DISTILLATION COLUMN DYNAMICS

AN ANALYTICAL STUDY

By

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PREFACE

A revolutionary method for predicting the transient behavior of a distillation column has been developed. This new method is based on the concept that the separation that occurs in a section of a distillation column can be described by a parameter that remains constant for small changes in column conditions. The driving force for the separation is the difference between the equilibrium composition and the actual composition of passing streams. The results obtained with this new concept have been shown to agree favorably with experimental data.

I am deeply indebted to Professor R. N. Maddox for the guidance and advice which he has given to me and for serving on my Thesis Review Committee; and also to Professors J. H. Erbar and W. C. Edmister for serving on my Thesis Review Committee. I would also like to thank the Graduate School of Oklahoma State University for the privilege of studying for the Master of Science degree, the School of Chemical Engineering for the financial support that I received during the first year of study, and the National Aeronautics and Space Administration for the Traineeship which provided financial support during the second year of study.

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CHAPTER I

INTRODUCTION

In recent years, with the development of better controlling devices and analytical instruments, the desirability of having a mathematical model which will enable the prediction of the transient behavior of a distillation column, has increased to the point of almost being a necessity. Such a method must be able to predict accurately the effect of a change in operating variables on the product composition. The predictions should be equally accurate during the transient period and at the final steady-state. In this respect, if a change in the feed composition, reflux rate, or reboiler duty is experienced, the model should enable the prediction of the changes in the operating variables which are required to maintain a product of a specified composition. The model should also enable reliable prediction of the time at which the column will again come to a desired degree of steady-state. In order for the model to be useful for design purposes, only the data which are normally obtained from a steady-state computer solution should be required to use the model. A model with this feature can be used to design the control system for the column during the preliminary stages of column design and thus prevent overdesign of the control system.

The model should also be simple enough that it can be used by plant operating personnel and compact enough that it can be programmed on a computer which can be economically installed in a plant. The time required to use the model on the plant computer should also be at a minimum. These properties, which will permit in-plant use of the model, are desirable so that the effect of a change in operating conditions can be predicted as soon as the change is noticed. This ability to make an immediate change in the operating variables will permit closer control of the distillation column and could eventually lead to complete computer control.

Any model which is developed for the prediction of the transient behavior of a distillation column should, in addition to reliably predicting the transient behavior, be simple enough to be used for in-plant operations, require only that data which is normally obtained from plant columns or from computer calculations, and be versatile enough that the simultaneous changing of several operating variables can be investigated. The purpose of this project has been to develop a mathematical model of a distillation column that will satisfy these conditions.

CHAPTER II

REVIEW OF THE LITERATURE

Prior to 1934 almost no work had been done in the field of developing mathematical models of industrial processes. In 1934 Ivanhoff (11) presented a paper in which he made the first attempt at developing a mathematical model from a strictly empirical point of view. From the discussion accompanying the article, the results of his experiments appear to have been widely accepted. Several other early authors (1, 27) also approached the development of dynamic models from an empirical point of view. These men would statistically correlate the behavior of a process with changes in independent variables and thus develop an approximate model of the process. Several other researchers (7, 10, 12, 16) approached the problem of developing a dynamic model by constructing small scale plants and then developing a model from the results obtained. Although these early workers were not interested in the control of distillation columns, but in transient systems in general, their works formed the foundation of modern process dynamics.

In 1947 Marshall and Pigford (15) proposed the first mathematical model of a distillation column. Their model was based on the equilibrium stage as shown in Figure 1. According to the equilibrium tray concept, each tray must be considered individually, and the differential equation that predicts the transient behavior must be written for each component in the form

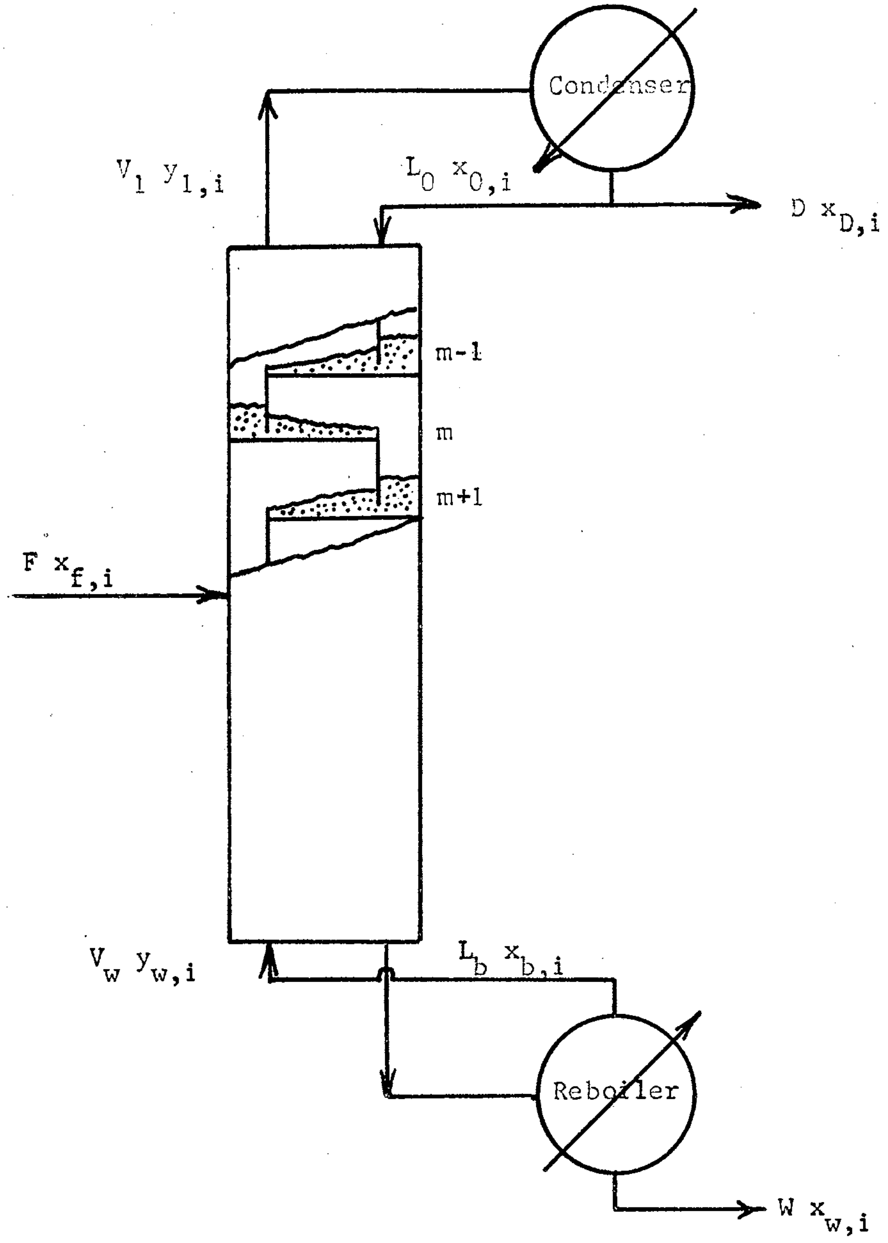

Figure 1. A Schematic Diagram of a Distillation Column Having Trays

$$\frac{d(\delta_n^L x_n)}{dt} + \frac{d(\delta_n^V y_n)}{dt} = L_{n-1} x_{n-1} + V_{n+1} y_{n+1} - (L_n x_n + V_n y_n) \qquad (1)$$

$\frac{d(\delta_n^L x_n)}{dt}$ = change in liquid holdup of a component on tray n with time.

$\frac{d(\delta_n^V y_n)}{dt}$ = change in vapor holdup of a component above tray n with time.

$L_{n-1} x_{n-1} + V_{n+1} y_{n+1}$ = rate at which a component flows on to tray n.

$L_n x_n + V_n y_n$ = rate at which a component flows away from tray n.

While this concept is theoretically sound, there are several drawbacks to using it. The most significant of these drawbacks is the vast number of equations that must be solved. This problem is perhaps best illustrated by an example. If the column of interest has n trays and i components, then the number of differential equations that must be solved is n times i. Thus the model is severely limited in its utility by its complexity. Since neither digital nor analog computers were well developed at the time that Marshall and Pigford developed the plate-to-plate model, a rigorous solution of the equations was almost impossible. The difficulty in using the Marshall and Pigford model was compounded further by the fact that the trays are not normally equilibrium ones. Thus some method of estimating the efficiency, or the approach to equilibrium, of each tray was required. In order to make their model more useful, Marshall and Pigford made the following assumptions:

1. constant molal overflow
2. negligible vapor holdup above a tray
3. that the degree of equilibrium between the liquid on the tray and the vapor above the tray could be represented by a straight pseudo equilibrium line

While these assumptions enabled Marshall and Pigford to obtain an analytical solution to the differential equations, the accuracy of the model was reduced by them. The assumption of negligible vapor holdup is normally a good assumption, but since the assumption of constant molal overflow requires that the molal heats of vaporization of the components be equal and the assumption of a straight equilibrium line requires that the concentration of the component be small, the integrated equations are normally too restricted to be successful on actual systems.

Some time after Marshall and Pigford developed their model, Rose and his co-workers (20, 21, 22, 23) applied the basic equation, equation (1), to a batch distillation column. In this application, Rose et al avoided the assumptions that limited the usefulness of the Marshall and Pigford equations by programming the differential equations on a digital computer. They were, however, confronted by the problem of excessive computer time.

About the same time that Rose et al were publishing their work, Robinson and Gilliland (19) developed an approximate graphical method for predicting the approach to steady-state of a distillation column. Their method was restricted to the cases where the column was upset by a change in the feed composition, and like the previous models was based on the equilibrium tray concept.

Voetter (24) was perhaps the first to combine experimental data with a theoretical analysis. He compared the equations of Marshall and Pigford with experimental data that he obtained on a sixty tray Oldershaw distillation column. The experimental and the theoretical values compared excellently during the early portion of the transient period, but as the column approached steady-state the experimental and the theoretical values differed considerably. Voetter's experimental results were for a single section column under the influence of a step change, but he mathematically extended the results to a complete fractionation column under the influence of a frequency response function. In 1957 Wilkinson and Armstrong (25, 26) presented some additional experimental data that were obtained on a five tray four-inch in diameter column which was operating on the carbon tetrachloride-benzene binary system. The equations they presented were only adaptations of the Marshall and Pigford equations and the assumption of a straight equilibrium line was still required. This work was, however, performed on a complete column. In 1961 Armstrong and Wood (2) published experimental as well as theoretical results for a twenty-one tray distillation column. The purpose of their work was to determine the effect of changing the reflux rate. At the top of the column the experimental and the theoretical values were in good agreement, but at the bottom of the column the experimental and theoretical values did not agree well.

In 1961 Baber (3, 4, 5) presented the most extensive experimental and theoretical study that has been published. He programmed a series of differential equations that were developed by Lamb and Pigford (13), but were based on the earlier Marshall and Pigford equations, on an analog computer. The results obtained on the computer were then compared with experimental data which he obtained. The experimental data were obtained on a five tray, single section, distillation column. The method of operating the column was to allow the column to come to steady-state at total reflux and then change one of the operating variables; either the reflux rate, the reflux composition, or the vapor rate. The flow rates and compositions of the various streams were determined before the step change was made and the compositions were measured at intervals throughout the transient period. When the column reached steady-state, the flow rates and the compositions were again measured. For some of the experimental runs, Baber was able to get good agreement between the experimental and the computer values, but for most of the runs he was unable to obtain good agreement.

At the Baltimore meeting of the American Institute of Chemical Engineers, Marr (14) suggested a new concept for predicting the transient behavior of a distillation column. He suggested that in order to get away from the conventional and complicated plate-to-plate model, some parameter which could be used to describe the degree of separation that was occurring in a distillation column should be developed. Marr however did no more than to suggest the idea and no further work was done on the model until Reynolds (18) began his work.

Reynolds envisioned a distillation column as being composed of several sections in which there could be any number of trays. According to the section concept, as shown in Figure 2, a section of a distillation column is that part of the column which lies between the points at which either feed streams enter or product streams leave the column. According to Reynolds, the rate at which mass is transferred from the vapor phase to the liquid phase can be expressed by the equation

$$N^{V}_{n,i} = -J_{n,i} \; (y^* - y)_{n,i} \qquad (2)$$

where $J_{n,i}$ is the parameter which describes the degree of separation occurring in a section and $(y^* - y)_{n,i}$ is the driving force for mass transfer in the section.

The reader will notice that equation(2) is identical in form with the equation that is normally used for mass transfer

$$N = k(y^* - y)$$

There are, however, some fundamental differences between equation (2)

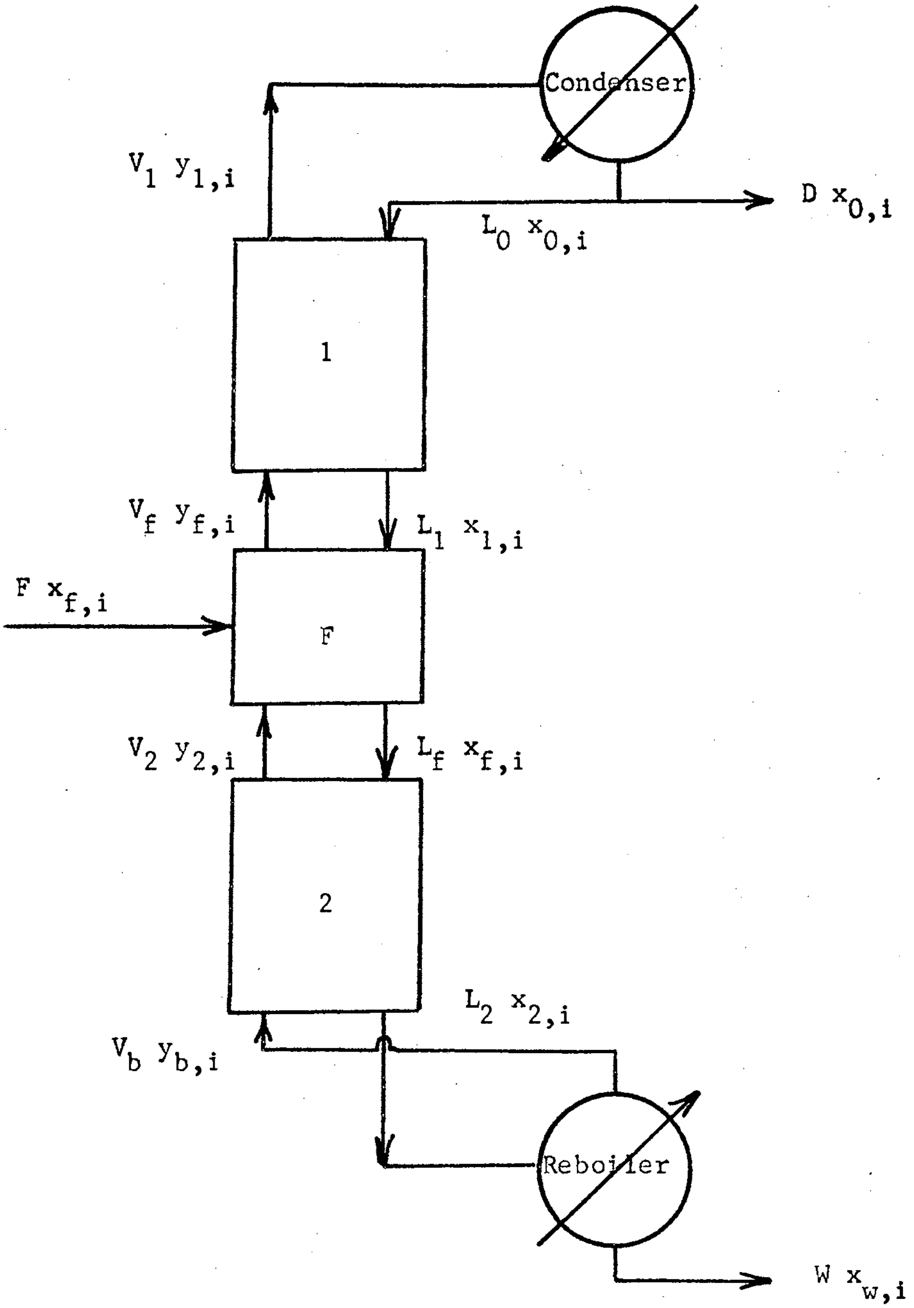

Figure 2. A Distillation Column According to the Section Concept

and the conventional mass transfer equation. In deriving the conventional equation, the coefficient k is related to the diffusivity of the components being transferred. The coefficient in equation (2), however, is not related directly to the physical properties of the component being transferred. The coefficient, $J_{n,i}$, is, as its definition says, a parameter that describes the degree of separation that occurs in a section and as such is merely an empirically determined factor.

Using this idea for the rate of mass transfer in the section, Reynolds developed a set of differential equations for the transient behavior of the liquid and vapor streams leaving the section. In developing the equations Reynolds made two major assumptions. The first of these assumptions was that $J_{n,i}$ remained constant for small changes of column conditions and the second was that of constant molal overflow throughout the section. After developing the model, Reynolds attempted to prove the model by comparing the values predicted with the model with experimental data, but was unable to obtain good agreement. Since the basic concept underlying Reynolds' work still seemed to have merit, the present project was begun in order to develop a model which would successfully reproduce experimental data.

CHAPTER III

DEVELOPMENT OF THE MODEL

Since Reynolds was unable to get good agreement between the results that his model predicted and the experimental results and because the basic idea of using a section concept rather than a plate concept still appeared to be reasonable, the present project was begun. The basic idea suggested by Marr and developed by Reynolds was used, but an entirely different method of attack was used.

Assuming that the basic idea of the model developed by Reynolds is valid; i.e., that the net rate at which mass is transferred from the vapor phase to the liquid phase in a section can be represented by equation (2), a material balance can be made on the vapor stream entering and leaving a section. Since the general law of conservation of matter applies; i.e., that the difference between the input and the output is the accumulation, the following equations expressing the input, the output, and the accumulation are valid:

$$\text{input} = V_{n+1}\, y_{n+1,i} \tag{3}$$

$$\text{output} = V_{n+1}\, y_{n+1,i} + \frac{\partial(V_n\, y_{n,i})}{\partial z}\, dz + N^V_{n,i} \tag{4}$$

$$\text{accumulation} = \frac{\partial(\delta^V_n\, y_{n,i})}{\partial t} \tag{5}$$

$$\delta^V_n = f^V_n \rho^V_n S z \tag{6}$$

The symbols appearing in equations (3), (4), and (5) and in the remainder of this thesis are defined in the Nomenclature section. The terms in equation (4) may need further explanation than is supplied by the equation itself. Thus, in order to further the meaning of the equation, the explanation that follows is presented. The output that is calculated in equation (4) is the sum of all of the material that leaves the vapor phase, either by flow or by mass transfer. The rate at which a component flows from the section is equal to the flow rate in $V_{n+1}\, y_{n+1,i}$ plus the increase in the stream flow rate that occurs in the section $\frac{\partial(V_n\, y_{n,i})}{\partial z}\, dz$, and the vapor phase is represented by the term $N^V_{n,i}$. If equations (3), (4), and (5) are substituted into a material balance, the resulting equation is

$$\frac{\partial(\delta^V_n\, y_{n,i})}{\partial t} = - \frac{\partial(V_n\, y_{n,i})}{\partial z}\, dz - N^V_{n,i} \tag{7}$$

A partial differential equation that represents the behavior of the composition of the vapor stream passing through the column can now be obtained by substituting equation (2) into equation (7). The partial differential equation that results from this substitution is

$$\frac{\partial(\delta^V_n\, y_{n,i})}{\partial t} = - \frac{\partial(V_n\, y_{n,i})dz}{\partial z} + J_{n,i}(y^* - y)_{n,i} \tag{8}$$

A partial differential equation for the liquid stream that is analogous to equation (8) for the vapor stream can be obtained by making a material balance on the liquid stream passing through the section. In this material balance the input, output, and accumulation are represented by the equations

$$\text{input} = L_{n-1}\, x_{n-1,i} \tag{9}$$

$$\text{output} = L_{n-1}\, x_{n-1,i} + \frac{\partial(L_n\, x_{n,i})}{\partial z}\, dz + N^L_{n,i} \tag{10}$$

$$\text{accumulation} = \frac{\partial(\delta_n^L x_{n,i})}{\partial t} \tag{11}$$

$$\delta_n^L = f_n^L \rho_n^L \, Sz \tag{12}$$

The terms that appear in equation (10) are like those that appeared in equation (4) except they apply to the liquid phase rather than the vapor phase. The equation that results from the substitution of equations (9), (10), and (11) into a material balance equation is

$$\frac{\partial(\delta_n^L x_{n,i})}{\partial t} = - \frac{\partial(L_n x_{n,i})}{\partial z} dz + N_{n,i}^L \tag{13}$$

Equation (13), which is similar to equation (8), is a partial differential equation that represents the behavior of the composition of the liquid stream passing through a section of a distillation column.

Since the partial differential equations obtained for the liquid and vapor streams leaving a section of the column cannot, under normal circumstances, be integrated exactly some simplifications of the equations are necessary. First, the partial derivatives $\frac{\partial(L_n x_{n,i})}{\partial z}$ and $\frac{\partial(V_n y_{n,i})}{\partial z}$ can be replaced by the approximations

$$\frac{\partial(V_n y_{n,i})}{\partial z} = \frac{(V_n y_{n,i} - V_{n+1} y_{n+1,i})}{\Delta z} \tag{14}$$

$$\frac{\partial(L_n x_{n,i})}{\partial z} = \frac{(L_n x_{n,i} - L_{n-1} x_{n-1,i})}{\Delta z} \tag{15}$$

In order for the approximations represented by equations (14) and (15) to be valid, the change in height Δz must be small. Since the groups $\delta_n^V y_{n,i}$ and $\delta_n^L x_{n,i}$ are now functions of time only, the partial derivatives with respect to time can be replaced with total derivatives. Using this change from partial to total derivatives, the approximations of equations (14) and (15), the assumption of constant molal holdup in a section, and the assumption of constant rate of interphase mass transfer in a section, equations (8) and (13) can be rewritten in the forms

$$\delta_n^V \frac{d(y_{n,i})}{dt} = -(V_n\, y_{n,i} - V_{n+1}\, y_{n+1,i}) + J_{n,i}(y^* - y)_{n,i} \qquad (16)$$

$$\delta_n^L \frac{d(x_{n,i})}{dt} = -(L_n\, x_{n,i} - L_{n-1}\, x_{n-1,i}) - N_{n,i}^L \qquad (17)$$

Up to this point no attempt has been made to relate the net rate at which mass is transferred from the liquid phase with the net rate at which mass is transferred from the vapor phase; this relationship will now be shown. For this purpose, consider a section of a column that is small enough that the molal holdups of the respective phases is negligible in comparison to the flow rates of the liquid and vapor streams. For such a section, equations (16) and (17) can be written

$$-(V_n\, y_{n,i} - V_{n+1}\, y_{n+1,i}) + J_{n,i}(y^* - y)_{n,i} = 0 \qquad (18)$$

$$-(L_n\, x_{n,i} - L_{n-1}\, x_{n-1,i}) - N_{n,i}^L = 0 \qquad (19)$$

Also for such a section, even under transient conditions, the over-all material balance can be written

$$L_n\, x_{n,i} + V_n\, y_{n,i} - (L_{n-1}\, x_{n-1,i} + V_{n+1}\, y_{n+1,i}) = 0 \qquad (20)$$

Summing equations (18) and (19) and the subsequent use of equation (20) yields the equation

$$N_{n,i}^L = J_{n,i}(y^* - y)_{n,i} \qquad (21)$$

Now by using equation (21), equation (17) can be rewritten

$$\delta_n^L \frac{d(x_{n,i})}{dt} = -(L_n\, x_{n,i} - L_{n-1}\, x_{n-1,i}) - J_{n,i}(y^* - y)_{n,i} \qquad (22)$$

Equations (16) and (22) are valid for any system which meets the assumptions that were made in deriving them; however, they cannot be used in this present form because no method for evaluating $J_{n,i}$, the parameter that describes the degree of separation which occurs in the column, has been developed. In order to evaluate $J_{n,i}$ the assumption that it remains constant for small changes in column conditions must be made. In addition since the function $J_{n,i}(y^* - y)_{n,i}$, which represents the net rate of mass transfer between phases, is based on passing streams which cannot be measured some method of approximating the driving force for mass transfer must be developed. Reynolds attempted to use both the driving force at the top of the section and the average driving force (Reynolds defined the average driving force as the arithmetic average of the driving forces at the top and bottom of the column.) but did not get good results with either. In order to obtain a new method for representing the driving force for mass transfer, the line of reasoning which is described below was used.

If a section of the column is considered to be subdivided into an infinite number of subsections (as shown in Figure 3), the driving force for one of these infinitesimal subsections can be represented by the equation

$$(y^* - y)_{m,i} = (Kx)_{m-1,i} - y_{m+1,i} \tag{23}$$

If the number of subsections for which the driving force applies is increased to two, then the driving force for the two subsections m and m-1 can be approximated by the equation

$$(y^* - y)_{\left.\begin{matrix}m\\m-1\end{matrix}\right\},i} = (Kx)_{m-2,i} - y_{m+1,i} \tag{24}$$

If a similar line of reasoning is used to extend the interval for which the driving force applies to the entire section, the driving force for the section can be approximated by the equation

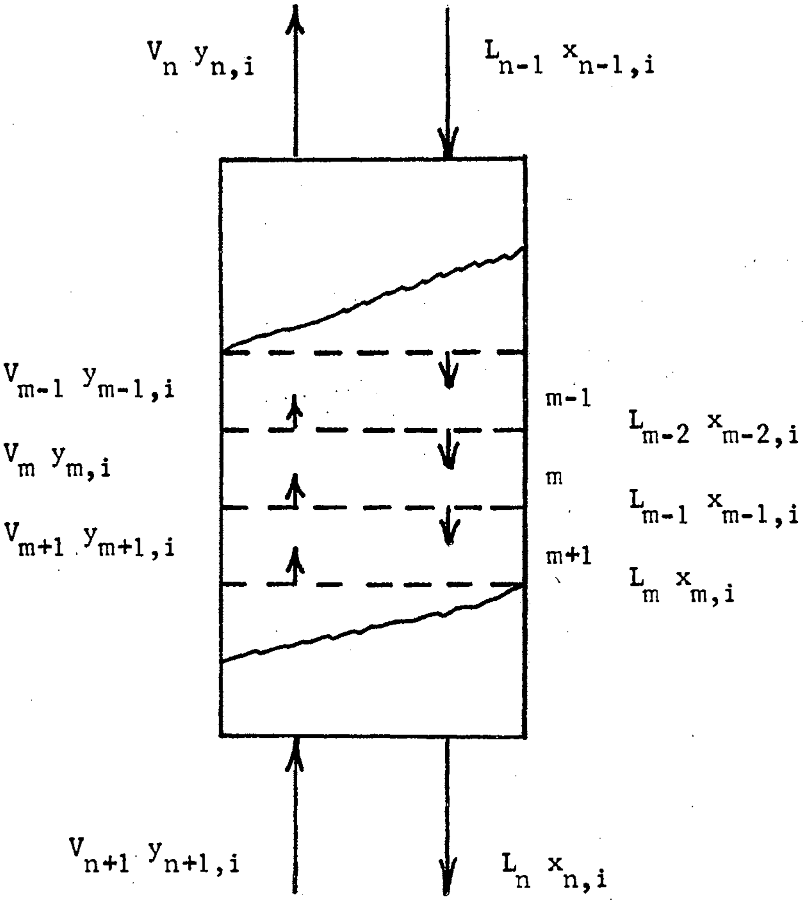

Figure 3. A Section of A Distillation Column Divided Into Subsections

$$(y^* - y)_{n,i} = (Kx)_{n-1,i} - y_{n+1,i} \qquad (25)$$

Thus equation (2) can be rewritten in the form

$$N^V_{n,i} = - J_{n,i} \left[(Kx)_{n-1,i} - y_{n+1,i} \right] \qquad (26)$$

Using equation (26), equations (18) and (22) can be rewritten in the form

$$\delta^V_n \frac{d(y_{n,i})}{dt} = - (V_n \, y_{n,i} - V_{n+1} \, y_{n+1,i}) + J_{n,i} \left[(Kx)_{n-1,i} - y_{n+1,i} \right] \qquad (27)$$

$$\delta^L_n \frac{d(x_{n,i})}{dt} = - (L_n \, x_{n,i} - L_{n-1} \, x_{n-1,i}) - J_{n,i} \left[(Kx)_{n-1,i} - y_{n+1,i} \right] \qquad (28)$$

Now by assuming that $J_{n,i}$ is constant for small changes in column conditions, a solution to the transient behavior of the compositions of the vapor and liquid streams leaving the column can be obtained by integrating equations (27) and (28). In most cases the integration cannot be performed analytically and either numerical or graphical techniques must be used. Regardless of which technique is used, the value of $J_{n,i}$ must be obtained. Equation (27) must be equal to zero at the steady-state since by definition $\frac{d(y_{n,i})}{dt} = 0$ at the steady-state. Thus by using the initial conditions in the column, a value for $J_{n,i}$ can be calculated using the equation

$$J_{n,i} = \frac{(V_n \, y_{n,i} - V_{n+1} \, y_{n+1,i})}{(Kx)_{n-1,i} - y_{n+1,i}} \qquad (29)$$

Likewise, since the time derivative for the liquid phase must be zero at steady-state, equation (28) can be rearranged so that the initial liquid flow rates can be used to obtain $J_{n,i}$. Thus a value for $J_{n,i}$ can also be obtained using the initial conditions and the equation

$$J_{n,i} = \frac{- (L_n \, x_{n,i} - L_{n+1} \, x_{n-1,i})}{(Kx)_{n-1,i} - y_{n+1,i}} \qquad (30)$$

Equations (29) and (30) reveal that the only information that is required to obtain a value for $J_{n,i}$ is that information that is normally obtained from a computer solution. Likewise, equations (27) and (28) reveal that the only information, other than that which can be obtained from a computer solution, that is required to use the model is the liquid holdup. In addition, the data required to use the model are normally obtained on a distillation column. At this point, the reader will recall that one of the requirements of a successful model, as described in the Introduction, was that the model be derived from the data normally obtained on a distillation column or from a computer solution to the steady-state case. In comparison to this relatively easy to use model, the plate-to-plate models require, in addition to the data required by the present model, an extensive knowledge of the physical construction of the column itself. This knowledge of the physical construction of the column is required because the liquid holdup on each tray must be known and the dynamics of the liquid flowing across the trays must be known to calculate the efficiencies.

Another advantage which the present model has over the more complicated model is that while the plate-to-plate model requires a set of equations, which includes an equation for each component, for every tray, the present model requires a set of equations only for each section, and a section may include any number of trays. Thus for a simple fractionator which has only two sections, a solution to the unsteady-state problem can be obtained on the smallest of computers using the present model. The plate-to-plate model however would require one of the largest and fastest computers available. Due to this ease of calculation, the computer required by the present model is small enough to be installed in a plant, whereas the size computer required by the plate-to-plate model would not normally be installed in a plant.

Since the vapor and liquid holdup terms in equations (27) and (28) do not appear in equations (29) and (30), a logical conclusion would be that they do not have any effect on the final steady-state values, but only serve as time constants. A numerical integration of equations (27) and (28) using several different holdups, has shown this conclusion to be valid. A solution to the same problem was also obtained for the plate-to-plate model (3). The results of both of these solutions, along with the plot of the experimental data (3) are shown in Figure 4. The experiments applying the data will not be discussed here, but will be discussed in complete detail in Chapter V. As can be seen in Figure 4, the transient solution obtained with the present model is one which has a first order time constant. Also, the solution obtained with the present model can be made to coincide with the experimental data by merely changing the holdup, while the plate-to-plate model does not follow the experimental data at all. The purpose of this comparison has not been to point out the fact that the plate-to-plate model does not approximate the curves, because it does in many cases, but to point out the fact that the present model can be made to follow the experimental data by merely changing the holdup term.

In this chapter, a model for the transient behavior of a distillation column which can be used easily on a small computer and which requires only the data which are normally obtained on a distillation column or from a computer solution at the initial steady-state, has been developed. Within the assumptions that $J_{n,i}$, the parameter which describes the degree of separation in a section of a distillation column, remains constant for small changes in operating conditions and that the molal holdup in a

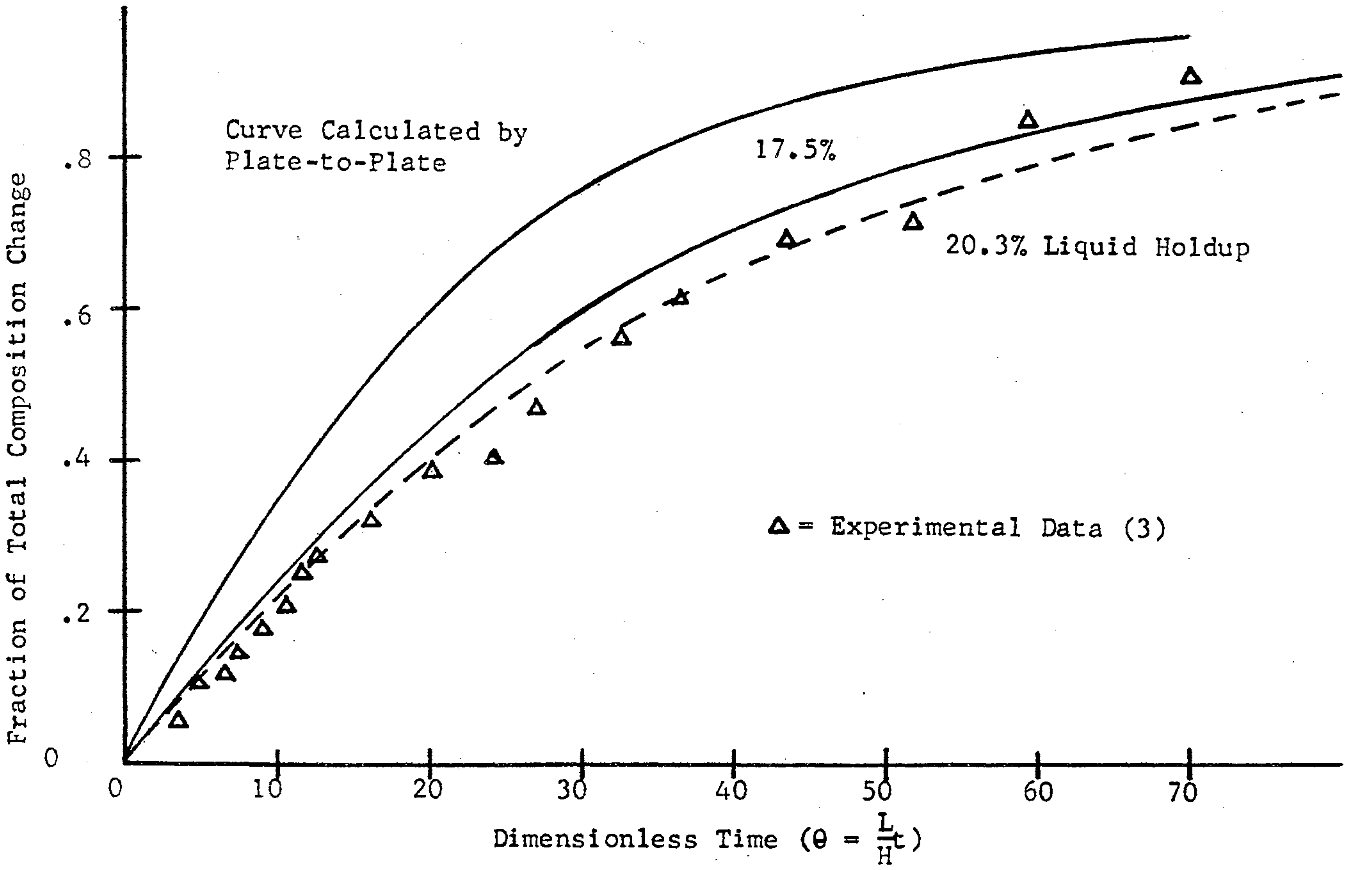

Figure 4. Fraction of Total Change as a Function of Time

section remains constant during the transient period, the model will enable the accurate prediction of the transient behavior of a distillation column.

CHAPTER IV

EXTENSION OF THE MODEL TO A COMPLETE COLUMN

In order for the method developed in the preceding chapter to be useful in practical situations, the model must be developed for a complete fractionation column like the one shown in Figure 5. Since the column has only one feed and two product streams it can be easily divided into two sections, a stripping section and a rectifying section.

Referring again to Figure 5, the unsteady-state behavior of the rectifying section may be represented by the equations

$$\delta_n^V \frac{d(y_{1,i})}{dt} = -(V_1 y_{1,i} - V_f y_{f,i}) + J_{1,i}\left[(Kx)_{0,i} - y_{f,i}\right] \tag{31}$$

$$\delta_n^L \frac{d(x_{1,i})}{dt} = -(L_1 x_{1,i} - L_0 x_{0,i}) - J_{1,i}\left[(Kx)_{0,i} - y_{f,i}\right] \tag{32}$$

If there is no holdup in the condenser, the material balance for the condenser can be written

$$Dx_{D,i} + L_c x_{c,i} = V_1 y_{1,i} \tag{33}$$

If the accumulator is completely mixed and has a constant molal holdup, then the differential equation that predicts the composition of the stream leaving the accumulator is

$$\delta_a^L \frac{d(x_{0,i})}{dt} = L_c x_{c,i} - L_0 x_{0,i} \tag{34}$$

If there is no holdup in the feed section then the material balance equations for the feed section can be written

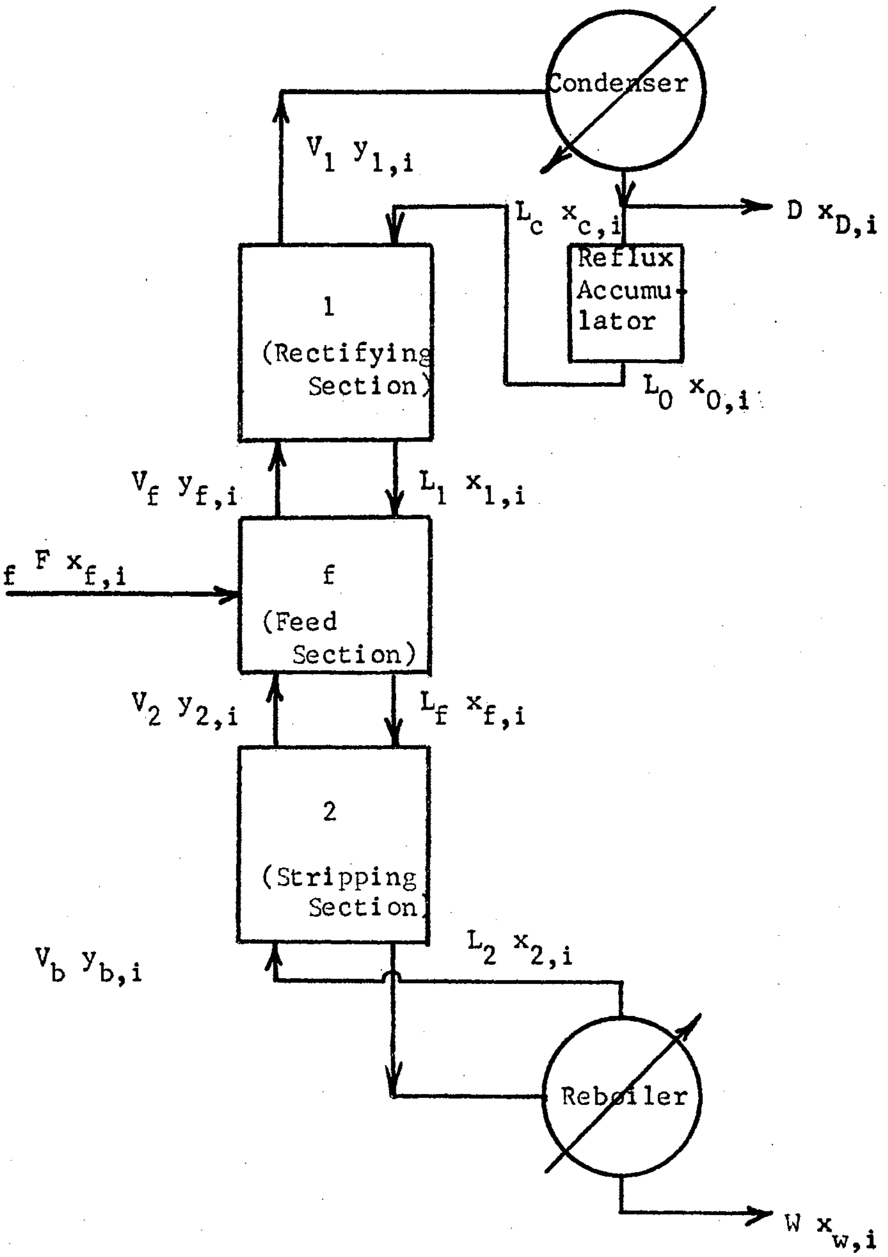

Figure 5. A Simple Fractionation Column

$$L_f x_{f,i} = L_1 x_{1,i} + \gamma_f F x_{f,i} \qquad (35)$$

$$V_f y_{f,i} = V_2 y_{2,i} - (1-\delta_f) F y_{f,i} \qquad (36)$$

where δ_f is the fraction of the feed that is liquid and $(1-\gamma_f)$ is the fraction of the feed that is vapor. In obtaining these equations the feed section has been considered to be a mixing section is which no liquid is vaporized and no vapor is condensed.

In the stripping section, that is, the section of the column below the feed section, the following equations are valid:

$$\delta_2^V \frac{d(y_{2,i})}{dt} = -(V_2 y_{2,i} - V_b y_{b,i}) + J_{2,i} \left[(Kx)_{f,i} - y_{b,i}\right] \qquad (37)$$

$$\delta_2^L \frac{d(x_{2,i})}{dt} = -(L_2 x_{2,i} - L_f x_{f,i}) - J_{2,i} \left[(Kx)_{f,i} - y_{b,i}\right] \qquad (38)$$

If the reboiler holdup, like the condenser holdup, is considered to be negligible and the reboiler is treated as an equilibrium stage, the material balance equation can be written

$$W x_{w,i} = L_2 x_{2,i} - V_b y_{b,i} \qquad (39)$$

In equation (39) the vapor leaving the reboiler is considered to be in equilibrium with the liquid leaving the reboiler.

The above equations can be used, with an over-all material balance for the column, to obtain a solution for the transient behavior of the column. One problem which arises, however, is that of determining the internal flow rates at any time. The most accurate way of determining the internal flow rates is to make a heat balance for the column during the solution of the differential equations. While this method is undoubtedly the most accurate, it also increases the complexity of the problem.

Another way that has been proposed to obtain the internal flow rates is to first determine the initial flow rates by making a heat balance and then to assume that the flow rates change to their final values immediately after the step change. If the step change is of a relatively small order of magnitude, the internal flow rates can be assumed to have the same relationship with the external flow rates after the change as they did before the change. If the above assumptions are valid, the flow rate of the liquid leaving the rectifying section can be expressed as

$$L_1 = L_0(1 - P) \tag{40}$$

In equation (40), the term P is defined by the equation

$$P = \left.\frac{(L_0 - L_1)}{L_0}\right|_{t<0} \tag{41}$$

Once the internal liquid rate is determined with equation (40), the internal vapor rate can be determined with a material balance.

Although the above approximate method is valid for small changes in column conditions, the heat balance should be used to obtain more accurate results. In fact, the approximate method should only be used when absolutely necessary, in order to conserve either computer time or space.

Use of the equations developed in this section will allow the accurate prediction of the transient behavior of a simple fractionation column if the underlying assumptions are valid. The most important of these assumptions is that $J_{n,i}$ is a constant during the transient period.

CHAPTER V

DISCUSSION OF TESTS FOR THE PROPOSED MODEL

In order to prove the model that has been developed in this thesis, two different types of tests have been used. The first type of proof was to compare results obtained with the present model with the experimental results obtained by Baber (3) on the acetone-benzene system. The other type of test was to calculate an initial steady-state solution for the propane-n-butane system at a given feed rate and composition in a simple fractionation column. These initial steady-state data were used to determine a value for $J_{n,i}$, the parameter that describes the degree of separation in the column. The equations developed in Chapter IV were then used to predict the final steady-state to which the system would go after a change in the feed composition. The results of this prediction were then compared with the values obtained from a steady-state solution using the new feed composition. The results of these tests of the model are presented in Chapter VI. The steady-state model that was used to calculate the steady-state values was one developed by Erbar and Maddox (9).

The experimental data obtained by Baber were obtained on a column of the type shown in Figure 6. Baber performed three different types of experiments in order to obtain data for as many types of perturbations as possible. The three types of experiments were different in that a different variable was changed in each type of experiment. The three variables that were changed were the reflux composition, the reflux rate,

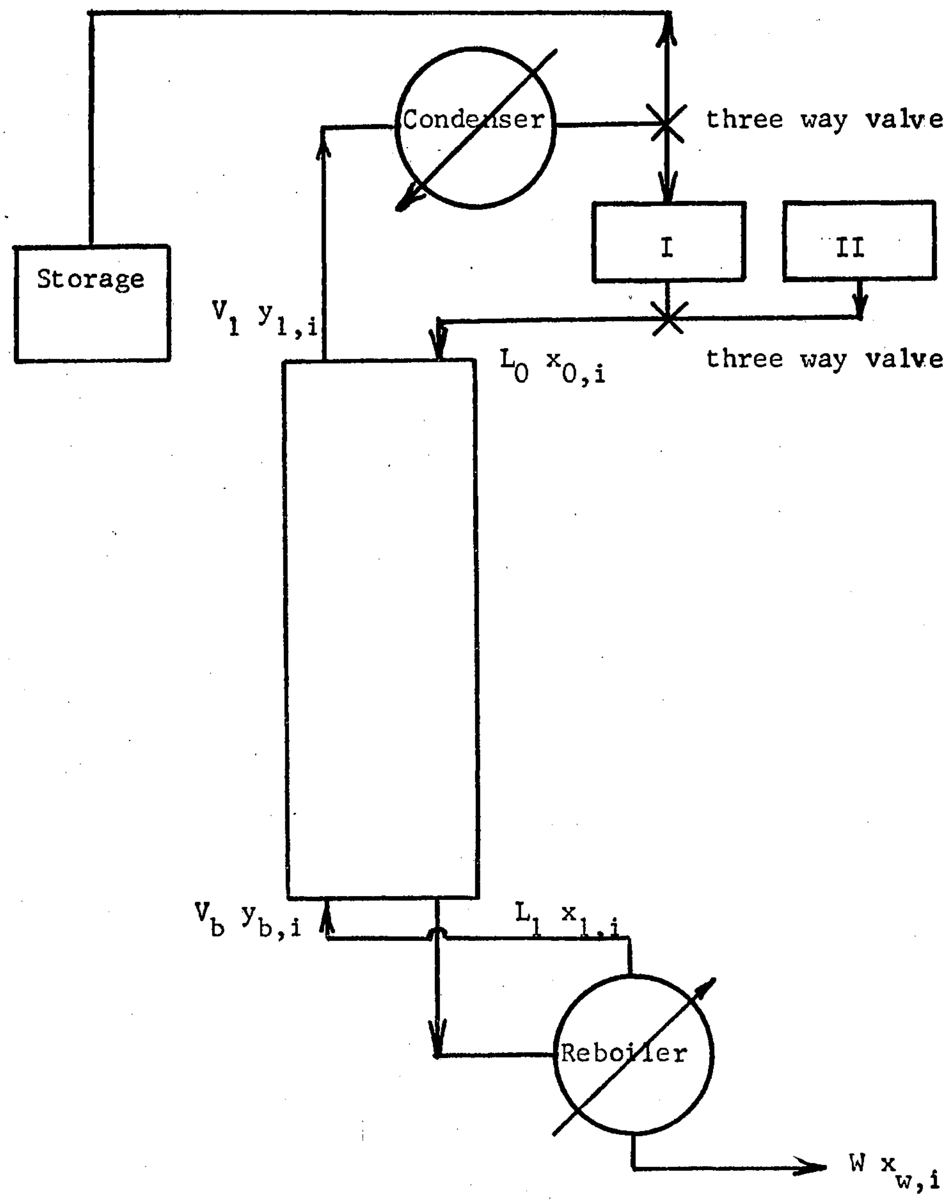

Figure 6. Distillation Column Used by Baber to Obtain Experimental Data

and the vapor boilup rate. These runs were designated the D-runs, the B-runs, and the M-runs by Baber. In the D-runs the column was allowed to reach steady-state at total reflux and then the composition of the reflux was changed with special precautions being taken to insure that the reflux rate did not change. This change in reflux composition without a change in the reflux rate was accomplished by taking reflux from tank II in Figure 6 instead of tank I. During these D-runs, the reboiler duty was held constant and no bottoms product was removed.

In the B-runs the reflux rate was increased, but the reflux composition was not changed. This change was accomplished by sending the condensed vapors to the storage tank rather than tank I. The reflux was still taken from tank I and thus the reflux composition did not change. In these runs, like the D-runs, the reboiler duty was held constant, but a small amount of bottoms product was removed in order to keep the reboiler holdup constant.

In the M-runs the reboiler duty was decreased, and thus the internal vapor rate was decreased, while the reflux rate and composition were held constant. This change was accomplished by decreasing the steam rate to the reboiler and sending the condensed vapors to the storage tank. In these runs, like the B-runs, a small amount of bottoms product was removed to keep the reboiler holdup constant.

Since a small amount of bottoms product was withdrawn in the B-runs and in the M-runs, the composition of the vapor could not be assumed to be the same as the liquid leaving the bottom tray; and since Baber published neither the compositions nor the relationship between the vapors leaving the reboiler and the bottoms product, the vapor composition could not be calculated. This lack of information on the composition of the vapor stream entering the column greatly restricts the utility of the B- and M-runs in proving the proposed model. The value of $J_{n,i}$ was, however, calculated for each run in order to see how much it varied.

Since, during the D-runs, the reflux composition was held constant, the composition of the vapor leaving the reboiler was assumed to be the same as the liquid leaving the bottom tray, and the changes in the flow rates were assumed to occur immediately after the step change, the differential equations describing the transient behavior of the column became amenable to analytical solution. The actual integration process appears in the Appendix, but the final equation obtained for the liquid is

$$x_1 = \left[\frac{L_0\, x_0 - J\, K_0\, x_0}{L_1 - J}\right]\left[1 - \exp -\left(\frac{L_1 - J}{\delta^L_1}\, t\right)\right] + x^o_1 \exp -\left(\frac{L_1 - J}{\delta^L_1}\, t\right) \qquad (42)$$

For the vapor, the integrated equation is

$$y_1 = y^o_1 \exp -\left(\frac{V_1}{\delta^V_1}\, t\right) + \left[1 - \exp -\left(\frac{V_1}{\delta^V_1}\, t\right)\right]\left[\frac{J_1\, (Kx)_0 \{\delta^V_1\, (L_1 - J_1\, (Kx)_0) - \delta^L_1\, (V_2 - J_1\, (Kx)_0)\} - (J_1 - V_2)\, \delta^L_1\, L_0\, x_0}{V_1\, \delta^L_1\, (L_1 - J_1)}\right] -$$

$$\left[\frac{[J_1 - V_1][x^o_1 (L_1 - J_1) - L_0\, x_0 + J_1\, (Kx)_0][\delta^L_1]}{[\delta^V_1\, (L_1 - J_1) - \delta^L_1\, (V_1)][L_1 - J_1]}\right]\left[\exp -\left(\frac{L_1 - J_1}{\delta^L_1}\, t\right) - \exp -\left(\frac{V_1}{\delta^V_1}\, t\right)\right] \qquad (43)$$

In equations (42) and (43), the compositions and other data are for the most volatile component, acetone. Equations (42) and (43) can now be used to predict the behavior of the liquid and vapor streams leaving the column and thus to compare the proposed model with experimental data.

CHAPTER VI

DISCUSSION OF THE RESULTS OF THE TESTS CONDUCTED TO PROVE THE PROPOSED MODEL

The tests which were described in the previous chapter proved rather conclusively that the model developed in Chapter III is an excellent method for predicting the transient behavior of a distillation column. The tests on the computer solution have shown that the model can, by use of computer values for the initial steady-state, be used to predict the final steady-state values and the tests on experimental data (3) have shown that the experimental data curve can be reproduced if the proper holdup is used. Thus, the model has been proven experimentally to possess the power to predict the transient behavior of a distillation column in the preliminary stages of design. Table I contains the results of the test on the computer data and Figure 4, which appeared in Chapter III, shows that the experimental data can be reproduced if the proper holdup term is used. The results in Table I indicate that, while the compositions of the internal streams predicted by the proposed model and those predicted by the steady-state computer solution differ considerably, the difference between the product values is markedly smaller. The method by which the final steady-state values predicted by the proposed model were obtained is illustrated in the Appendix.

The data from Baber's experimental runs were used for three purposes. The first purpose was to determine whether or not $J_{n,i}$ the parameter which

TABLE I

RESULTS OF COMPARISON OF PROPOSED MODEL WITH STEADY-STATE COMPUTER SOLUTION*

Table Ia

Feed Compositions and Flow Rates

Variable	Before Change	After Change
Feed flow rate (# moles/hr.)	100	100
Mole per cent propane	25	30
Mole per cent n-butane	75	70
Feed condition	bubble point	bubble point

Table Ib

Compositions of Product Streams and Internal Streams as Calculated With Erbar-Maddox Method and Proposed Model at Initial and Final Steady-States

Stream	Initial Steady State**			Final Steady-State		
	Erbar-Maddox	Proposed Model	Difference	Erbar-Maddox	Proposed Model	Difference
D	.89391	.89391	-	.9185	.9651	-.0466
L_1	.26552	.26552	-	.45831	.36586	.09245
V_f	.48920	.48920	-	.62296	.58136	.04160
L_f	.25454	.25454	-	.34965	.31940	.03025
V_2	.48881	.48881	-	.62296	.58101	.04195
L_2	.06072	.06072	-	.16079	.12955	.03124
V_w	.08898	.08898	-	.23170	.18712	.04458
W	.03549	.03549	-	.09792	.07850	.01942

*Change in column conditions effected by changing the feed composition.

**Compositions given are mole fraction propane.

describes the degree of separation occurring in the section remains essentially constant. This was done by calculating a value for $J_{n,i}$ for each of the runs of a particular type and then calculating the mean value and the standard deviation. The complete results of these calculations are shown in Table II, but the mean values and the standard deviations are as follows: for the D-runs the mean value of $J_{n,i}$ was 107.2 and the standard deviation was 23.5: for the B-runs the mean value of $J_{n,i}$ was 110.1 and the standard deviation was 14.7: and for the M-runs the mean value of $J_{n,i}$ was 104.2 and the standard deviation was 12.1. Obviously, the B- and M-runs would have been better to test the ability of the proposed model, to predict the transient behavior but as was mentioned above, the composition of the vapor entering the column after the run was begun was not known. Using equation (42), the ability of the proposed model to predict the final steady-state from initial steady-state values and final flow rates was tested. The results with the present model were compared with the experimental results as were the results obtained by Baber with the plate-to-plate model. The complete results of these tests are presented in Table III; however, a summary of the results is given below. The average difference between the values calculated with the present model and the experimental values was 2.9 mole per cent while the average difference between the values calculated with the plate-to-plate model and the experimental values was 1.9 mole per cent. In addition to predicting the final steady-state values as well as the plate-to-plate model, the present model produces curves which follow the experimental data more closely. This observation is borne out by the curves in Figures 4 and 7.

The results given above for both the computer calculations and the

TABLE II

VALUES OF $J_{n,i}$ FOR THE INITIAL STEADY-STATES OF THE EXPERIMENTAL RUNS BY BABER (3)

Run No.	$J_{n,i}$ (moles/hr. mole fraction)
D-2	88.0
D-3	70.5
D-4	98.5
D-5	94.4
D-7	104.3
D-8	96.1
D-10	144.8
D-11	121.5
D-12	142.7
D-13	111.0
B-1	103.5
B-2	102.3
B-3	112.7
B-4	113.7
B-6	97.3
B-7	106.1
B-8	131.0
B-9	105.8
B-10	138.1
B-11	90.3
M-1	95.1
M-3	103.4
M-4	115.0
M-5	117.3
M-6	106.9
M-7	96.8
M-8	127.5
M-9	95.4
M-10	84.5
M-11	113.0
M-12	97.7
M-13	98.1

TABLE III

COMPARISON OF VALUES PREDICTED BY PROPOSED MODEL WITH EXPERIMENTAL (3) VALUES AND THOSE PREDICTED BY PLATE-TO-PLATE MODEL (3)

Run No.	Change Predicted by		Experimental Change*
	Proposed Model*	Plate-to-Plate*	
D-2	-.119	-.0211	-.010
D-3	-.093	-.087	-.021
D-4	-.045	-.039	-.008
D-5	-.062	-.118	-.049
D-7	-.083	-.111	-.093
D-8	-.031	-.024	-.031
D-10	-.095	-.104	-.126
D-11	-.046	-.019	-.024
D-12	-.067	-.056	-.042
D-13	-.061	-.040	-.025

*Mole fraction acetone in liquid leaving bottom of column

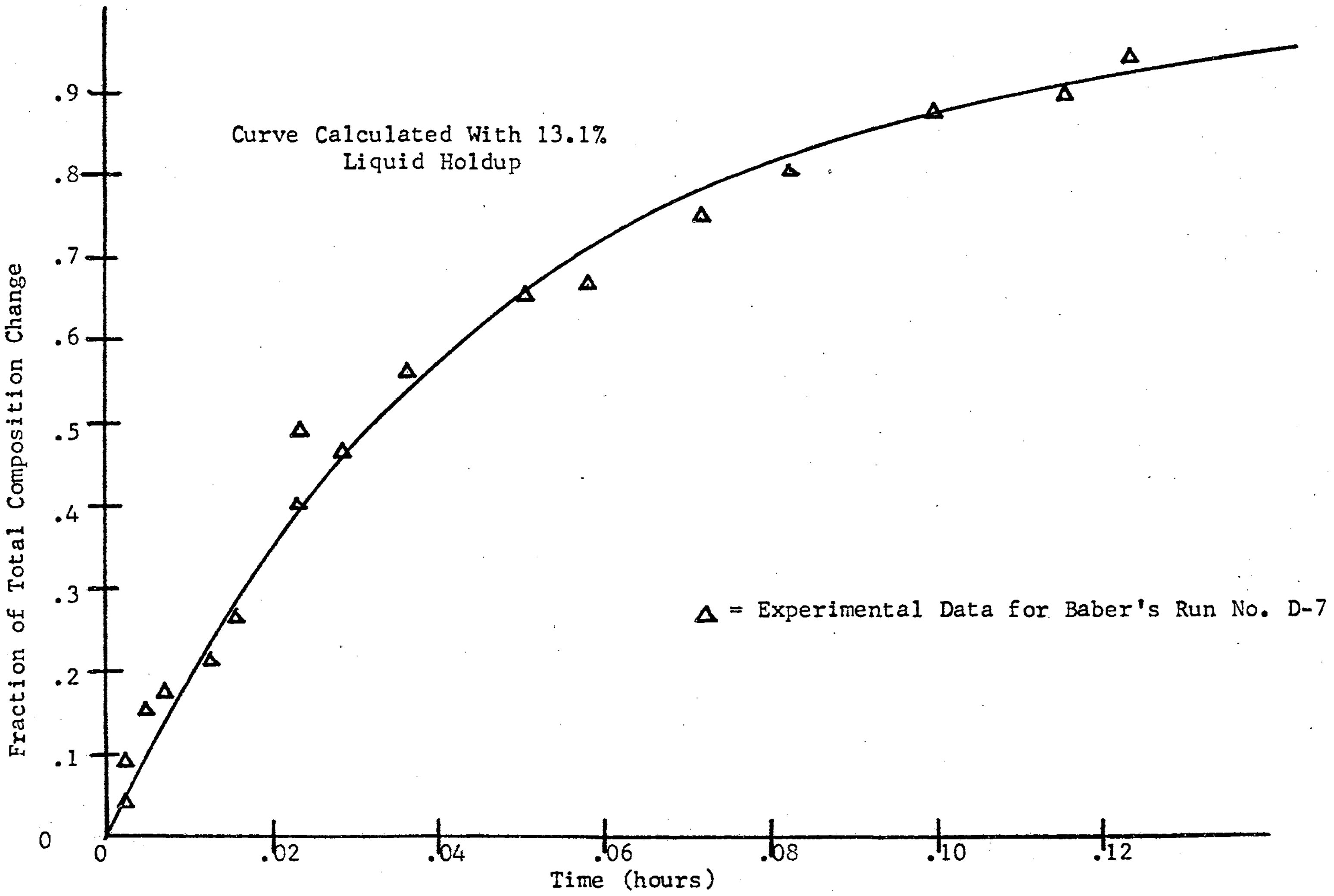

Figure 7. Fraction of Total Change as a Function of Time

experimental tests indicate how necessary it is to accurately know the initial flow rates and compositions and the final flow rates of the various streams. This observation is supported by the fact that changing the internal flow rate in the column used by Baber as little as six moles per hour changes the final steady-state composition by approximately four mole per cent. Another reason is that since $J_{n,i}$ is of the same order of magnitude as the flow rates, an error in the initial flow rates, which is not compensated for in the final flow rates, will cause a relatively large error in the final composition predicted by the model.

CHAPTER VII

RECOMMENDATIONS AND CONCLUSIONS

From the results of the series of tests that were conducted on the model that was developed in this thesis, several conclusions seem to be warranted about the model. First and foremost, the results indicate that the basic concept that the separation that occurs in a distillation column can be represented by a parameter that describes the degree of separation in the column is valid. Even though the results in some of the tests are not exactly correct, they are comparable in accuracy to the results obtained with the more complicated plate-to-plate model. In fact, in most cases the curves predicted by the present model follow the experimental data curves more closely than the curves predicted by the plate-to-plate model. This ability to reproduce the experimental curves leads directly to the conclusion that the transient behavior of a single section distillation column is a first order function, which can be represented by a first order time constant.

Since the present model appears to be so promising, the process of testing it should be continued. This continuation of the testing program is recommended because, in the opinion of the author, the current program has not been extensive enough. Future work on the testing of the model should be conducted on multicomponent systems rather than the conventional binary ones and should include experimental work. The use of multicomponent systems is recommended for two reasons. The first reason is that since the model will eventually be used to evaluate multicomponent systems, such a system should undoubtedly be used to prove the model. The other reason for obtaining experimental data on a multicomponent system is that, while transient data for binary systems, such as the data obtained by Baber, are available, there are no sources of transient behavior data for multicomponent systems listed in the literature.

NOMENCLATURE

Major Symbols

English Letters

D = rate at which distillate is produced, moles/hour.

F = feed rate to the column, moles/hour.

f_n^L = fraction of the section that is filled with liquid.

$f_n^V = (1 - f_n^L)$ fraction of the section that is filled with vapor.

J = the parameter which describes the degree of separation occurring in the section, moles/hour-mole fraction.

K = vapor-liquid equilibrium coefficient.

L = liquid flow rate, moles/hour.

N = net rate of mass transfer between phases, moles/hour.

$P = (L_0 - L_1)/L_0$

S = cross sectional area of the column, sq. ft.

V = vapor flow rate, moles/hour.

x = liquid composition, mole fraction.

y = vapor composition, mole fraction

z = height of the section, ft.

Greek Letters

δ = holdup in a section or on a tray, moles.

γ = fraction of the feed that is liquid.

$1-\gamma$ = fraction of the feed that is vapor.

ρ = molal density, moles/cu. ft.

Subscripts

a = accumulator.

b = vapor leaving the reboiler.

c = condensate.

d = distillate.

f = feed section.

i = component number.

m = subsection number.

n = section number.

b = bottoms.

$*$ = equilibrium value.

Superscripts

L = liquid phase.

o = initial condition.

V = vapor phase.

Groups

$\frac{d}{dt}$ = total derivative with respect to time.

$\frac{\partial}{\partial t}$ = partial derivative with respect to time.

$\frac{\partial}{\partial z}$ = partial derivative with respect to distance.

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APPENDIX

APPENDIX A

INTEGRATION OF EQUATIONS (27) AND (28) FOR THE CONDITIONS OF BABER'S (3) D-RUNS

The D-runs made by Baber were performed on a column like the one illustrated in Figure 6, and during these runs the following variables were held constant: $(Kx)_0$, $J_{1,1}$, V_1, V_2, L_0, and L_1. Since no bottoms product was removed, $y_2 = x_1$. Due to the constancy of the variables tested and the equality of y_2 to x_1, equations (27) and (28) can be integrated, analytically.

Taking equation (27) and (28) and using the equality of y_2 and x_1, then for any component the resulting equations are

$$\delta_1^V \frac{dy_1}{dt} = - V_1 y_1 + (J_1 - V_2) x_1 + J_1 (Kx)_0 \qquad \text{(A-1)}$$

$$\delta_1^L \frac{dx_1}{dt} = - (L_1 - J_1)x_1 + (L_0 x_0 - J_1 (Kx)_0) \qquad \text{(A-2)}$$

Since equation (A-2) contains only one independent and one dependent variable and is a linear first order equation, it can be integrated easily For ease in handling, let

$$\beta = L_0 x_0 - J_1 (Kx)_0 \qquad \text{(A-3)}$$

$$\alpha = L_1 - J_1 \qquad \text{(A-4)}$$

Thus, by use of equation (A-3) and (A-4) equation (A-2) becomes

$$\delta_1^L \frac{dx_1}{dt} = \beta - \alpha x_1 \qquad \text{(A-5)}$$

Equation (A-5) can now be integrated by using the techniques of separation of variables. The equation that results from this integration is

$$- \ln (\beta - \alpha x) = \frac{\alpha t}{\delta_1^L} - \ln C_1 \qquad \text{(A-6)}$$

Equation (A-6) can be written in simplified form as

$$- \quad x_1 = C_1 \exp -\left(\frac{\alpha}{\delta_1^L} t\right) \qquad \text{(A-7)}$$

By use of the initial conditions that $x_1 = x_1^o$ at $t = 0$, equation (A-7) becomes, on evaluation of C_1,

$$x_1 = \frac{1}{\alpha} \left[1 - \exp -\left(\frac{\alpha}{\delta_1^L} t\right) \right] + x_1^o \exp -\left(\frac{\alpha}{\delta_1^L} t\right) \qquad \text{(A-8)}$$

Now that an expression for x_1 has been obtained, equation (A-1) can be written in a form that contains only y_1 and t. The equation that results from the substitution of (A-8) into (A-1) is

$$\frac{dy_1}{dt} + \Omega y_1 = \xi + \frac{\eta \beta}{\alpha} \left[1 - \exp -\left(\frac{\alpha}{\delta_1^L} t\right) \right] + x_1^o \exp -\left(\frac{\alpha}{\delta_1^L} t\right) \qquad \text{(A-9)}$$

where

$$\eta = \frac{J_1 - V_2}{\delta_1^L} \qquad \text{(A-10)}$$

$$\Omega = \frac{V_1}{\delta_1^L} \qquad \text{(A-11)}$$

$$\xi = \frac{J_1 (Kx)_0}{\delta_1^L} \qquad \text{(A-12)}$$

Equation (A-9) can now be integrated by use of the integrating factor $e^{\int \Omega dt} = e^{\Omega t}$. This integration yields the equation

$$y_1 = e^{-\Omega t}\left\{\left[\frac{\xi}{\Omega} e^{\Omega t} + \frac{\eta\beta}{\alpha\Omega} e^{\Omega t} - \frac{\eta\left[\left(x_1^o - \frac{\beta}{\alpha}\right) \exp -\left(\frac{\alpha}{\delta_1^L} - \Omega\right)t\right]}{\left[\frac{\alpha}{\delta_1^L} - \Omega\right]}\right.\right. + C_2 \qquad \text{(A-13)}$$

Substitution of the initial value that $y_1 = y_1^o$ and of the values for α, β, η, ξ, and Ω into equation (A-13) yields the equation

$$y_1 = y_1^o \exp -\left(\frac{V_1}{\delta_1^V} t\right) + \left[1 - \exp -\left(\frac{V_1}{\delta_1^V} t\right)\right]\left[\frac{J_1 (Kx)_0\left\{\delta_1^V (L_1 - J_1 (Kx)_0) - \delta_1^L (V_2 - J_1 (Kx)_0)\right\} - (J_1 - V_2)\,\delta_1^L L_0 x_0}{V_1\,\delta_1^L (L_1 - J_1)}\right] -$$

$$\left[\frac{[J_1 - V_1]\left[x_1^o (L_1 - J_1) - L_0 x_0 + J_1 (Kx)_0\right]\left[\delta_1^L\right]}{\left[\delta_1^V (L_1 - J_1) - \delta_1^L (V_1)\right]\left[L_1 - J_1\right]}\right]\left[\exp -\left(\frac{L_1 - J_1}{\delta_1^L} t\right) - \exp\left(-\frac{V_1}{\delta_1^V} t\right)\right] \qquad \text{(A-14)}$$

Substitution of the values of α and β into equation (A-8) yields the equation

$$x_1 = x_1^o \exp -\left(\frac{L_1 - J_1}{\delta_1^L} t\right) + \frac{L_0 x_0 - J_1 (Kx)_0}{L_1 - J_1} \exp -\left(\frac{L_1 - J_1}{\delta_1^L} t\right) \qquad \text{(A-15)}$$

Equation (A-14) and (A-15) can now be used to predict the compositions of any column which operates under the assumptions that were made in obtaining the solution.

APPENDIX B

DESCRIPTION OF THE SOLUTION TO THE EXAMPLE WORKED WITH THE COMPUTER SOLUTION

In order to solve this problem, a solution to the initial steady-state problem had to be obtained. This solution was obtained using the method of Erbar and Maddox that was described in Chapter V. This computer program required vapor-liquid equilibrium data and enthalpy data for each of the components. The vapor-liquid equilibrium data were obtained from the Engineering Data Book (17) and the enthalpy data were obtained from Applied Hydrocarbon Thermodynamics by W. C. Edmister(8).

Once the initial conditions had been determined, the effect of the change in feed composition was calculated with the following equations, which are the steady-state forms of the equations derived in Chapter IV for the simple fractionation column:

$$-(V_1\, y_{1,1} - V_f\, y_{f,1}) + J_{1,1}\, (Kx)_{0,1} - y_{f,1} = 0 \qquad (1)$$

$$(L_1\, x_{1,1} - L_0\, x_{0,1}) + J_{1,1}\, (Kx)_{0,1} - y_{f,1} = 0 \qquad (2)$$

$$-(V_2\, y_{2,1} - V_b\, y_{b,1}) + J_{2,1}\, (Kx)_{f,1} - y_{b,1} = 0 \qquad (3)$$

$$(L_2\, x_{2,1} - L_f\, x_{f,1}) + J_{2,1}\, (Kx)_{f,1} - y_{b,1} = 0 \qquad (4)$$

In addition, the normal material balance equations were used. In this example, the column was assumed to have no accumulator and the reboiler was assumed to act as an equilibrium stage.

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