L-3  | 312 |
| Peak Area #8 | L-4  | 318 |
| Peak Area #9 | L-5  | 332 |

### G. C. Analysis Extracted Unsaps Calculation:

**S-96C and A-30F** See Figures 49 and 50.

| Peak Area #1 | L-1  | 239 |
| Peak Area #2 | L-2  | 290 |
| Peak Area #3 | L-3  | 312 |
| Peak Area #4 | L-4  | 318 |
| Peak Area #5 | L-5  | 332 |

Peak Areas are converted to weight per cent. This weight per cent is divided by the calculated unsaps per cent to obtain actual weight per cent of unsaps distribution in fatty acid sample.

Fatty acid samples are corrected for unsaps. Content as follows:
Figure 47. Chromatogram of Crude Fatty Acid
Figure 48. Chromatogram of Feed to A-30
Figure 49. Chromatogram of Unsaps in Feed to A-30
Figure 50. Chromatogram of Unsaps in Crude Fatty Acid
C14 Less 1/2 L-1
C16 Less 1/2 L-1
C18 Less 1/2 L-2
C20 Less 1/2 L-2

**Calculation of UNSAPS Per Cent In S-96C**

\[
100 - \left( \frac{\Delta N - RAN}{1.995} \right) + RA\% = \text{Unsaps, (\%)}
\]

RAN = RA\% \times 1.855

**Calculation of UNSAPS Per Cent In Feed**

\[
100 - \left( \frac{\Delta N - RAN}{XAN} \right) + RA\% = \text{Unsaps, (\%)}
\]

RAN = RA\% \times 1.855

XAN derived from Figure 51.
Figure 51. Acid Number Correlation for Calculation of Unsaps in Feed to A-30
BIOGRAFICAL SKETCH

Henry Ray Wengrow was born on April 20, 1938, in Savannah, Georgia. He was raised in Allendale and Columbia, South Carolina and graduated from Dreher High School, Columbia, South Carolina in June, 1956. He received a Bachelor of Science in Chemical Engineering from the University of South Carolina in June, 1960. He also received the degree Master of Science in Chemical Engineering and held a National Science Foundation Co-operative Fellowship at the University of South Carolina.

He enrolled at the University of Florida in September, 1961, to begin study for the degree Doctor of Philosophy. He was employed in May, 1963, by the University of Florida as a full-time Engineering Assistant and taught under-graduate and graduate courses. Since August, 1964, he has been employed by The Glidden Company, Organic Chemicals Division, Jacksonville, Florida.

He is married to the former Miss Vicki Lee Kligerman of Miami Beach, Florida.

He is a member of Tau Beta Pi, Omicron Delta Kappa, Phi Epsilon Pi, Sigma Xi, and the American Institute of Chemical Engineers.
This dissertation was prepared under the direction of the Chairman of the Candidate's Supervisory Committee, and has been approved by all members of that committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

April, 1966

Dean, College of Engineering

Dean, Graduate School

SUPERVISORY COMMITTEE:

Chairman

[Signatures]