



A study of the reversing of relative volatilities by extractive distillation  
by An-I Yeh

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in  
Chemical Engineering  
Montana State University  
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**Abstract:**

The separation of the close-boiling mixture, m-xylene-o-xylene; three binary azeotropes: ethanol-water, methyl acetate-methanol, acetone-methanol, and four ternary azeotropes: n-propyl acetate-n-propanol-water, isopropyl acetate-isopropanol-water, n-butyl acetate-n-butanol-water, isobutyl acetate-isobutanol-water has been enhanced by extractive distillation. The azeotropes have been negated and the relative volatilities of key components have been reversed by the agents used.

The plot of polar interaction versus hydrogen bonding, called polarity diagram, was used to compare the affinity of agents for key components. Thus the key component which will be the overhead product can be predicted. The three solubility parameters were used to describe the intermolecular forces occurring between agents and key components in extractive distillation. The MOSCED model was used to calculate the activity coefficients of the key components using the properties of the pure compounds. The calculated values fitted the experimental data well. The advantage of this model was to calculate the relative volatilities of key components in the presence of the agent using the properties of pure compounds instead of using the properties of mixtures.

Temperature inversion, where the overhead temperature was higher than the stillpot temperature, was observed for the acetone-methanol system when ketones were used as the agents. The data showed that the temperature inversion could be caused by the dissolving of the vapor of key components in the liquid agents.

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BY EXTRACTIVE DISTILLATION

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of the requirements for the degree

of

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in

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APPROVAL

of a thesis submitted by

An-I Yeh

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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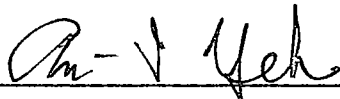
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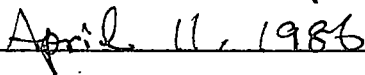
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## ABSTRACT

The separation of the close-boiling mixture, m-xylene-o-xylene; three binary azeotropes: ethanol-water, methyl acetate-methanol, acetone-methanol, and four ternary azeotropes: n-propyl acetate-n-propanol-water, isopropyl acetate-isopropanol-water, n-butyl acetate-n-butanol-water, isobutyl acetate-isobutanol-water has been enhanced by extractive distillation. The azeotropes have been negated and the relative volatilities of key components have been reversed by the agents used.

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Temperature inversion, where the overhead temperature was higher than the stillpot temperature, was observed for the acetone-methanol system when ketones were used as the agents. The data showed that the temperature inversion could be caused by the dissolving of the vapor of key components in the liquid agents.

## I. INTRODUCTION

Separation processes are those operations which transfer a mixture of substances into two or more products which differ from each other in composition. Often separation itself can be the main function of an entire process. The need for separation processes can account for most of the cost of a pure substance. A simple schematic of a separation process is shown in Figure 1. The feed may consist of one or of several streams of matter. There must be at least two product streams which differ in composition from each other. This follows from the fundamental nature of a separation. The separation is caused by the addition of a separating agent, which takes the form of another stream of matter or/and energy. Usually the energy input required for the separation is supplied by the separating agent, and the separating agent could cause the formation of a second phase of matter.

We can categorize separation processes in several ways: (i) mechanical vs. diffusional processes, (ii) equilibration processes vs. rate-governed processes, (iii) energy-separating-agent vs. mass-separating-agent process. A separation device which receives a heterogeneous feed consisting of more than one phase of matter and singly serves to separate the phases from each other is called a mechanical separation process. Mechanical processes are important industrially but are not a primary concern of this study. Diffusional separation processes receive a homogeneous feed and involve a



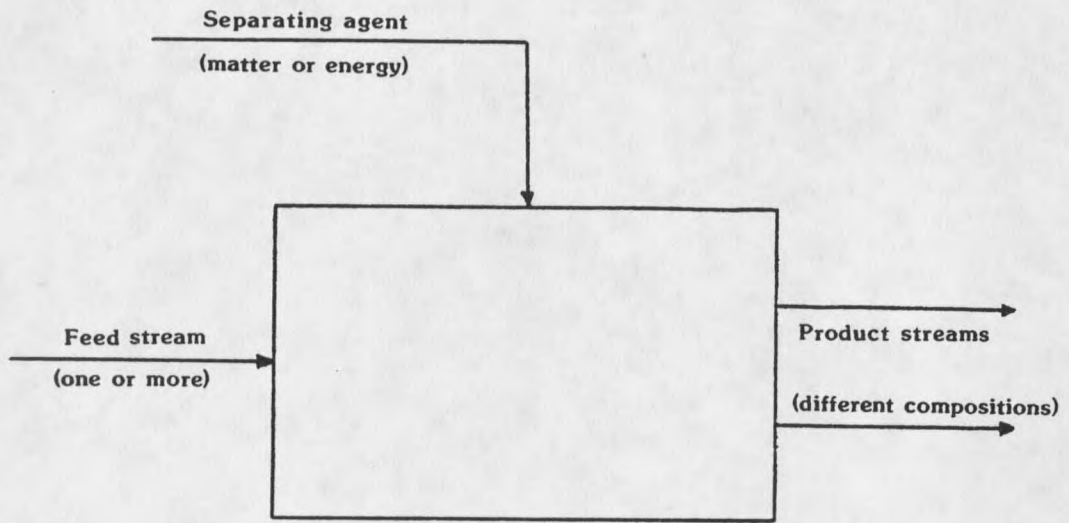


Figure 1. General separation process.

diffusional transfer of matter from the feed stream to one of the product streams. Most diffusional separation processes operate through equilibration of two immiscible phases which have different compositions at equilibrium. They are the principal subject matter of this study. On the other hand, some separation processes work by virtue of difference in transport rate through some medium under the impetus of an imposed force, resulting from a gradient in pressure, temperature, composition, electric potential, or the like. These are the rate-governed processes. Energy-separating-agent processes use energy as the separating agent such as distillation. In mass-separating-agent processes, matter is used as the separating agent such as liquid-liquid extraction.

#### Separation Factor

The degree of separation which can be obtained with any particular separation process is indicated by the separation factor. Since the object of a separation device is to produce products of differing compositions, it is logical to define the separation factor in terms of product compositions.

$$\alpha_{ij}^s = \frac{x_{i1}/x_{j1}}{x_{i2}/x_{j2}} \quad (1)$$

The separation factor  $\alpha_{ij}^s$  between components  $i$  and  $j$  is the ratio of the mole fractions of those two components in product 1 divided by the ratio in product 2. The separation factor will remain unchanged if all

the mole fractions are replaced by weight fractions, by molar flow rates of the individual components, or by mass flow rates of the individual components.

An effective separation is accomplished to the extent that the separation factor is significantly different from unity. If  $\alpha_{ij}^s = 1$ , no separation of components  $i$  and  $j$  has been accomplished. If  $\alpha_{ij}^s > 1$ , component  $i$  tends to concentrate in product 1 more than component  $j$  does, and component  $j$  tends to concentrate in product 2 more than component  $i$  does. On the other hand, if  $\alpha_{ij}^s < 1$ , component  $j$  tends to concentrate preferentially in product 1. By convention, components  $i$  and  $j$  are generally selected so that  $\alpha_{ij}^s$ , defined by Equation 1, is greater than unity.

The separation factor reflects the differences in equilibrium compositions and transport rates due to the fundamental physical phenomena underlying the separation. It can also reflect the construction and flow configuration of the separation device. For this reason it is convenient to define an inherent separation factor, which we shall denote by  $\alpha_{ij}$ . This inherent separation factor is the separation factor which would be obtained under idealized conditions, as follows:

1. For equilibration separation processes, the inherent separation factor corresponds to those product compositions which will be obtained when simple equilibrium is attained between the product phases.
2. For rate-governed separation processes, the inherent separation factor corresponds to those product compositions which will occur in the presence of the underlying physical transport mechanism alone, with no

complication from competing transport phenomena, flow configurations, or other extraneous effects.

Both the inherent separation factor  $\alpha_{ij}$  and the actual separation factor  $\alpha_{ij}^s$ , based on the actual product compositions through Equation 1, can be used for the analysis of separation processes. When  $\alpha_{ij}$  can be derived relatively easily, the most common approach is to analyze a separation process on the basis of the inherent separation factor  $\alpha_{ij}$  and allow for deviations from ideality through efficiencies. This procedure is advantageous since  $\alpha_{ij}$  is frequently insensitive to changes in mixture composition, temperature, and pressure.

### Fractional Distillation

The ultimate application of distillation is for the purpose of separating two or more components occurring in a mixture to produce products which meet certain specifications. These specifications may be sales specifications which require certain purity or characteristics based on boiling range, or process specifications which require purity or concentration with respect to one or more components for use in subsequent processes. The economic consideration of yield of material of specified characteristics has resulted in the development of the fractional distillation which may be of the stage type or differential type.

A conventional fractionating column is shown in Figure 2. From a simplified point of view, multi-stage fractional distillation may be considered to be a process in which a series of flash vaporization

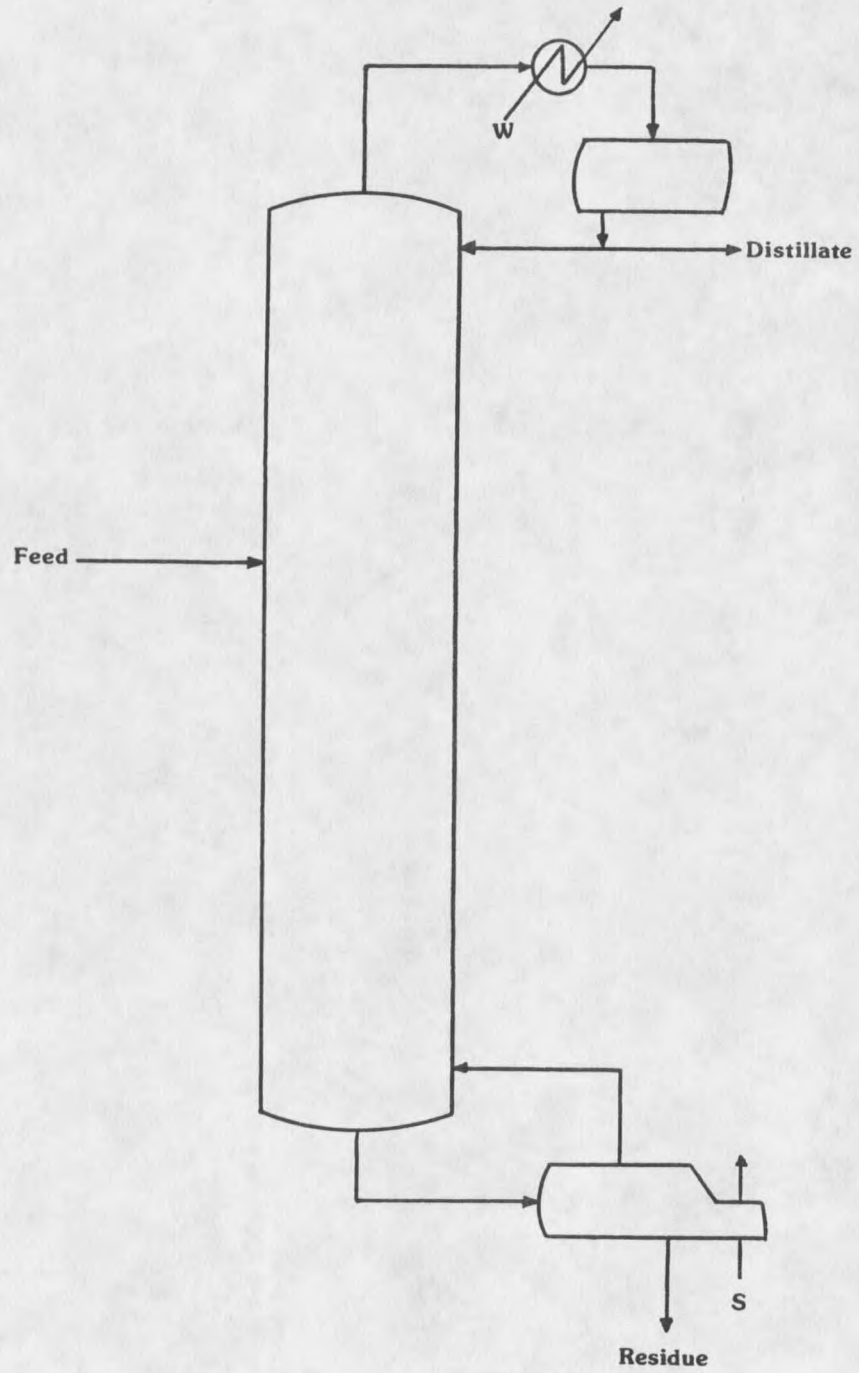


Figure 2. Conventional fractionating column.

stages are arranged in series in such a manner that the products from each stage are fed to adjacent stages. The vapor produced in one stage is conducted to the stage above and the liquid to the stage below. In turn, this stage receives the liquid from the stage above and the vapor from the stage below as its feed material. In this arrangement the concentration of the lower boiling component(s) is being increased in the vapor from each stage in the direction of vapor flow and decreased in the liquid in the direction of the liquid flow. Because the lower boiling constituents are concentrating in the vapor from each successive stage, the temperature decreases from stage to stage and reaches the minimum as the final vapor is produced from the process. Similarly, the temperature increases along with the direction of flow of the liquid, and the maximum temperature is reached at the point where the liquid product is withdrawn from the process. Since temperature is a measure of the level of heat energy, it is obvious that heat energy is necessary to the distillation process. In addition to the heat energy involved in maintaining a temperature differential, an amount of heat energy roughly equivalent to the latent heat of the vapor evolved from the last stage (with respect to vapor flow) must be supplied. This heat energy may be supplied in the feed, in the last stage from which the liquid product is withdrawn, or in both places.

In general, fractional distillation can apply when:

1. The components have appreciable differences in volatility or the relative volatility of the components to be separated is 1.05 or greater.
2. There is no azeotrope formation.

3. There is no chemical reaction between components.
4. There is no decomposition or polymerization of one or more of the components.
5. The components are capable of vaporization at practical temperature and pressure.

However, in some cases, distillation techniques other than fractional distillation have to be used for a specific separation. Those cases are (a) two or more of the components to be separated have but slight difference in volatility (relative volatility approximately equal to unity) and their vapor pressure curves are essentially of the same shape; (b) two or more of the components form a homogeneous minimum azeotrope which is not pressure sensitive or which is pressure sensitive but will not provide sufficient relative volatility change near  $x_i = 1$  or  $x_i = 0$ ; (c) one or more of the compounds will decompose or change chemically at temperature and pressure within economic distillation ranges.

#### Extractive and Azeotropic Distillation

Azeotrope is a synonym for constant-boiling mixture, a specific mixture of two or more components, which cannot be readily separated by ordinary distillation. Also, it is very difficult to separate mixtures whose components boil very close together. These are the cases a and b for which fractional distillation is not applicable. The separation can be sometimes greatly facilitated by adding a third component, called herein an "agent". In these cases two methods, namely azeotropic and

extractive distillation, have been developed commercially. Azeotropic and extractive distillation are old processes which have become widely used since about 1930. In 1908 Guillaume [1] patented an extractive distillation process for the removal of fusel oil from fermentation alcohol. Extractive and azeotropic distillation have the property in common that a substance not normally present in the mixture to be separated is added to increase the difference in volatility of the most difficultly separable components. Benedict and Rubin [2] have defined extractive and azeotropic distillation. Extractive distillation is distillation in the presence of a substance which is relatively non-volatile compared to the components to be separated and which, therefore, is charged continuously near the top of the distilling column so that an appreciable concentration is maintained on all the plates of the column. Azeotropic distillation is the process in which the substance added forms an azeotrope with one or more of the components and by virtue of this fact is present on most of the plates of the column in appreciable concentration. Applications of azeotropic and extractive distillation have continued to expand because many very close boiling mixtures may be separated economically by use of those techniques. The separation of such mixtures by conventional distillation methods is usually uneconomical because of the large number of plates which would be required to affect such separation. For a separation of a binary mixture, both overhead and bottoms products are specified to have 99% purity. Figure 3 shows the number of theoretical plates as a function of relative volatility. It can be seen that the theoretical plates number approaches infinite as the relative volatility



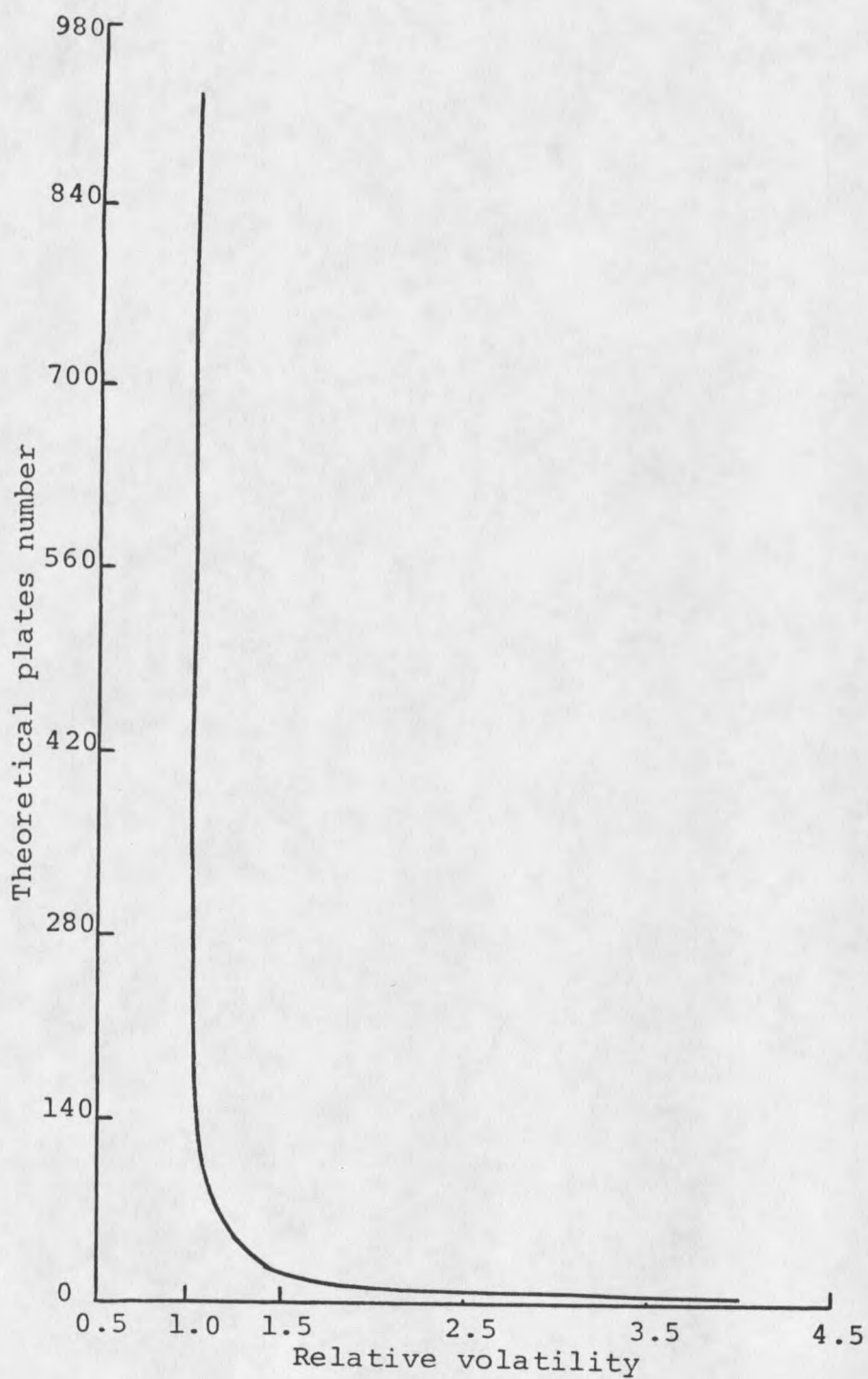


Figure 3. Number of theoretical plates as a function of the relative volatility. In a separation of a binary mixture, the overhead and bottoms products are specified to have 99% purity.

becomes closer to unity. That is the situation for the presence of a minimum-boiling azeotrope. The theoretical plates number drops rapidly when the relative volatility increases to about 1.25. If the plate efficiency is 75% and the column cost is linearly proportional to the plate number, the comparison of the column cost for different relative volatilities is shown in Table I. The column cost is a relative value which is based on a value of relative volatility of 1.05. The linear proportionality of column cost to plate number occurs up to some point. Beyond that point, the column will become more expensive than the linearly proportional price. In addition, higher pressure drop accompanys more plates. This causes more heat requirement to evaporate the liquid mixture and operational difficulties. Therefore, it is very advantageous to increase the relative volatility.

In azeotropic distillation the agent has about the same vapor pressure as the feed components and is removed with the overhead product with which it forms a minimum-boiling azeotrope. Figure 4 shows the schematic of dehydration of ethanol with benzene by azeotropic distillation. In column I the minimum ternary azeotrope, ethanol-water-benzene, comes out as the overhead product. Ethanol is obtained from the bottoms. Benzene is recovered from column II and then recycled. Water is removed from column III. In extractive distillation the agent has a low vapor pressure, so the agent is added near the top of the column and removed with the bottom product. The agent flows down the column, washing the ascending vapors and absorbing one of the components preferentially. A typical scheme for separating a binary mixture, components A and B, by extractive distillation is shown in Figure 5. In

Table I. Column cost for different relative volatility.

<u>Relative volatility</u>	<u>Plate number</u>	<u>Column cost</u>
1.01	1231.5	490.25
1.02	618.8	246.34
1.03	414.5	165.01
1.04	312.4	124.36
1.05	188.4	100.00
1.06	210.3	83.72
1.08	159.2	63.38
1.10	128.5	51.15
1.12	108.1	43.03
1.15	87.7	34.91
1.17	78.0	31.05
1.20	67.2	26.75
1.30	46.7	18.59
1.40	36.4	14.49
1.80	20.8	8.28
2.00	17.7	7.05
2.40	14.0	5.57
2.80	11.9	4.74
3.00	11.2	4.46
3.50	9.7	3.86
4.00	8.8	3.50

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The column cost is a relative value based on a value of relative relative volatility of 1.05.

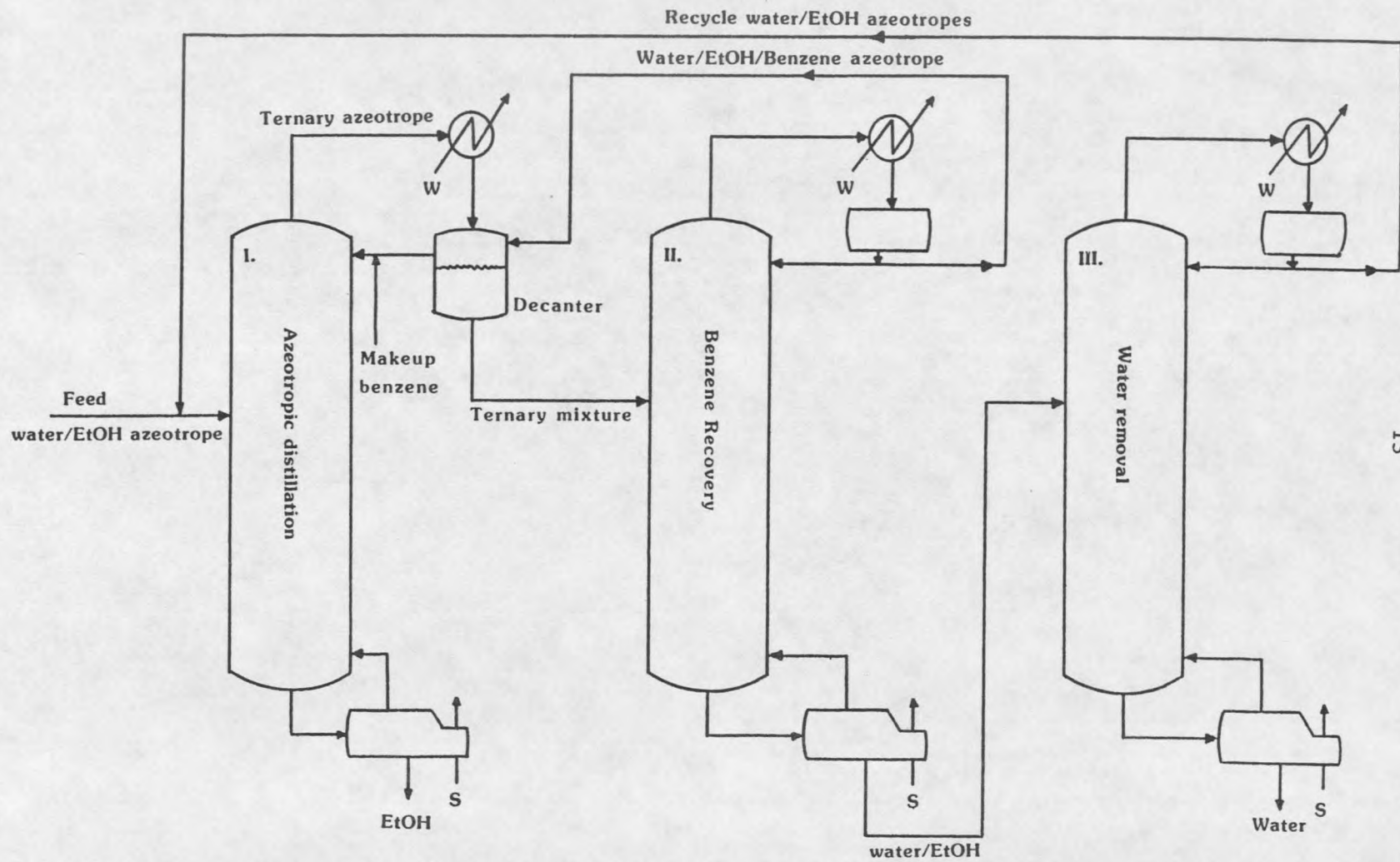


Figure 4. Azeotropic distillation scheme for ethanol dehydration with benzene.

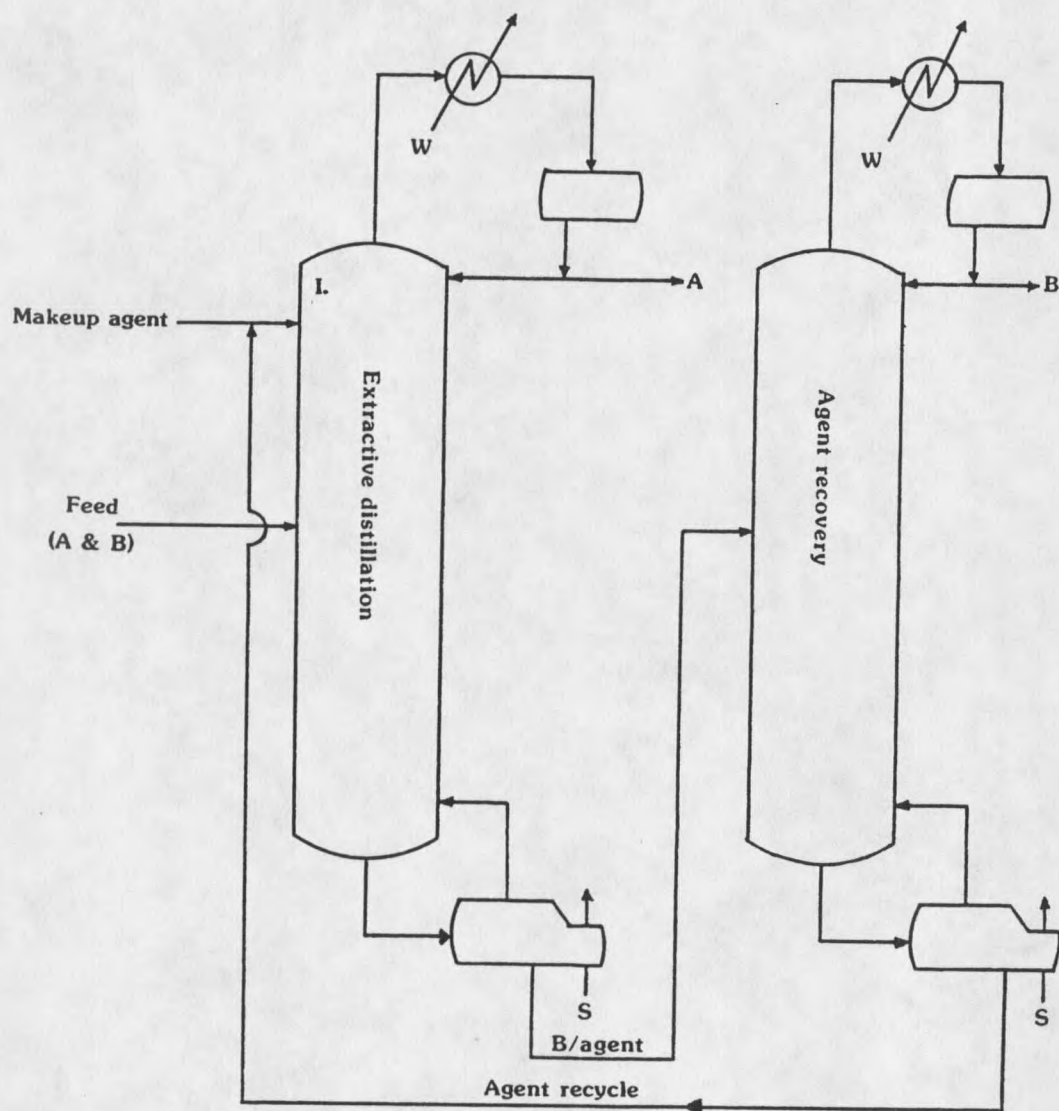


Figure 5. Schematic diagram of an extractive distillation process.

column I, component A is obtained as overhead product. The bottom product, mixture of component B and the agent, is fed to the second column and B is obtained as overhead product. The agent is recovered and recycled.

Obviously, for azeotropic or extractive distillation to be economically attractive, the improvement in relative volatility, and resulting saving in column height and steam and water costs, should more than offset the added costs of recirculating the agent, recovering it from the products, and providing make up agent because of losses in recirculation. In azeotropic distillation an agent immiscible with the overhead product can be separated by decantation, and with a hydrocarbon overhead product a water-soluble agent can be used and then recovered by washing the overhead product with water. As shown in Figure 4, three columns are needed to complete the separation of water and ethanol, agent recovery, and water removal. In extractive distillation, agent recovery from the bottoms product is easily affected in a separate stripping column because of the agent's low vapor pressure. As shown in Figure 5, only two columns are required to complete the separation of a binary mixture and agent recovery. Comparing Figures 4 and 5 shows that the capital cost for extractive distillation could be lower than that for azeotropic distillation.

The principal difference between the processes of azeotropic and extractive distillation is that the agent is almost entirely recovered in the distillate in azeotropic distillation, and in extractive distillation the agent is recovered in the residue or bottoms. Also, the optimum point of adding of the agent to the column is different for

the two types of processes. Gerster [3] illustrated the difference between these two methods by the various special-agent distillations required at Celanese's Bishop, Texas plant. If the feed is a close-boiling hydrocarbon pair, the differences in the nature of the feed components are usually comparatively small, so that the agent is required to improve the relative volatility over the entire height of the column. This is achieved best in extractive distillation where the agent enters at, or near, the top and is discharged at the bottom of the column. Azeotropic distillation is particularly useful where the feed component selected to come overhead as an azeotrope with the agent is present in the feed in small amount. In such an instance the amount of agent needed to be circulated is small, resulting in only small additional steam costs because of the presence of the agent and in a low-agent recovery cost.

In many industrial mixtures the key components under consideration can be separated either by extractive or azeotropic distillation by the selection of the proper agent, and the economic comparison of the processes will usually indicate the one more suitable for the purpose. Another important consideration in the selection of a process is the thermal stability of the components, particularly that of the heavy key and heavier key components. If one of these components is unstable or tends to decompose, polymerize, or otherwise react at a higher temperature level, it is better to use azeotropic distillation to keep the bubble-point temperature of the bottoms at its lowest point. A heavy agent would increase the bubble point above this temperature and could have a deleterious effect on the components in the residue.

Treybal [4] has pointed out that extractive distillation is generally considered to be more desirable than azeotropic distillation since (i) there is a greater choice of agents because the process does not depend upon the accident of azeotrope formation and (ii) generally smaller quantities of agent must be vaporized. Due to the increase in energy costs, extractive distillation is worth considering even when the conventional approach is feasible. Sucksmith [5] has shown that 42 million Btu/hour are required to separate the mixture of n-heptane and toluene by conventional distillation; only 18 million Btu/hour are required for the same separation by extractive distillation. If an agent provides approximately 40% greater relative volatility, Bojnowski and Hanks [6] suggested that the extractive distillation could be considered instead of conventional fractional distillation.

#### Behavior of Agents

An effective agent for an extractive distillation is one which is attractive to one or more of the components. This attraction of the agent for these components reduces the volatility of the agent as well as the volatility of the components to which it is attracted. It is desirable that the attraction occur in the natural direction, that is, that the agent be attracted to the relatively heavy components. However, this is not a necessary condition for the behavior of the agent. Many separations are carried out in which one of the relatively light components is attracted by the agent and removed in the bottoms product with the agent. In this case, the energy consumption for



recovering the agent in a stripping column can be reduced due to lower bubble point of the mixture of the agent and the relatively light component.

A variety of theories has been advanced for the roles of the agent in azeotropic and extractive distillation. In the case of extractive distillation, attraction of the agent for certain components of the mixture is commonly attributed to one or more or a combination of the following phenomena: (1) hydrogen bonding, (2) polar characteristics of the agent and components of the mixture, (3) the formation of weak unstable chemical complexes, and (4) chemical reactions between the agent and one or more of the components of the mixture.

In the case of azeotropic distillation, the agent should have the capacity to reduce the tendency of attraction between molecules. For example, a nonpolar agent may be added to a mixture of polar molecules in order to increase the volatilities of the more polar compounds relative to the less polar compounds.

Although any one theory does not sufficiently explain all applications of azeotropic and extractive distillation, the theories do provide qualitative values for the selection of agents. The role of polarity has been elucidated by Hopkins and Fritsch [7] who described the use of products obtained by oxidation of selected hydrocarbons. Because of the dissimilarities in molecular structure, the oxidation products can be arranged in the order of increasing polarity [8], namely, esters, oxides, aldehydes, ketones, acetals, and alcohols. In any class of compounds, the polarity is inversely proportional to the molecular weight, the polarity of straight-chain molecules is greater.

than that of branched-chain structures, and olefinic compounds are more polar than their corresponding paraffin derivatives.

### Choice of Agents

Among the desirable features for an agent are the following:

1. It should have a high capacity for the species being separated by it. The higher the agent capacity, the lower the agent circulation rate required.
2. It should be selective, having a wider range of temperature and concentration of miscibility with one or more of the components being separated while having a small range of the miscibility with other components.
3. It must have a low molar latent heat since it is to be vaporized.
4. It should be chemically stable, i.e., it should not undergo irreversible reactions with components of the feed stream or during recovery.
5. It should be easily separable from the components with which it associates. Thus it can be reused again and again.
6. It should be nontoxic and noncorrosive and should not be a serious contaminant to the process stream being handled.
7. It should be inexpensive to keep the cost of maintaining agent inventory and of replacing lost agent low.
8. It should have a low enough viscosity to be pumped and flow by gravity easily.
9. It should have a density different enough from that of the feed

stream for the phases to counterflow and separate readily.

10. It should not form so stable an emulsion that the phases cannot be separated adequately.

11. It should be completely soluble with the components in the distilling system at the temperature and concentrations in the column.

The selection of the agent can be based upon its ability to modify the relative volatility of the system. However, its final selection must be determined through economic evaluation wherein all variables and criteria are considered in conjunction with selectivity to determine the minimum operating and investment cost for the process. Colburn and Schoenborn [9] and others have analyzed the selection of agents on the cost basis.

In some cases an agent mixture may be used to derive properties that cannot be achieved with pure agents. Gerster [10] discussed agent selection in more detail. Obviously no agent will be best from all of these viewpoints, and the selection of a desirable agent involves compromises between these various factors, e.g., between capacity and selectivity.

It is necessary to emphasize that the whole process must be considered in the selection of an effective agent, and the recovery process must be included in the evaluation. An agent must have the best selectivity of all of those of an entire group considered, but it might be more difficult to be separated from the components with which it associates than an agent having low selectivity, and economic considerations might prove the use of the latter to be more feasible.

































































































































































































































































































































































































