Separation of formic acid/3-methyl-2-butanone, formic acid/acetic acid/4-methyl-2-pentanone, formic acid/4-methyl-2-pentanone and m-xylene/o-xylene by extractive distillation
by George Bentu

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University

Abstract:

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APPROVAL

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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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ABSTRACT

Extractive distillation processes were developed to break the formic acid-3-methyl-2-butanone azeotrope, and the close boiling mixtures of formic acid-4-methyl-2-pentanone, acetic acid-4-methyl-2-pentanone, and m-xylene-o-xylene. Initial screening of potential extractive agents was carried out for each system in an Othmer vapor-liquid equilibrium still. More than one hundred and twenty agents were investigated overall. Subsequent testing of effective agents was carried out in two perforated-plate columns, which after calibration were found to have the equivalent of 3.5 and 7.3 theoretical plates.

BACKGROUND

Distillation is a method of separating the components of a solution which depends upon the distribution of the substances between a gas and a liquid phase, applied to cases where all components are present in both phases. Instead of introducing a new substance into the mixture in order to provide the second phase, as is done in gas absorption or desorption, the new phase is created from the original solution by vaporization or condensation. By repeated vaporizations and condensations or by appropriate manipulation of the phases it is possible to make as complete a separation as may be desired, recovering both components of the mixture in as pure a state as it is desired.

The advantage of such a separation method is that in distillation the new phase provided differs from its original by its heat content. On the other hand, desorption or absorption operations depend on the introduction of a foreign substance, therefore these operations provide a new solution which in turn may have to be separated by one of the diffusional operations unless the new solution is useful directly.

On the other hand, there are certain limitations to distillation as a separation process. In distillation, the availability to choose from a great variety of solvents, in order to provide the greatest possible separation effect, is not possible. The gas created from a liquid by application of heat consists only of the components constituting the liquid. Since the gas is chemically similar to the liquid, the change in composition resulting from the distribution of the components between the two phases is usually not very great.

Nevertheless, the direct separation, ordinarily possible by distillation, into pure products requiring no further processing has made this one the most important of the mass-transfer operations [1].

Due to the ease with which industrial size processes can be conducted and because of its commercial value to the chemical industry, distillation methods are the most widely used techniques for effecting liquid separations [2,3].

In practice, there are two principal methods by which distillation may be carried out. One of the methods is based on the return of part of the condensate to the still under the conditions that the returning liquid is brought into close contact with the vapors on their way to the condenser. The other method is based on the production of a vapor by boiling the liquid mixture to be separated and condensing the vapors without allowing any liquid to return to the still. Either of these methods may be conducted as a batch process or as a continuous process [4].

Distillation utilizes vapor and liquid phases at essentially the same temperature and pressure. Various kinds of devices such as dumped or ordered packings and plates or trays are used to bring the two phases into intimate contact. Trays are stacked one above the other and enclosed in a cylindrical shell to form a column. A typical plate-type distillation column and major external accessories is shown in Figure 1 on page 4 [5].

The "plate" where the feed material, which is to be separated, is introduced into the column is referred to as the feed plate. Because of the difference in gravity between vapor and liquid phases, liquid runs down the column while vapor flows up the column, contacting liquid at each tray.

Liquid reaching the bottom of the column is partially vaporized in a heated reboiler to provide boil-up, which is sent back up the column. The remainder of the bottom liquid is withdrawn as bottoms, or bottom product. Vapor reaching the top of the column is condensed to liquid in the overhead condenser. Part of the liquid is returned to the column as reflux to provide liquid overflow. The remainder of the overhead stream is withdrawn as distillate, or overhead product.

The flow pattern in a distillation column provides counter-current contacting of vapor and liquid streams on all the plates in the column. Vapor and liquid phases on a given tray approach thermal, pressure, and composition equilibriums to an extent dependent upon the efficiency of the contacting plate [5].

The lower boiling components tend to concentrate in the vapor phase, while the higher-boiling components tend toward the liquid phase. The result is a vapor phase that becomes richer in lower-boiling components as it goes up the column and a liquid phase that becomes richer in higher-boiling components as it goes downward. The overall separation achieved between the distillate and the bottoms depends primarily on the relative volatilities of the components, the number of contacting plates, and the ration of the liquid-phase flow rate to the vapor-phase flow rate.

When the liquid mixture to be separated forms no azeotrope(s) and the difference in the volatilities of its components is significant (greater than 1.00), fractional distillation is a very attractive technique. In order for the method mentioned previously to be very effective, no reaction can occur between components nor can decomposition or polymerization of one or more of the components occur and the components must be capable of vaporizing at feasible temperature and pressure.

The technology of distillation has developed two modified forms for the cases in which techniques other than simple fractional distillation must be used due to its ineffectiveness. They are extractive and azeotropic distillation techniques.

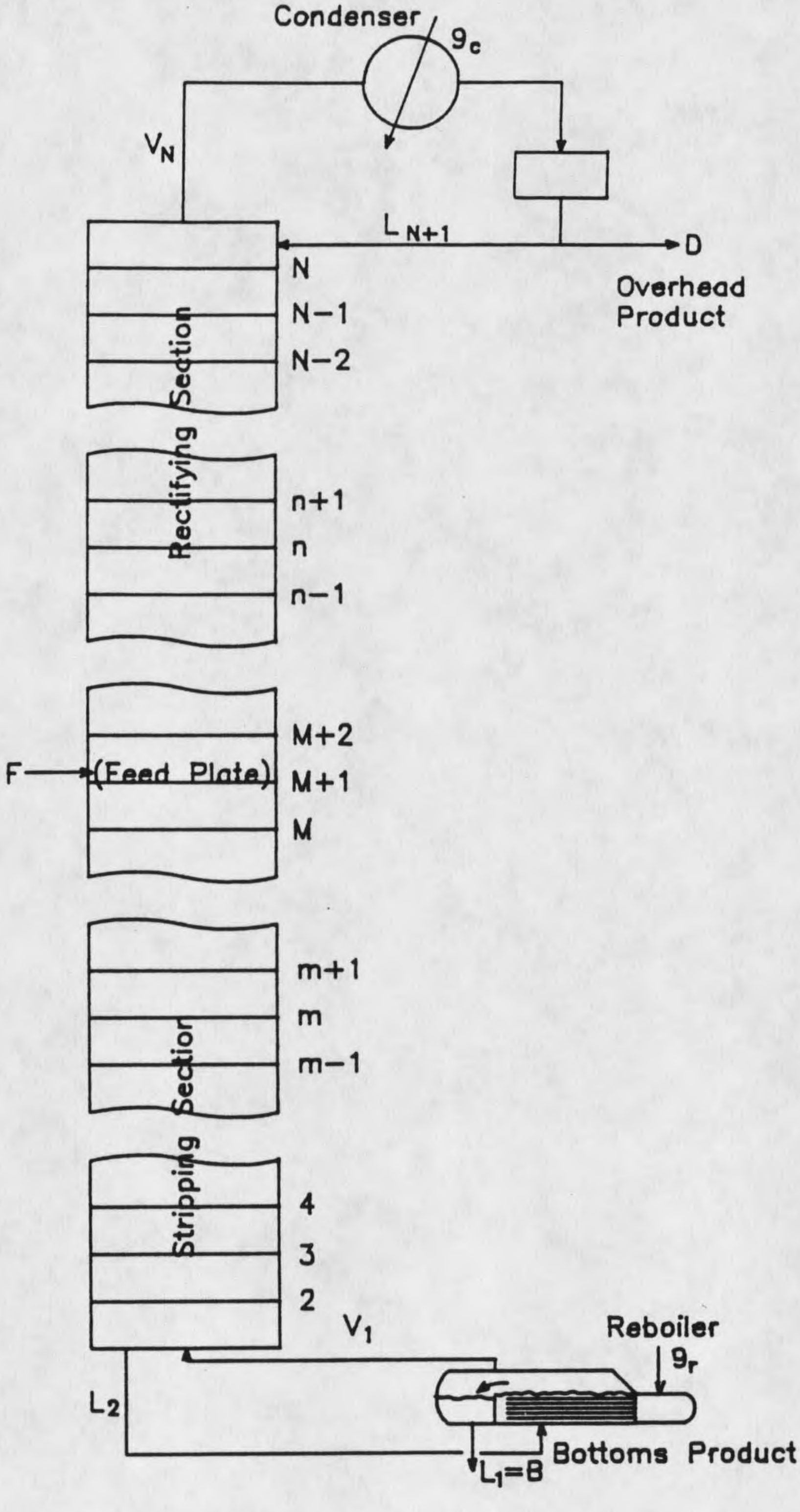


Figure 1. Fractional distillation column.

Extractive Distillation

Extractive distillation is the process in which a high-boiling solvent is added to a plate in a column to alter the relative volatilities of the components to be separated. The alteration of volatilities is desired because of the presence of an azeotrope or similarities in the vapor pressures of the feed components. The solvent usually boils at a temperature far above the feed components, which makes formation of new azeotropes impossible. Also, any azeotropes present in the untreated feed disappear in the presence of solvent. The absence of azeotropes plus the fact that the solvent can be recovered by simple distillation makes extractive distillation a more widely useful process than azeotropic distillation. A typical configuration for an extractive distillation process is shown in Figure 2 on page 6. Distillation proceeds as described previously in the first column with the exception of the addition of the extractive agent near its top. The addition of the extractive agent takes place a couple of plates below the top in order to avoid carryover into the overhead product. The second column is used to recover the extractive agent from the bottoms product.

Some of the drawbacks on extractive distillation include larger plates for the columns and the recovery of the agent requires an additional column. To process the same amount of material, larger plates for the columns are required due to an additional volume of liquid, caused by the addition of the agent to the system. The extractive agent may also lower plate efficiency by increasing viscosity.

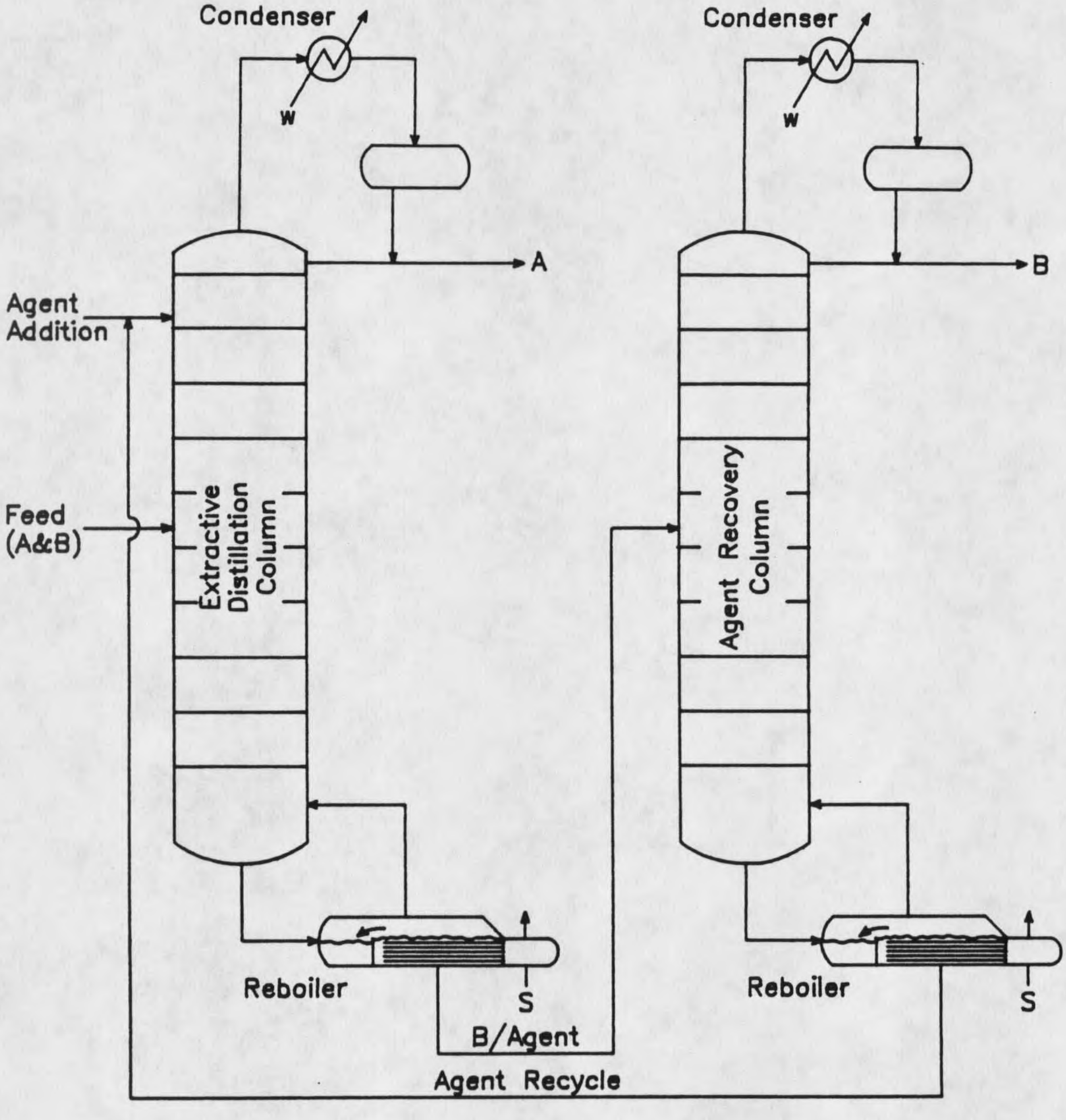


Figure 2. Extractive distillation column

Azeotropic Distillation

In order to form an azeotrope, the boiling points of the pure components of the mixture to be separated must be sufficiently close. A mixture of close boiling components may form an azeotrope when only small deviations from ideal liquid solutions occur. On the other hand, a mixture of wide boiling components may not exhibit an azeotrope even though they form a very nonideal liquid.

Azeotropes can make a given separation impossible by simple distillation in a particular pressure range. However, azeotropes may be utilized to separate mixtures not ordinarily separable by simple distillation or to increase recovery yield of some components from certain mixtures.

In azeotropic distillation the solvent is added at the main feed plate to form an azeotrope with one of the feed components. The azeotrope formed is usually removed as the distillate.

Selection of Extractive Agent

The number of possible solvents available for separation by extractive distillation is usually much larger than for an azeotropic separation because of less severe volatility restrictions, which only include that the solvent boil sufficiently higher than feed components to prevent formation of an azeotrope and the solvent boiling point not be so high that sensible-heat requirements of the solvent cycle become unreasonably large.

A general approach to selection of a solvent is to chose a compound that is similar to the higher boiling component and then go up the homologous series of that compound until a homolog is found that boils high enough to make a solvent-nonsolvent azeotrope impossible.

An actual search for a suitable solvent usually means that many compounds of differing structures must be screened.

The selection of an extractive agent is determined by important factors such as effectiveness, chemical compatibility, company preference, and economics. A modified list of criteria reported by Paffhausen [6] which have been previously suggested by Berg [7] and Yeh [8] is given in Table 1 below.

Table 1. Favorable Characteristics of an Extractive Agent

---

1. It should have a high boiling point, considerably higher than the components to be separated. This is to insure that it is not carried into the overhead product and is easily separable from the bottoms product.
2. It should have a high capacity for the component it is to associate with in the separation. The higher this capacity the less solvent may be used. This results inwer recycle rates for the solvent, smaller column plate, and less energy consumption.
3. It should be highly selective. That is, it should have a maximum effect on one of the components to be separated and a minimum effect on the other.
4. It should not associate so strongly with either of the components so as to render them inseparable.
5. It should mix well with the feed stream and have a viscosity low enough for pumping and gravity flow within the column.
6. It is desirable that the agent be attracted to the higher boiling component so that the separation may occur in the natural direction.
7. It should be chemically stable at the operating temperatures and pressures of the system so that it will withstand extended recycling through the system without decomposition.
8. It should not be an agent so harsh as to cause decomposition of the components to be separated at the temperatures and pressures of the system.

Table 1 Continued

9. It should be non-toxic, non-corrosive, and not be a serious contaminant to the system being handled.
10. It should not be so expensive as to render the process uneconomical.

As one can easily tell by examining this list it is not an easy decision to make when selecting the right extractive agent. The agent with the most favorable characteristics does not always have to be the choice of a company. In some instances a company will choose an agent that can be obtained at a lower buying cost. Therefore, in the end the process will be more economical [9].

THEORETICAL ASPECTS

Thermodynamics of Vapor-Liquid Equilibrium

The most common liquid mixture separation technique used by chemical process industries is distillation, a diffusional operation [10]. Design of these distillation processes requires accurate quantitative data regarding the equilibrium properties of the mixture to be separated. Although many methods for estimation of these properties are available, there is no substitute for reliable experimental data. In the case of extractive distillation, literature concerning estimation of the properties is practically non-existent and of little use since it is unable to predict many of the chemical complications, like the chemical properties of a system that encourage areotrope formation. For this reason, experimental data is a must for designs utilizing extractive distillation.

The distillation process is dependent upon a lack of equilibrium between the liquid and vapor phases coming into contact. If the two phases were in equilibrium, there would be no net diffusion between the phases and no separation would be possible. After intimate contacting of a liquid and gas not initially in equilibrium, under ideal conditions we could bring the two phases to a state of thermodynamic equilibrium. For every component in a mixture, the condition for thermodynamic equilibrium is given by equation (1) [10]:

$$f^{l}_{i} = f^{v}_{i} \text{ (for all components } i = 1,2,3,\ldots,n) \quad (1)$$

where f_i = fugacity of component i at the temperature, pressure, and composition of the system

v = vapor phase

1 = liquid phase

It is important to note that fugacity is a function of temperature, pressure and composition. Although any measure for composition may be used (provided the basis is consistent), the vapor mole fraction y_i is generally used for the vapor phase and the liquid mole fraction x_i is used for the liquid phase. Because fugacity is a function of temperature, pressure, and composition, it is convenient to define some terms relating these conditions. The functions used are the fugacity coefficient for the vapor phase, and the activity coefficient for the liquid phase [10,11]. For the vapor phase:

$$\Phi_i - \frac{f_i^v}{y_i P} \tag{2}$$

where ϕ_i = vapor phase fugacity coefficient of in in the mixture

P = total pressure of the system

f_i = fugacity of in in the mixture

For the liquid phase:

$$\gamma_i - \frac{a_i}{x_i} - \frac{f_i^1}{x_i f_i^0} \tag{3}$$

where γ_i = liquid phase activity coefficient

a_i = activity of component i

f^0_i = standard state fugacity of component i at the system temperature and at some arbitrary pressure and composition chosen for convenience.

Although the above development can be valid if used currently, more simplified view of nonideal mixture is preferred for our case. What is being done when relatively volatility values are obtained for both the Othmer still and the perforated plate column is simply a comparison of the presence of the two components of interest on an extractive agent-free basis. It is only accurate as an "empirical" comparison of the data obtained from the two techniques.

In order to obtain a more rigorous thermodynamic evaluation of the systems in question, one must look more closely at the total mixture that is present. Upon addition of an extractive agent to a binary system, a ternary or higher system is formed. In order to obtain valid activity coefficients, vapor-liquid equilibrium data on every possible binary combination should be obtained at many different compositions and temperatures. In order to fit the data to an equation for the activity coefficient, reduction of this data is done, i.e., by using Barker's method along with an optimization technique such as the Complex Method of Box [12,13]. The above mentioned reduction method may be used to obtain the binary parameters for the Wilson equation. Once these parameters are known, they are used in the actual equation [14]:

$$\ln \gamma_i = 1 - \ln \sum_j x_j \Lambda_{ij} - \Sigma \frac{X_k \Lambda_{ki}}{\Sigma_j x_j \Lambda_{kj}} \quad (4)$$

where Λ = symbol for a Wilson parameter

Note that $\Lambda_{ij} = 1$ for $i = j$. All indices in the equation refer to the same species and all summations are over all species. For each i-j pair there are two parameters since $\Lambda_{ij} \neq \Lambda_{ji}$. For example, in a ternary system the three possible i-j pairs are associated with the parameters Λ_{12}, Λ_{21}; Λ_{13}, Λ_{31}; and Λ_{23}, Λ_{32}. From this an actual activity coefficient, γ_i, for ternary systems or higher is obtained. The "empirical" results obtained on the extractive agent free basis were considered sufficient for the goals of this thesis.

Relative Volatility

One numerical measure of the difference in liquid and vapor compositions is called the separation factor or, particularly in the case of distillation, the relative volatility, α. The relative volatility is probably the single most useful measure of separation for a distillation process. Relative volatility quantitatively shows the ease of separation of a component i from a second component j using the ratio of their volatilities.

This ratio is defined as [4]:

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} \qquad (5)$$

where α_{ij} = relative volatility of component i in j

y_i, y_j = vapor mole fractions at equilibrium

x_i, x_j = liquid mole fractions at equilibrium

The value of α will ordinarily change as x varies from 0 to 1.0. If $y = x$, $\alpha = 1.0$ and no separation is possible. This is the situation encountered with an oceotrope. The larger the value of α above unity, the greater the degree of separability.

By convention, the value of α_{ij} is taken such that the volatility of component j is always less than that of i, i.e., α_{ij} is greater than or equal to unity. Although the relative volatility, given by α, for a nonideal mixture may vary greatly according to liquid composition, for an ideal mixture this value is nearly constant when temperature is constant. For purposes of later discission, equation (5) above may be put into a more suitable form. Assume that the vapor phase behaves ideally and neglect the Poynting corrections for the pure liquid fugacity. Next, by taking into account the vapor pressures and the liquid and vapor mole fractions in terms of components i and j we obtain:

$$\gamma_i = \frac{y_i P}{x_i P_{vpi}} \qquad (6)$$

and

$$\gamma_j = \frac{y_j P}{x_j P_{vpj}} \qquad (7)$$

where P = total pressure of the system

P_{vpi} = vapor pressure of component i

P_{vpj} = vapor pressure of component j

y_i, y_j = vapor mole fractions at equilibrium

x_i, x_j = liquid mole fractions at equilibrium

Substitution of these values in equation (5) yields the following expression for relative volatility which is also valid:

$$\alpha_{ij} = \frac{\gamma_i P_{vpi}}{\gamma_j P_{vpj}} \tag{8}$$

The Fenske Total-Reflux Equation

Total reflux represents one limiting case in the operation of fractionating columns. Under conditions of total reflux, the minimum number of theoretical plates required to effect a separation is given by the Fenske total-reflux equation [5]:

$$N_m = \frac{\ln\,[(x_d/x_b)_i/(x_d/x_b)_j]}{\ln \alpha_{ij}} \tag{9}$$

where $(x_d/x_b)_i$ = mole fraction ratio of component i in the distillate to that in the bottoms

$(x_d/x_b)_j$ = mole fraction ratio of component j in the distillate to that in the bottoms

N_m = minimum number of plates required

The relative volatility in equation (9) must either be constant or represented by the geometric mean to be strictly valid. The geometric mean for relative volatility is given by [5]:

$$\alpha_{ij} = (\alpha_{ij,top}\ \alpha_{ij,middle}\ \alpha_{ij,bottom})^{1/3} \tag{10}$$

where top, middle, and bottom = column position

Since the work of this thesis involves calculations of relative volatilities using a distillation column, it is convenient to rearrange equation (9) to the form:

$$\alpha_{ij} = [(x_d/x_b)_i/(x_d/x_b)_j]^{1/Nm} \qquad (11)$$

In order to use this equation, the number of theoretical plates must be estimated by calibration of the column (see Calibration of the Perforated-Plate Column).

Figure 3 on page 16 depicts the number of theoretical plates needed to separate a binary mixture into 99% products as a function of relative volatility. As the relative volatility approaches unity the number of theoretical plates approaches infinity. The number of plates required decreases rapidly when the relative volatility value is around 1.3 and above. Assuming that plate efficiency is 75% and that column cost is linearly proportional to the number of theoretical plates, a comparison of column cost versus relative volatility and plate number is given in Table 2 on page 17.

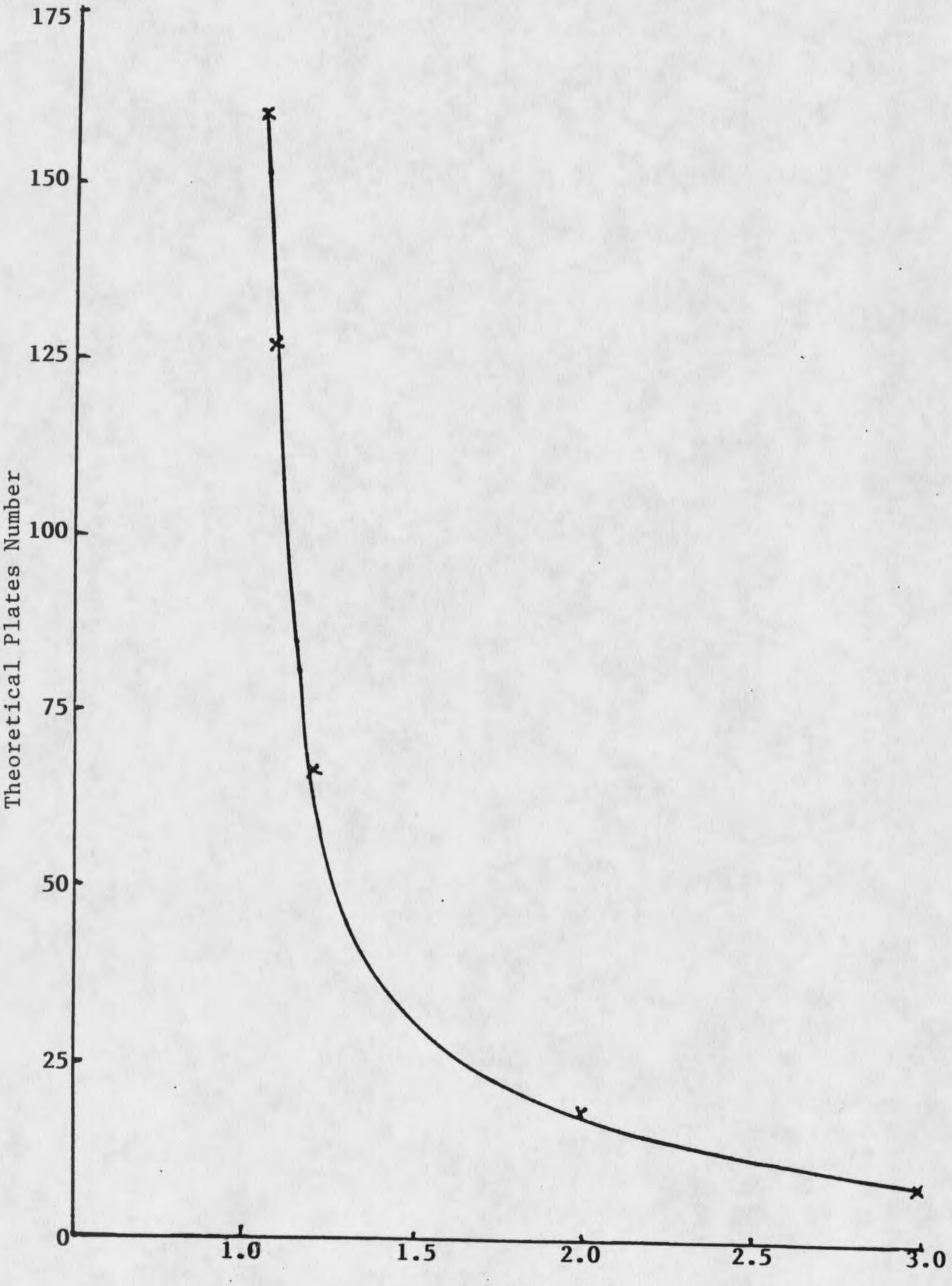


Figure 3. Number of theoretical plates as a function of relative volatility. In a separation of a binary mixture, the overhead and bottoms products are specified 99%.

Table 2. Relative Volatility vs. Theoretical Plates vs. Column Cost.
Plates required to achieve 99% pure overhead and bottom products.

Relative volatility	Theoretical plates required	Column cost*
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	210.3	100.0
1.06	188.4	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
1.20	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

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

The theoretical plates required to achieve 99% pure distillate and bottoms products have been calculated using the Fenske equation with geometric mean relative volatilities. When interpreting Table 2 it is important to note that the numbers are for total reflux and in terms of theoretical plates. Since neither of these apply to a real industrial process, the number of actual plates would be considerably higher. Mixtures with a relative volatility less than 1.1 are considered extremely difficult to separate and the process is usually uneconomical.

Altering Relative Volatility

From the Fenske equation it is apparent that the key to separating an azeotropic mixture, or one having a very low relative volatility, is to increase its separation factor, or its relative volatility. There are three possibilities by which this might be accomplished. First, one could alter the correction factors for the components, given by $_i$ and ϕ_i, used to obtain equations (6) and (7). However, these values are very close to unity at moderate pressure and do not appreciably effect the relative volatility. Second, one might choose to alter the ratio of the pure component vapor pressures. Reducing the operating temperature of the column, the column pressure is reduced, this ratio will increase which will enhance the separation. This change is usually not appreciable enough to significantly affect the separation [15]. The third alternative is to change the ratio of the liquid phase activity coefficients. This can be achieved by addition of an extractive agent and may significantly affect the relative volatility. The latter case provides a case for extractive distillation.

Selectivity

The ability of an agent to preferentially enhance the volatility of one component in a mixture over that of another is called selectivity. This is an important characteristic of an extractive agent based on its relative volatility. An expression used to define selectivity is given by Anderson and Prausnitz [15]:

$$S_{ij} = [\alpha_{ij}]_P/[\alpha_{ij}]_A \tag{12}$$

where S_{ij} = selectivity of agent on component i relative to component j

$[\alpha_{ij}]_P$ = relative volatility in the presence of agent

$[\alpha_{ij}]_A$ = relative volatility in the absence of agent

In order to maximize selectivity it is desirable for the agent to increase the volatility of one component while decreasing the volatility of the other.

Factors Affecting Selectivity

The selectivity an extractive agent exhibits towards other components is the result of molecular interaction. Two broad classifications of these interactive forces are generally recognized to be physical and chemical forces [16,17]. Physical forces, sometimes called van der Waals forces, are broken into three groups:

(1) Dispersion forces. It is due to attractive forces between nonpolar molecules. It is a result of momentarily induced dipoles which occur when the electron clouds of two molecules temporarily overlap.

(2) Induction forces. This is the result of a molecule with a permanent dipole inducing a dipole in another molecule. This primarily occurs between polar and nonpolar molecules.

(3) Orientation forces. This causes molecules which have permanent dipoles to interact and orient themselves with respect to one another.

Chemical complexing suitable for extractive distillation occurs as a result of hydrogen bonding and acid-base interactions. The hydrogen bonding is the most important of the two. Liquids have been classified according to the strength and number of hydrogen bonds that their molecules may form [18]. As a result liquid materials have been placed into one of five classes, which are given here in order of decreasing ability to form strong hydrogen bonds as reported by Berg [19]:

(I) Liquids capable of forming three dimensional networks of strong hydrogen bonds. Examples of strong hydrogen bonds are: O-HO, N-HO, O-HN.

(II) Liquids composed of molecules containing both active hydrogen atoms and donor atoms (oxygen, nitrogen, and fluorine).

(III) Liquids composed of molecules containing donor atoms but no active hydrogen atoms.

(IV) Liquids composed of molecules containing active hydrogen atoms but no donor atoms.

(V) All other liquids which have no hydrogen-bond forming capabilities.

By identifying the hydrogen bonding characteristics and polarity of a successful extractive agent, one may be able to identify groups of compounds that may also be used successfully as extractive agents for similar chemical systems.

Two other important effects on agent selectivity are temperature and fraction of extractive agent present. Due to the fact that higher temperatures tend to disrupt the process of chemical complexing, lower temperatures are preferred. This would imply the use of vacuum distillation, the implementation of which would depend upon economics. Also, selectivity can be improved by increasing the volume fraction of solvent in the mixture to be separated. If carried to an extreme, this effect produces diminishing returns and may lead to immiscibility within the system. An immiscible system is undesirable in that it will cause unstable operation of the distillation column.

Use of Solubility Parameters and Polarity Diagrams

Intermolecular forces of repulsion are a phenomenon related to the inability of two molecules to occupy the same space. As two molecules are separated by distance the force of repulsion becomes very small. Therefore, it is generally considered insignificant as related to extractive distillation. It is the attractive forces resulting from a molecule's polarity and hydrogen bonding that are important.

When considering extractive distillation using a binary feed mixture, there are three possible attractive molecular interactions to be considered: molecular interactions between components of the feed mixture, molecular interactions between the extractive agent and one of the feed components, and molecular interactions between the extractive agent and the second of the feed components. Since interactions between feed components can only be altered by the introduction of extractive agents, only interactions between extractive agents and feed components will be considered.

Yeh [8] reported considerable success in predicting the degree of attraction between extractive agents and mixture components using solubility parameters. In his studies, the dispersion force, δ_d, hydrogen bonding, δ_h, and polarity, δ_p, solubility parameters were used in conjunction with specific volumes of liquids to explore the degree of attractive molecular interactions. However, it was found that differences in the dispersion force parameters were negligible and unsuitable for further investigation.

RESEARCH OBJECTIVES

The objective of this research is to find extractive agents which will effectively separate the following close boiling systems: 3-methyl-2-pentanone/formic acid, 4-methyl-2-pentanone/formic acid, m-xylene/o-xylene. The extractive agents may be either pure compounds or mixtures of compounds. They should be chemically and thermally stable, easily recoverable, and should not react with or cause decomposition of the mixtures to be separated.

SYSTEMS TO BE SEPARATED

Formic Acid/3-Methyl-2-Butanone

3-Methyl-2-butanone has a molecular weight of 86.31, a specific gravity of 0.802, and a boiling point (B.P.) of 94.5^{0}C. Formic acid has a molecular weight of 46.03, specific gravity of 1.22, and a boiling point of 100.8^{0}C. Industrial uses for formic acid are in textile dyeing and finishing (21%), pharmaceuticals (20%), rubber intermediates (16%), leather and tanning treatment (15%), and catalysts (12%) [9].

When together, 3-methyl-2-butanone and formic acid form a maximum azeotrope boiling at 102^{0}C. The azeotrope consists of 85 weight percent formic acid and 15 weight percent 3-methyl-2-butanone. Separation is achieved by distillation with any one of a number of extractive agents being used.

Formic Acid/Acetic Acid/4-Methyl-2-Pentanone

4-Methyl-2-pentanone has a molecular weight of 100.16 and a boiling point of 117^{0}C. Over 80% of the total compound produced annually is used as a general solvent in coating processes, and processes for making adhesives, pesticides and rubber processing chemicals. Formic acid was previously discussed. Acetic acid has a molecular weight of 60.05 and a boiling point of 117.9^{0}C. It is used industrially in production of vinyl acetate (52%), acetic anhydride(16%), acetic esters and glycol ether acetates (10%), dimethyl terephthalate/purified terephthalic acid (9%), miscellaneous (7%), textile processing (2%), and the remaining 4% is exported.

The compounds boil so close together that they are difficult to separate by conventional rectification. Extractive distillation would be an attractive method of effecting the separation of 4-methyl-2-pentanone from formic acid and acetic acid if suitable extractive agents can be found.

Formic Acid/4-Methyl-2-Pentanone

The components of the system were previously discussed. The components boil so close together that they are difficult to separate by conventional rectification. Extractive distillation would be an attractive method of effecting the separation of 4-methyl-2-pentanone from formic acid if suitable extractive agents can be found.

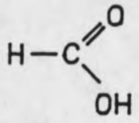
m-Xylene/o-Xylene

m-Xylene, boiling point of 139.1^0C, and o-xylene, boiling point of 144.4^0C, are difficult to separate by rectification due to their close boiling points. Extractive distillation would be an attractive method of effecting the separation of m-xylene from o-xylene if suitable extractive agents can be found. The mixture is to be separated using certain esters as the agent in the extractive distillation.

For convenience, the chemical structures of components for the azeotropic systems studied and important extractive agents are shown in Figures 4 and 5 on pages 25 and 26.

B.P. = 100.8 °C

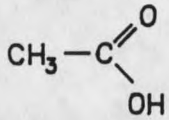
MW = 46.03



<u>Formic Acid</u>

B.P. = 117.9 °C

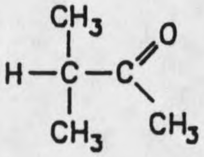
MW = 60.05



<u>Acetic Acid</u>

B.P. = 94.5 °C

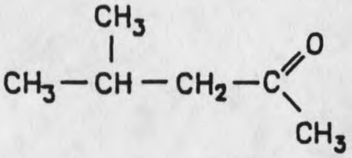
MW = 86.31



<u>3-Methyl-2-Butanone</u>

B.P. = 117 °C

MW = 100.16

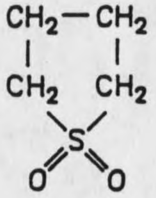


<u>4-Methyl-2-Pentanone</u>

Figure 4. Structures and physical data for key components [9,22,23].

B.P. = 285 °C

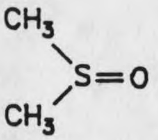
MW = 120.17



Sulfolane

B.P. = 189 °C

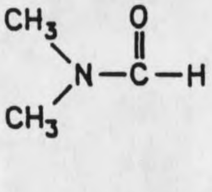
MW = 78.13



Dimethylsulfoxide (DMSO)

B.P. = 153 °C

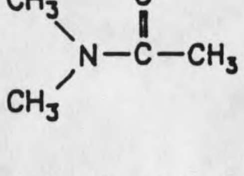
MW = 73.10



Dimethylformamide (DMFA)

B.P. = 166 °C

MW = 87.12



Dimethylacetamide (DMAA)

Figure 5. Structures and physical data for key agents [9,22,23].

EXPERIMENTAL AND ANALYTICAL EQUIPMENT

Othmer Vapor-Liquid Equilibrium Still

In order to find successful extractive agents capable of breaking azeotropic systems by extractive distillation, initial screening was done in an Othmer vapor-liquid equilibrium still. The data obtained from the Othmer still only suggests potential extractive agents for the system in question. At this point, further investigation of these potential agents is necessary in order to decide which extractive agent would be best for the system to be separated. Figure 6 on page 28 illustrates the Othmer still used for prescreening of potential agents.

The azeotropic mixture to be separated is introduced to the still along with a known volume fraction of agent to be tested. The volume introduced to the still must be sufficient to maintain a liquid level between points A and B during operation. A heating coil supplies heat for vaporization of the liquid to the bottom of the still. In order to prevent condensation of the vapor leaving the still before it reaches the primary condenser the first still has heating coils over the entire length and the outside of the second still is covered with insulation. The condensing vapor continuously flushes the vapor sampling tube and returns to the stillpot by means of an overflow tube. A vent placed on the overflow tube maintains atmospheric pressure in the still. The vent is equipped with an additional condenser so that no material is lost from the system to the atmosphere.

Equilibrium is achieved after allowing the still to reflux its contents for several hours. Vapor and liquid samples may then be taken from their respective sampling parts for analysis on the gas chromatograph. The Othmer still in effect represents one equilibrium stage or one theoretical plate. The relative volatility of the components for one equilibrium stage may be

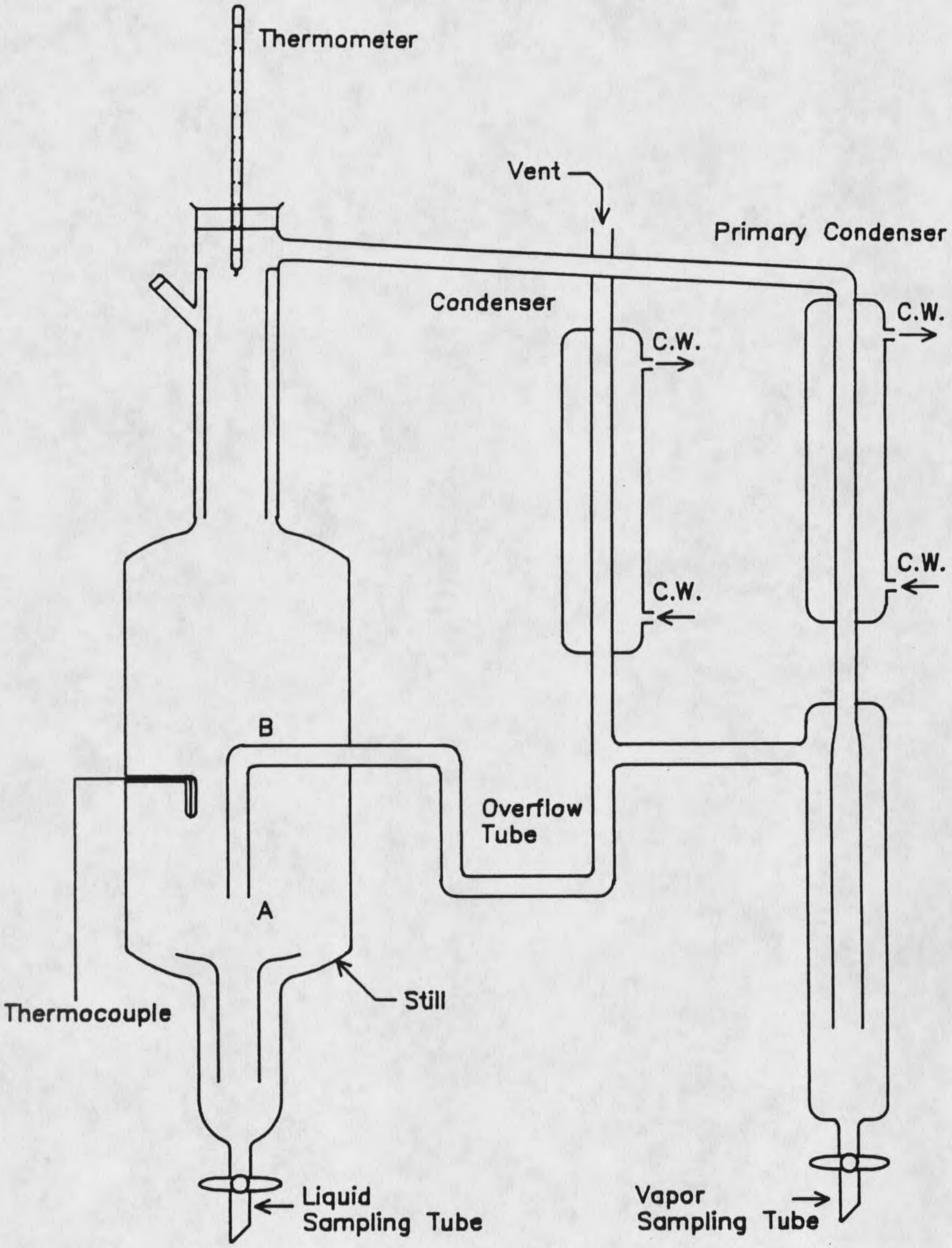


Figure 6. Othmer vapor-liquid equilibrium still.

determined from the analysis of the vapor and liquid samples on the gas chromatograph. As a further aid in the analysis of the data, a thermometer and thermocouple are available for measurement of vapor and liquid temperatures, respectively.

Perforated-Plate Column

The agents, screened in the Othmer still, for which high relative volatilities were obtained, were tested in the perforated-plate column. For reasons of simplicity as well as for conservation of chemical materials the distillation column was operated in a semi-batch fashion. As shown by Szabados [20], the batch operation does not significantly affect experimental results. Figure 7 on page 30 illustrates the column setup.

The column is mainly a stripping column with a rectification section above the extractive agent feed point. The main components of the column and a brief description, as reported by Rall [21], are listed below:

(1) A Corad condensing head. Cooling water is channeled through this glass jacketed head to provide a heat sink for condensing the vapor reaching the top of the column.
Vertical glass ridges separate various areas on the inside of the head allowing calculation of boil-up rates and reflux ratios. Liquid falling from any of the areas inside the head may be channeled by means of a glass point to the overhead collection tube. By changing the area of the Corad head directed at the sample collection tube, the reflux ratio may be changed. Available reflux ratios are: 30:1, 20:1, 10:1, 3:1, and 2:1. The head is also fitted with a thermometer port for overhead temperature measurement.

(2) Perforated-plate column. Two Oldershaw perforated-plate columns comprised the contacting portion of the column. The two columns are both 20 inches long, each containing

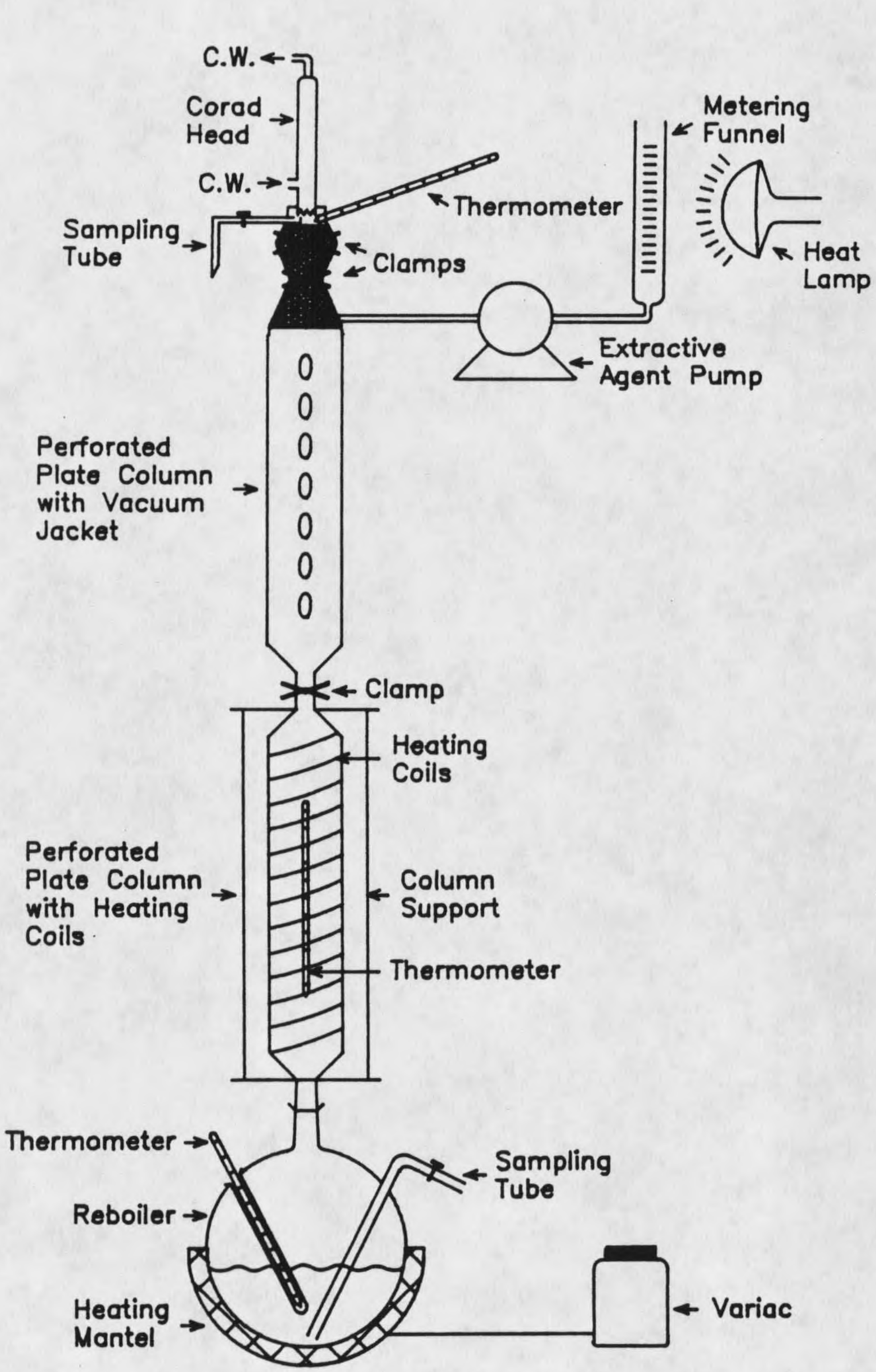


Figure 7. Batch-wise extractive distillation column.

8 actual plates with a 1.5 inch separation between plates. Liquid height on each of the plates is about 3/8 inch. The only difference between the two columns is that the upper column is silvered and vacuum jacketed and the lower column has heating coils. The purpose of the vacuum jacket and the heating coils is to minimize heat loss.

(3) Reboiler. The reboiler consists of a 5 liter round bottom flask equipped with a sampling tube and thermal well. Heat is electrically supplied by a full Glas-Col mantle which also acts as insulation for the flask. Heat through the mantle is controlled using a variac, an adjustable power transformer. Adjusting the power controls boil-up rates.

(4) Extractive agent pump. Preheated extractive agent to an adjustable micro-bellows metering pump by means of a calibrated 200 ml. glass funnel. The extractive agent enters the column between the connecting section and perforated-plate column sections. The connecting section is three inches of empty column to prevent any extractive agent from being carried off with the overhead product. To assure that the extractive agent does not cool before entering the column, a heating lamp maintains the temperature of extractive agent in the glass funnel and the pumping lines to the column are insulated.

In addition to the components mentioned, three thermometers are required to measure overhead, bottoms, and extractive agent temperature.

Extractive Agent Recovery

When necessary, extractive agents may be recovered by a simple distillation process. Recovery of extractive agents serves two purposes. One is to conserve the supply of available extractive agent. Another is to verify the stability of the extractive agent since it must be recovered and recycled in an industrial process.

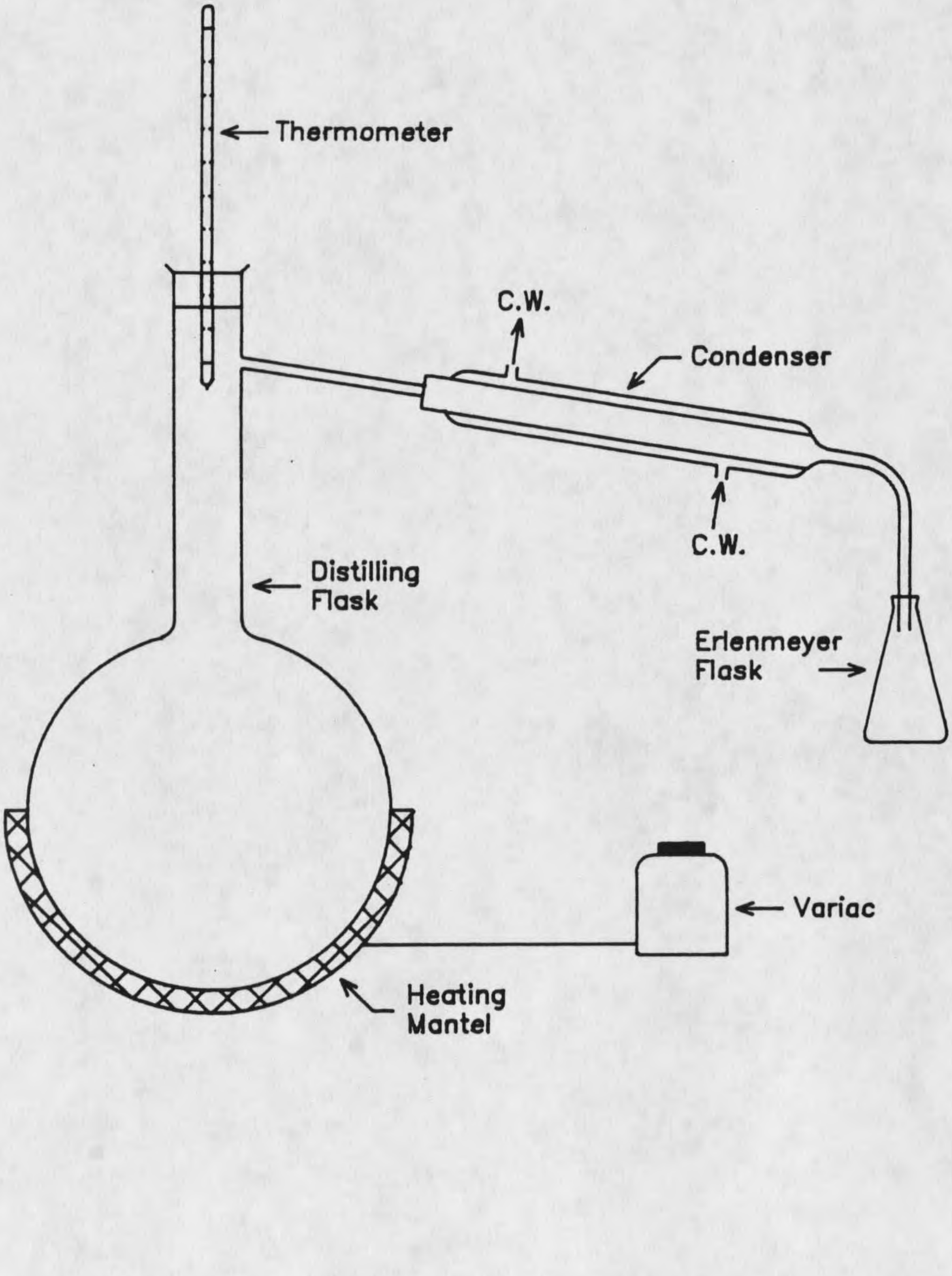


Figure 8. Agent recovery by simple distillation.

Figure 8 on page 32 is a typical scheme for agent recovery in laboratory. After an extractive distillation column run was completed, the resulting bottoms mixture was emptied into a 2 liter distilling flask. Using a heating mantle and variac, the bottoms mixture is driven from the flask as vapor, which is then condensed and collected in an Erlenmeyer flask. When the distillation is complete, the temperature of the vapor will rise sharply indicating that only extractive agent remains in the flask.

Gas Chromatograph

A gas chromatograph was used to analyze the bottoms and overhead products from experimental runs in both the Othmer vapor-liquid equilibrium still and perforated-plate column. The gas chromatograph used was a Varian Aerograph model 1400. Data was output to a Spectra-Physics Chromjet integrator in form of peak heights and are percentages. Area percents for components in the overhead and bottoms products were used to calculate relative volatility in the Othmer stills, and were used in conjunction with the Fenske equation to calculate average relative volatility in the perforated-plate columns.

EXPERIMENTAL PROCEDURE

Operation of the Othmer Still

Fifty grams of the close boiling mixture to be studied is charged to the Othmer still along with fifty grams of pure extractive agent or extractive agent mixture. The charge is refluxed for six hours to assure that a state of equilibrium has been reached. Samples taken from the condensed overhead vapor and from the bottoms product are analyzed on the gas chromatograph. In order to prepare the still for another charge, the still is flushed with acetone and blown dry with compressed air.

Analysis of the samples on the gas chromatograph gives accurate data on the effectiveness of the extractive agent on the mixture to be separated, and also discloses the amount, if any, of decomposition in the system. The amount of decomposition in the system may be determined by the reading of peaks, other than the ones expected, obtained from the gas chromatograph output.

Calibration of the Perforated-Plate Column

Since the experimental apparatus was modified by addition of another perforated-plate column section, none of the previous calibrations could be used. Therefore, for the experiments of this thesis, a new calibration of the perforated-plate column was necessary.

A mixture of 40 grams m-xylene (B.P. 139.1^0C) and 40 grams of o-xylene (B.P. 144.4^0C) was charged to the Othmer still and refluxed for 5 hours. Analysis of the overhead and bottoms products revealed 52.9% m-xylene and 47.1% o-xylene in the vapor, 49.9% m-xylene and 50.1% o-xylene in the liquid. This gives a relative volatility of 1.127.

A charge of 100 grams of m-xylene and 100 grams o-xylene was charged to the perforated plate column, with only one of the column sections available (vacuum jacketed column). The column was operated at total reflux for 3 hours with a boil-up rate of 60 ml. per minute. Product samples were taken and analysis revealed 55% m-xylene and 45% o-xylene in the vapor, 44.5% m-xylene and 55.5% o-xylene in the liquid. Using the Fenske equation, and the data obtained from the perforated plate column, (α = 1.127), the number of theoretical plates in the column was found to be 3.5.

The identical procedure was repeated with both sections of the column as part of the apparatus. The same charge was charged to the column and the column was operated at total reflux for 4 hours with a boil-up rate of 60 ml. per minute. Product samples were taken and analysis revealed 61.5% m-xylene and 38.5% o-xylene in the vapor, 39.9% m-xylene and 60.1% o-xylene in the liquid. Using the Fenske equation, and the data obtained from the perforated-plate column (α = 1.127), the number of theoretical plates in the column was found to be 7.3.

For the experiments involved in this thesis, only the column containing 7.3 theoretical plates was used.

Extractive Distillation in the Perforated-Plate Column

The purpose of carrying out a separation in the plate column is twofold. One is to reduce separation of the close boiling systems to practice. A second reason is to more accurately determine the relative volatility of the system components in the presence of the extractive agent. This is done using the Fenske equation.

Extractive distillation runs made in the perforated-plate column were done at total reflux in a semi-batch fashion. The operation is semi-batch in that the azeotropic mixture is introduced as an initial charge, but extractive agent is added continuously throughout the separation.

In order to have a successful separation, enough mixture should be on each plate. Not enough charge into the stillpot would lead to complete vaporization of the lower boiling component. Therefore, the bottoms would lack in composition of that component. Lack of, or a very low amount of one component in the bottoms makes it almost impossible to obtain a reading on the gas chromatograph and a value of relative volatility could

not be obtained. To insure a successful separation, 200 grams of the close boiling mixture was initially charged to the stillpot. Heat was applied to the stillpot and the vapors allowed to warm the column to its operating temperature. When vapor reached the top of the column, cold water was started to the overhead condenser and the column was then allowed to reflux in order to achieve operating conditions.

In the meantime, the extractive agent was being heated to a temperature close to the boiling points present in each mixture. The purpose of heating the extractive agent was so that upon addition, the efficiency of the column would not decrease because of having to compensate for a cooler temperature [9]. The warmed agent was then introduced to the metering flask from which the micro-bellows pump supplies feed to the top of the column. The time at which the extractive agent was introduced to the column was noted as the starting time for the run. Extractive agent was fed above the top plate of the column at a rate of approximately 60 ml. per minute. Since the flask from which the micro-bellows pump fed was calibrated, the rate at which the extractive agent was being fed to the column was easily verified. Overhead and bottoms samples were taken at half-hour intervals from the time at which agent addition began until steady state in the column was established. Steady state was considered to be established when the relative volatility for the system was constant. Heat to the column was adjusted to achieve a boil-up rate of between 40 ml. and 60 ml. per minute. This gave an agent addition to boil-up ratio of between 1:3 and 1:4 as desired. Measurement of the boil-up rate was achieved by counting drops of liquid which fell from any of the points on the Corad head and accounting for the portion of surface area which they represented. It was found that there were approximately 22 drops per milliliter and this was used as a conversion factor.

As the distillation progressed, the ever-increasing concentration of the extractive agent in the bottoms mixture would increase the temperature in the stillpot. If the temperature became too high, this would sometimes cause decomposition of the close boiling components that were being separated. For this reason, distillation runs with higher extractive agent addition rates were avoided.

After each run the perforated-plate column was allowed to cool, flushed with acetone, and blown dry with compressed air in preparation for the next run.

RESULTS

Formic Acid/3-Methyl-2-Butanone

The formic acid/3-methyl-2-butanone was initially separated using various extractive agents in the Othmer still. Table 3 below and on the following pages lists compounds that were used with the key component of sulfolane to form extractive agent mixtures which were successful at increasing the relative volatility in the Othmer still. Table 5 on page 48 contains similar data except the key component in the extractive agent mixtures is dimethylsulfoxide [24,25].

Table 3. Effective agents for formic acid/3-methyl-2-butanone containing sulfolane [24].

Compounds	Ratios	Relative volatilities
Sulfolane, Adipic acid	$(1/2)^2(3/5)^2$	3.2 3.6
" , Azelaic acid	" "	2.6 2.3
" , Benzoic acid	" "	1.8 2.7
" , p-tert. Butyl benzoic acid	" "	1.9 2.4
" , Cinnamic acid	" "	2.6 2.6
" , Decanoic acid	" "	2.6 2.4
" , Ethylene glycol diacetate	" "	3.2 2.8
" , Glycerine triacetate	" "	2.3 2.7
" , Hexanoic acid	" "	1.9 2.5
" , p-Hydroxy benzoic acid	" "	2.4 3.0
" , Itaconic acid	" "	3.0 3.0
" , Malic acid	" "	2.5 2.3
" , Neodecanoic acid	" "	1.9 2.7
" , m-Nitrobenzoic acid	" "	1.6 1.5

Table 3 - Continued

Compounds	Ratios	Relative volatilities	
Sulfolane, Octanoic acid	$(1/2)^2(3/5)^2$	2.2	2.8
" , Phenyl acetic acid	" "	1.3	1.9
" , Sebacic acid	" "	2.7	2.5
" , o-Toluic acid	" "	1.7	1.5
" , m-Toluic acid	" "	2.4	2.0
" , Adipic acid, Ethyl phenyl acetate	$(1/3)^3(2/5)^3$	2.8	2.0
" , Azelaic acid, Isobutyl heptyl ketone	" "	2.0	2.1
" , Benzoic acid, Acetophenone	" "	2.7	1.9
" , p-tert. Butyl benzoic acid, Dipropylene glycol dibenzoate	" "	2.1	1.5
" , Cinnamic acid, Diethylene glycol dimethyl ether	" "	2.8	2.1
" , Decanoic acid, Cyclohexanone	" "	2.3	2.1
" , Ethylene glycol diacetate, 2-Methoxy-ethyl ether	" "	2.8	2.8
" , Glutaric acid, Ethylene glycol diacetate	" "	2.3	2.8
" , Glycerine triacetate, Butyl benzoate	" "	2.3	2.0
" , Heptanoic acid, Ethyl benzoate	" "	1.9	1.8
" , Hexanoic acid, Methyl benzoate	" "	1.7	1.7
" , p-Hydroxy benzoic acid, 3-Heptanone	" "	1.3	1.4
" , Itaconic acid, Diethylene glycol diethyl ether	" "	2.7	2.1
" , Malic acid, 2-Methoxy ethyl ether	" "	3.1	3.0
" , Neodecanoic acid, Isophorone	" "	2.3	2.2
" , Phenyl acetic acid, 4-Methyl-2-pentanone	" "	1.7	1.5
" , Pelargonic acid, Benzyl benzoate	" "	1.6	1.7
" , Salicylic acid, Phenyl acetate	" "	1.5	1.5
" , Sebacic acid, Diisobutyl ketone	" "	2.0	2.1
" , o-Toluic acid, Ethylene glycol phenyl ether	" "	1.6	1.7
" , m-Toluic acid, Anisole	" "	1.5	1.7

The ratios and relative volatility values are easy to obtain from this table. For example, one half part of sulfolane with one half part of adipic acid with one part 3-methyl-2-butanone-formic acid mixture gives a relative volatility of 3.2 and 3/5 parts of sulfolane with 3/5 parts of adipic acid with one part 3-methyl-2-butanone-formic acid mixture gives a value of 3.6. In every example in Table 3, the starting material is the 3-methyl-2-butanone-formic acid azeotrope which possesses a relative volatility of 1.0. In both cases, the superscripts 2 and 3 mean that there are 2 or 3 components present in the extractive agent mixture.

Although several mixtures were effective in separating the formic acid/3-methyl-2-butanone system, some agents that might have been expected to be successful were not effective. Table 4 below lists these deficient agents. In general, an agent is considered not to be effective when either decomposition occurs or a relative volatility value of 1.0, or less, is obtained.

Table 4. Ineffective agents for formic acid/3-methyl-2-butanone.

Compounds
Sulfolane
" , Acetyl salicylic acid
" , Glutaric acid
" , Heptanoic acid
" , Pelargonic acid
" , Salicylic acid
" , Acetyl salicylic acid, Hexyl acetate
" , m-Nitrobenzoic acid, Adiponitrile
" , Octanoic acid, Butyl benzoate

The following table is interpreted the same way as Table 3, however, dimethylsulfoxide is the key component of the extractive agent mixtures in this case.

Table 5. Effective agents for formic acid/3-methyl-2-butanone using DMSO [25].

Compounds	Ratios	Relative volatilities	
Dimthylsulfoxide (DMSO), Benzoic acid	$(1/2)^2(3/5)^2$	5.2	4.3
DMSO, Decanoic acid	" "	4.3	4.1
" , Glutaric acid	" "	4.2	1.5
" , Heptanoic acid	" "	4.2	4.5
" , Hexahydro phthalic acid	" "	4.1	2.0
" , Hexanoic acid	" "	4.3	3.0
" , Itaconic acid	" "	3.2	3.6
" , Myristic acid	" "	2.0	1.6
" , Octanoic acid	" "	3.5	4.2
" , Neodecanoic acid	" "	2.4	3.9
" , p-Nitrophenyl acetic acid	" "	4.5	3.0
" , Pelargonic acid	" "	4.5	4.7
" , Phenyl acetic acid	" "	5.1	6.1
" , o-Toluic acid	" "	3.3	6.0
" , m-Toluic acid	" "	4.7	3.9
" , Benzoic acid, Isophorone	$(1/3)^3(2/5)^3$	3.5	5.3
" , Decanoic acid, Cyclohexanone	" "	2.1	1.7
" , Glutaric acid, Methyl salicylate	" "	1.7	1.7
" , Heptanoic acid, Ethyl benzoate	" "	2.4	3.0
" , Hexanoic acid, Methyl benzoate	" "	2.6	3.1
" , Itaconic acid, Methyl salicylate	" "	3.1	2.1
" , Myristic acid, 2-Methoxy ethyl ether	" "	1.8	1.6
" , Neodecanoic acid, Acetophenone	" "	3.2	2.0
" , p-Nitrophenyl acetic acid, Hexyl acetate	" "	3.6	2.2
" , Octanoic acid, Butyl benzoate	" "	4.0	4.6
" , Pelargonic acid, Adiponitrile	" "	3.8	2.2
" , Phenyl acetic acid, Diisobutyl ketone	" "	1.8	3.5
" , o-Toluic acid, Ethyl phenyl acetate	" "	2.9	3.3
" , m-Toluic acid, Diethyl maleate	" "	1.3	2.9

From the values obtained by initial screening in the Othmer still, an extractive agent mixture was chosen from each table for testing in the perforated plate column. Table 6 and

Table 7 contains the results obtained using the agents chosen from Table 3 and 7, a 50-50 volume % mixture of sulfolane and ethylene glycol diacetate and a 50-50 volume % mixture of DMSO and heptanoic acid, respectively.

Table 6. Column results for formic acid/3-methyl-2-butanone using sulfolane [24].

Agent	Column	Time, hrs.	Weight % Ketone	Weight % Formic acid	Relative volatility
50% Sulfolane, 50% Ethylene glycol diacetate	Overhead	1/2	98.1	1.9	1.37
	Bottoms		22.1	77.9	
"	Overhead	1	96.7	3.3	1.36
	Bottoms		15.6	84.3	

Table 7. Column results for formic acid/3-methyl-2-butanone using DMSO [25].

Agent	Column	Time, hrs.	Weight % Ketone	Weight % Formic acid	Relative volatility
50% DMSO, 50% Heptanoic acid	Overhead	1/2	57.4	42.6	1.33
	Bottoms		23.3	76.7	
"	Overhead	1-1/4	55	45	1.44
	Bottoms		15.4	84.6	

Formic Acid/Acetic Acid/4-Methyl-2-Pentanone

Preliminary data for the formic acid/acetic acid/4-methyl-2-pentanone system was obtained in the same manner as previously described. Table 8 contains compounds that were used with the key component of sulfolane to form extractive agent mixtures which were successful at separating formic acid/4-methyl-2-pentanone in the Othmer still [26].

Table 8. Effective extractive distillation agents for 4-methyl-2-pentanone from formic acid [26].

Compounds	Ratios	Relative volatilities	
Sulfolane	2 12/5	2.9	1.9
" , Adipic acid	$(1/2^2(3/5)^2$	4.0	2.6
" , Acetyl salicylic acid	" "	1.4	1.8
" , Azelaic acid	" "	1.3	1.5
" , Benzoic acid	" "	1.2	2.0
" , p-tert. Butyl benzoic acid	" "	2.4	-
" , Cinnamic acid	" "	2.1	1.2
" , Decanoic acid	" "	1.2	1.2
" , Glutaric acid	" "	2.2	3.1
" , Heptanoic acid	" "	1.6	1.6
" , Hexanoic acid	" "	1.3	1.2
" , Itaconic acid	" "	3.6	4.6
" , Malic acid	" "	2.2	2.5
" , Neodecanoic acid	" "	1.5	1.6
" , m-Nitrobenzoic acid	" "	1.1	1.4
" , Octanoic acid	" "	1.9	1.8
" , Pelargonic acid	" "	1.6	1.2
" , Salicylic acid	" "	1.2	1.3
" , Sebacic acid	" "	2.7	1.7
" , Thiosalicylic acid	" "	5.5	4.1
" , m-Toluic acid	" "	2.3	1.7
" , Azelaic acid, Ethylene glycol diacetate	$(1/3)^3(2/5)^3$	1.6	2.1
" , Adipic acid, Benzyl ether	" "	1.6	1.9
" , Benzoic acid, Dipropylene glycol dibenzoate	" "	1.0	1.2
" , Cinnamic acid, 2-Methoxyethyl ether	" "	2.1	2.6
" , Decanoic acid, Acetophenone	" "	1.1	1.5
" , Glutaric acid, Methyl isoamyl ketone	" "	1.3	1.9
" , Itaconic acid, Glycerol triacetate	" "	2.9	2.5
" , Malic acid, Ethylene glycol butyl ether acetate	" "	1.8	1.3

Table 8 - Continued

Compounds	Ratios	Relative volatilities	
Sulfolane, Octanoic acid, Isophorone	$(1/3)^3(2/5)^3$	2.2	1.5
" , Salicylic acid, Cyclopentanone	" "	1.2	1.2
" , Sbacic acid, Nitrobenzene	" "	1.6	1.3
" , Thiosalicylic acid, Diethyl maleate	" "	2.1	1.3

The values in this table are to be interpreted as previously described on page 46. As mentioned before, some of the tested extractive agents were not effective. The ineffective potential agents containing sulfolane are listed in Table 9 below.

Table 9. Potential agents containing sulfolane which are ineffective.

Compounds
Sulfolane, Acetyl salicylic acid, Benzyl acetate
" , p-tert. Butyl benzoic acid, Diethylene glycol diethyl ether
" , Heptanoic acid, Benzyl benzoate
" , Hexanoic acid, Ethyl benzoate
" , Myristic acid, Isobutyl heptyl ketone
" , Neodecanoic acid, Methyl salicylate
" , m-Nitrobenzoic acid, Dipropylene glycol methyl ether acetate
" , Pelargonic acid, 2-Undecanone
" , o-Toluic acid, Propiophenone
" , m-Toluic acid, Butyl ether
" , p-Toluic acid, Hexyl acetate

For the same system, Table 10 lists the compounds that were used with the key component of sulfolane to form extractive agent mixtures which were successful at separating acetic acid/4-methyl-2-pentanone in the Othmer still [26].

Table 10. Effective extractive distillation agents for 4-methyl-2-pentanone from acetic acid [26].

Compounds	Ratios	Relative Volatilities	
Sulfolane	2 12/5	1.7	2.7
" , Adipic acid	$(1/2)^2(3/5)^2$	1.2	2.5
" , Acetyl salicylic acid	" "	1.2	2.0
" , Azelaic acid	" "	2.1	2.9
" , Benzoic acid	" "	1.8	1.5
" , p-tert. Butyl benzoic acid	" "	3.8	2.0
" , Cinnamic acid	" "	1.5	1.2
" , Decanoic acid	" "	1.7	1.2
" , Glutaric acid	" "	1.7	1.5
" , Heptanoic acid	" "	1.4	1.7
" , Hexanoic acid	" "	1.3	2.8
" , Hexahydro phthalic acid	" "	2.8	1.5
" , Itaconic acid	" "	2.3	1.5
" , Myristic acid	" "	1.8	1.4
" , Neodecanoic acid	$(1/2)^2(3/5)^2$	1.4	1.7
" , Octanoic acid	" "	1.2	1.3
" , Pelargonic acid	" "	2.4	1.2
" , Salicylic acid	" "	1.4	1.4
" , Sebacic acid	" "	1.5	1.2
" , Tetrahydro phthalic acid	" "	1.5	1.4
" , Thiosalicylic acid	" "	2.1	1.6
" , o-Toluic acid	" "	2.9	1.2
" , m-Toluic acid	" "	1.7	1.3
" , p-Toluic acid	" "	1.5	1.3
" , Undecanoic acid	" "	1.9	1.2
" , Adipic acid, Anisole	$(1/3)^3(2/5)^3$	1.8	1.2
" , Acetyl salicylic acid, Methyl salicylate	" "	1.4	1.6
" , Azelaic acid, Ethylene glycol phenyl ether	" "	1.4	1.3
" , p-tert. Butyl benzoic acid, Isobornyl acetate	" "	1.4	3.3
" , Cinnamic acid, n-Butyl ether	" "	1.8	1.3
" , Decanoic acid, Adiponitrile	" "	2.5	1.5
" , Glutaric acid, Propiophenone	" "	2.3	1.3
" , Heptanoic acid, Methyl benzoate	" "	2.9	2.5
" , Hexahydro phthalic acid, Methyl benzoate	" "	1.4	1.5
" , Itaconic acid, Ethyl salicylate	" "	1.4	1.8

Table 10 Continued

Compounds	Ratios	Relative volatilities	
Sulfolane, Neodecanoic acid, Benzyl acetate	$(1/3)^3(2/5)^3$	1.6	1.2
" , Octanoic acid, Cyclohexanone	" "	3.1	2.7
" , Pelargonic acid, 2-Octanone	" "	1.2	2.2
" , Salicylic acid, Phenyl acetate	" "	1.5	1.4
" , Sebacic acid, 2-Heptanone	" "	3.0	1.8
" , Tetrahydro phthalic acid, Dipropylene glycol methyl ether	" "	1.5	2.6
" , Thiosalicylic acid, Diethylene glycol diethyl ether	" "	1.7	1.3
" , o-Toluic acid, 2-Methoxyethyl ether	" "	1.6	2.3
" , p-Toluic acid, Ethyl phenyl acetate	" "	1.4	1.2

The values in this table are to be interpreted as previously described. As mentioned before, some of the potential extractive agents proved to be ineffective. The ineffective potential agents containing sulfolane are listed in Table 11 below.

Table 11. Potential extractive distillation agents containing sulfolane which are ineffective for 4-methyl-2-pentanone from acetic acid.

Compounds
Sulfolane, Benzoic acid, Diethylene glycol dibenzoate
" , Hexanoic acid, Methyl benzoate
" , Myristic acid, Isobutyl heptyl ketone
" , m-Toluic acid, Ethylene glycol methyl ether acetate
" , Undecanoic acid, Benzonitrile

From the values obtained by initial screening in the Othmer still, an extractive agent mixture was chosen from each table for testing in the perforated plate column. Table 12 contains the results obtained using the chosen agents which were 50-50 volume % mixture of sulfolane and heptanoic acid, and 33-33-33 volume % mixture of sulfolane, heptanoic acid, and methyl benzoate, respectively.

Table 12. Column results for formic acid/acetic acid/4-methyl-2-pentanone using sulfolane [26].

Agent	Column	Time hrs.	Weight % Ketone	Weight % Formic acid	Relative volatility
50% Sulfolane, 50% Heptanoic acid	Overhead	0.5	40	60	1.69
	Bottoms		4.2	95.8	
"	Overhead	1.5	48.1	51.9	1.86
	Bottoms		3.5	96.5	
			Weight % Acetic acid		
33% Sulfolane, 33% Heptanoic acid, 33% Methyl benzoate	Overhead	0.5	69.2	30.8	1.74
	Bottoms		10.3	89.7	
"	Overhead	1.3	73.3	26.7	2.04
	Bottoms		6.7	93.3	

Formic Acid/4-Methyl-2-Pentanone

The formic acid/4-methyl-2-pentanone was initially separated using various extractive agents in the Othmer still. Table 13 lists compounds that were used with the key component of dimethylformamide to form extractive agent mixtures which were successful at increasing the relative volatility in the Othmer still. Table 14 contains similar data except the key component in the extractive agent mixtures is dimethylacetamide [27].

Table 13. Effective agents for formic acid/4-methyl-2-pentanone using DMFA [27].

Compounds	Ratios		Relative volatilities	
Dimethylformamide (DMFA)	1	6/5	2.0	1.9
DMFA, Hexanoic acid	$(1/2)^2$	$(3/5)^2$	1.7	1.3
" , Heptanoic acid	"	"	1.1	1.3
" , Itaconic acid	"	"	1.2	1.1
" , Neodecanoic acid	"	"	1.2	1.1
" , Octanoic acid	"	"	1.4	1.2
" , Pelargonic acid	"	"	1.2	1.1
" , Hexanoic acid, Methyl benzoate	$(1/3)^3$	$(2/5)^3$	1.6	1.4
" , Heptanoic acid, Ethyl benzoate	"	"	1.3	1.3
" , Itaconic acid, 2-Octanone	"	"	1.2	1.4
" , Neodecanoic acid, Benzyl acetate	"	"	1.1	1.4
" , Octanoic acid, Butyl benzoate	"	"	1.3	1.3
" , Pelargonic acid, Benzyl acetate	"	"	1.1	1.5

Table 14. Effective agents for formic acid/4-methyl-2-pentanone using DMAA [27].

Compounds	Ratios		Relative volatilities	
Dimethylacetamide (DMAA)	1	6/5	1.1	1.2
DMAA, Adipic acid	$(1/2)^2$	$(3/5)^2$	2.5	2.9
" , Acetyl salicylic acid	"	"	1.8	2.1
" , Azelaic acid	"	"	3.0	2.1

Table 14 Continued

Compounds	Ratios	Relative volatilities
DMAA, Benzoic acid	$(1/2)^2(3/5)^2$	3.0 2.9
" , o-tert. Butyl benzoic acid	" "	2.0 1.9
" , Cinnamic acid	" "	2.3 1.3
" , Decanoic acid	" "	1.5 1.5
" , Dodecanedioic acid	" "	1.6 2.1
" , Glutaric acid	" "	2.0 2.1
" , Heptanoic acid	" "	3.3 3.1
" , Hexanoic acid	" "	2.1 2.1
" , 4-Hydroxybenzoic acid	" "	1.5 1.6
" , Itaconic acid	" "	2.2 2.4
" , Malic acid	" "	2.4 2.5
" , Neodecanoic acid	" "	1.6 1.8
" , Neopentanoic acid	" "	1.5 1.6
" , m-Nitrobenzoic acid	" "	1.6 2.0
" , Octanoic acid	" "	1.6 2.1
" , Pelargonic acid	" "	1.7 2.1
" , Salicylic acid	" "	1.6 1.3
" , Sebacic acid	" "	1.3 1.6
" , o-Toluic acid	" "	1.9 1.9
" , m-Toluic acid	" "	2.1 1.9
" , p-Toluic acid	" "	1.7 1.5
" , 3,4,5-Trimethoxy benzoic acid	" "	1.9 1.5
" , Undecanoic acid	" "	1.6 2.2
" , Adipic acid, Diisobutyl ketone	$(1/3)^3(2/5)^3$	2.4 1.9
" , Acetyl salicylic acid, Acetophenone	" "	1.9 1.8
" , Azelaic acid, Adiponitrile	" "	2.6 2.4
" , Benzoic acid, Anisole	" "	1.3 1.6
" , o-tert. Butyl benzoic acid, Methyl salicylate	" "	2.0 1.7
, Cinnamic acid, Butyl ether	" "	2.5 2.8
" , Decanoic acid, Cyclo hexanone	" "	1.7 1.8
" , Dodecanedioic acid, Diisobutyl ketone	" "	1.4 1.4
" , Glutaric acid, Methyl isoamyl ketone	" "	1.9 2.7
" , Heptanoic acid, Ethyl benzoate	" "	2.6 2.1
" , Hexanoic acid, Methyl benzoate	" "	1.5 1.2
" , 4-Hydroxybenzoic acid, Ethylene glycol diacetate	" "	1.6 1.3
" , Itaconic acid, 2-Octanone	" "	1.7 2.9

Table 14. Continued

Compounds	Ratios	Relative volatilities	
DMAA, Malic acid, Diethylene glycol dibenzoate	$(1/3)^3(2/5)^3$	1.5	1.2
" , Neodecanoic acid, Isophorone	" "	1.8	1.5
" , Neopentanoic acid, 2-Heptanone	" "	1.3	1.4
" , m-Nitrobenzoic acid, Hexyl acetate	" "	1.7	1.3
" , p-Nitrobenzoic acid, Acetophenone	$(1/2)^3(2/5)^3$	1.1	1.1
" , Octanoic acid, Butyl benzoate	" "	1.7	1.6
" , Pelargonic acid, Benzyl benzoate	" "	1.1	1.2
" , Salicylic acid, Ethyl salicylate	" "	1.1	1.1
" , Sebacic acid, Ethyl butyl ketone	" "	2.1	1.3
" , o-Toluic acid, Diethylene glycol " , dimethyl ether	$(1/3)^3(2/5)^3$	1.7	1.7
" , m-Toluic acid, Diethylene glycol diethyl ether	" "	1.6	1.6
" , p-Toluic acid, Dipropylene glycol dibenzoate	" "	1.7	1.5
" , 3,4,5-Trimethoxy benzoic acid, Ethyl phenyl acetate	" "	1.6	1.5
" , Undecanoic acid, 2-Hydroxy acetophenone	" "	1.1	1.2

The values in these tables are to be interpreted as previously described.

From the values obtained by initial screening in the Othmer still, an extractive agent mixture was chosen from the tables for testing in the perforated plate column. Table 15 on page 59 contains the results obtained using the chosen agents which were 33-33-33 volume % mixture of dimethylacetamide, heptanoic acid, and methyl benzoate.

Table 15. Column results for formic acid/4-methyl-2-pentanone using DMAA.

Agent	Column	Time, hrs.	Weight % Ketone	Weight % Formic acid	Relative volatility
33% DMAA, 33% Heptanoic acid, 33% Methyl benzoate	Overhead	3/4	98.7	1.3	3.5
	Bottoms		10.3	89.7	
33% DMAA 33% Hytonoic acid 33% Methyl benzoate	Overhead	1.5	90.9	9.1	2.9
	Bottoms		4	96	

m-Xylene/o-Xylene

The m-xylene/o-xylene system was initially separated using various extractive agents in the Othmer still. Table 16 below and on pages 52 and 523lists compounds that were used with the key component of esters to form extractive agent mixtures which were successful at increasing the relative volatility in the Othmer still.

Table 16. Effective agents for m-xylene/o-xylene using esters [28].

Compounds	m-Xyl:o-Xyl	Relative Volatility
Diisononyl adipate	3:7	1.30
"	5:5	1.28
"	7:3	1.28
Benzyl acetate	3:7	1.29
"	5:5	1.17
"	7:3	1.12
Diethylene glycol ethyl ether acetate	3:7	1.18
"	5:5	1.23
Ethylene glycol diacetate	3:7	1.23
"	5:5	1.32

Table 16 Continued

Compound	m- Xyl:o-Xyl	Relative Volatility
Ethylene glycol diacetate	7:3	1.19
Ethylene glycol butyl ether acetate	3:7	1.29
"	5:5	1.20
"	7:3	1.10
Ethylene glycol ethyl ether acetate	3:7	1.25
"	5:5	1.16
Ethyl phenyl acetate	3:7	1.22
"	5:5	1.24
"	7:3	1.13
Glycerol triacetate	3:7	1.35
"	5:5	1.20
"	7:3	1.21
Isobornyl acetate	3:7	1.21
"	5:5	1.15
"	7:3	1.14
Benzyl benzoate	3:7	1.20
"	5:5	1.18
"	7:3	1.08
Ethyl benzoate	3:7	1.20
"	5:5	1.13
"	7:3	1.16
Methyl benzoate	3:7	1.21
"	5:5	1.26
"	7:3	1.25
Dipropylene glycol dibenzoate	3:7	1.15
"	5:5	1.17
Dimethyl glutarate	3:7	1.24
"	5:5	1.18
"	7:3	1.15
Dibutyl phthalate	3:7	1.36
"	5:5	1.30
"	7:3	1.24
Diethyl phthalate	3:7	1.34
"	5:5	1.33
"	7:3	1.32
Dihexyl phthalate	3:3	1.25
"	5:5	1.25
Diisodecyl phthalate	3:7	1.36
"	5:5	1.23
"	7:3	1.23
Ditridecyl phthalate	5:5	1.20

Table 16 - Continued

Compound	m-Xyl:o-Xyl	Relative Volatility
Dimethyl phthalate	5:5	1.34
Diisononyl phthalate	5:5	1.24
Dioctyl phthalate	3:7	1.26
"	5:5	1.24
"	7:3	1.21
Diisooctyl phthalate	3:7	1.24
"	5:5	1.26
Diundecyl phthalate	5:5	1.33
Triisononyl mellitate	3:7	1.23
"	5:5	1.26
"	7:3	1.20
Tributyl phosphate	5:5	1.17
"	7:3	1.22
Tricresyl phosphate	3:7	1.25
"	5:5	1.18
"	7:3	1.17
Methyl salicylate	3:7	1.22
"	5:5	1.19
"	7:3	1.35
Dimethyl sebacate	3:7	1.36
"	5:5	1.21
"	7:3	1.23
Dimethyl succinate	3:7	1.16
"	5:5	1.16
Triisononyl trimellitate	3:7	1.16
"	5:5	1.17
Diisononyl adipate - Dihexyl phthalate	3:7	1.15
" "	5:5	1.19
Diethylene - Dipropylene dibenzoates	3:7	1.23
" "	5:5	1.16
" "	7:3	1.18
Dimethyl glutarate - Dimethyl adipate	3:7	1.28
" "	5:5	1.32
" "	7:3	1.28
Dibutyl phthalate - Diisodecyl phthalate	3:7	1.21
" "	5:5	1.25
" "	7:3	1.13
Diethyl phthalate - Dihexyl phthalate	3:7	1.34
" "	5:5	1.34
" "	7:3	1.33
Diethyl phthalate - Diisodecyl phthalate	5:5	1.42

Table 16 <u>Continued</u>

Compound	m-Xyl:o-Xyl	Relative volatility
Diethyl phthalate - Diisodecyl phthalate	3:7	1.26
Dihexyl phthalate - Dibutyl phthalate	5:5	1.22
Dihexyl phthalate - Diisodecyl phthalate	3:7	1.33
" "	5:5	1.23
" "	7:3	1.23
Dihexyl phthalate - Diisononyl phthalate	3:7	1.26
" "	5:5	1.35
" "	7:3	1.21
Dihexyl phthalate - Diisooctyl phthalate	3:7	1.21
" "	5:5	1.28
" "	7:3	1.24
Dihexyl phthalate - Glycerol triacetate	3:7	1.18
" "	5:5	1.11
Diisodecyl phthalate - Diethyl phthalate	5:5	1.26
Ditridecyl phthalate - Diethyl phthalate	5:5	1.32
Diundecyl phthalate - Diethyl phthalate	5:5	1.26
Diundecyl phthalate - Dihexyl phthalate	5:5	1.34

The ratios and relative volatility values are easy to obtain from this table. In every case the starting material was a mixture of m-xylene and o-xylene in the ratio of 30% - 70%, 50% - 50%, or 70% - 30%. The relative volatilities are listed for all the mixtures investigated.

Several of those esters whose relative volatilities had been determined in the Othmer still were then evaluated in a glass perforated plate rectification column possessing 7.3 theoretical plates and the results listed in Table 17.

Table 17. Column results for m-xylene/o-xylene using esters [28].

Agent	Column	Time, hrs.	Weight % m-Xylene	Weight % o-Xylene	Relative volatility
50% Dimethyl adipate, 50% Dimethyl glutarate	Overhead	2	96.7	3.3	1.221
	Bottoms		87.2	12.8	
Dimethyl phthalate	Overhead	2.3	96.5	3.5	1.277
	Bottoms		82.2	17.8	
Diethyl phthalate	Overhead	1.5	96.9	3.1	1.231
	Bottoms		90.1	9.9	
50% Diethyl phthalate, 50% Dihexyl phthalate	Overhead	1.5	88.1	11.9	1.235
	Bottoms		79.2	20.8	
Dibutyl phthalate	Overhead	1	93.7	6.3	1.236
	Bottoms		75.7	24.3	
Dihexyl phthalate	Overhead	2	95.4	4.6	1.239
	Bottoms		81.3	18.7	
Diisooctyl phthalate	Overhead	1	92.2	7.8	1.215
	Bottoms		73.3	26.8	
Diisononyl phthalate	Overhead	1	93.9	6.1	1.240
	Bottoms		76.1	23.8	
Diisodecyl phthalate	Overhead	1.5	63.1	36.9	1.253
	Bottoms		23.7	76.3	

DISCUSSION

Data from the Othmer Still

From Tables 3, 5, 8, 10, 13, 14 and 16 one can easily notice that there are many potentially effective extractive agents for successfully separating the four close boiling systems examined in this thesis. For most of the extractive agents tested, two concentrations of agent were used. Testing of two concentrations was necessary in order to determine whether a low or a high concentration gives increased relative volatility. In some cases the higher concentration appears to give the highest value for relative volatility and in other cases the opposite is true. Selectivity increases by increasing agent concentration, therefore the relative volatility increases. Since the rate at which selectivity increases with concentration depends on the agent, it can only be determined experimentally. These occurrences may be due to temporary upset in operation of the Othmer still, decomposition, increasingly negative effect by one of the agents in the extractive agent mixture, and small amounts of water present in the initial "pure" mixtures.

As a conclusion of the above discussion, the data from the Othmer still is only preliminary data and not very conclusive. Relative volatility values calculated from the data obtained in the still only represent initial investigation of extractive agents which were shown to negate the azeotropes. These values may or may not be suitable for further investigation. Therefore, the values obtained from the Othmer still should not be taken for granted and should not be used in design.

Data from the Perforated-Plate Column

Data obtained from the perforated-plate column surpasses in accuracy the data obtained from the Othmer still. Equilibrium is achieved in a much shorter period of time in the perforated-plate column than in the still, therefore the possibility of decomposition is reduced considerably. Due to a shorter period of operation, the plate column may be monitored continuously for evidence of decomposition or system upset. Relative volatilities calculated using the Fenske equation represent the average of 3.5 or 7.3 equilibrium stages instead of one stage.

The formic acid/3-methyl-2-butanone system was tested with two extractive agent mixtures. The choice of the two mixtures was influenced by the relative volatility values obtained in the Othmer still and by their availability. The first agent mixture examined, a 50-50 volume % mix of DMSO and heptanoic acid, proved to give a high relative volatility value when used in the Othmer still. Using this agent mixture average relative volatility values of 1.33 after 30 minutes and 1.44 after 75 minutes were obtained. The second agent mixture, a 50-50 volume % mix of sulfolane and ethylene glycol diacetate, also proved to be a potential extractive agent when used in the Othmer still. Using this agent mixture average relative volatility values of 1.37 after 30 minutes and 1.36 after 60 minutes were obtained. With respect to both extractive agent mixtures, the relative volatility values obtained from the plate column are not very consistent with the values from the Othmer still. Even though the values obtained from the plate column (1.40 for the first extractive agent mixture and 1.37 for the second extractive agent mixture) are far from the values obtained from the Othmer still (4.2 for the first extractive agent mixture and 2.8 for the second extractive agent mixture), the values obtained from the plate column are considered to be very good by industry standards. In industry, relative volatility values of 1.3 and above are usually considered very good. Such good relative volatility values usually suggest that a very good separation of the system in question can be achieved.

The formic acid/acetic acid/4-methyl-2-pentanone was tested with 50-50 volume % mix of sulfolane and heptanoic acid, and 1/3 equal volume mix of sulfolane, heptanoic acid and methyl benzoate. For a 50-50 volume % mix of sulfolane and heptanoic acid, relative volatility values of 1.69 after 30 minutes and 1.86 after 90 minutes were obtained. These values not only agree with the values obtained from the Othmer still (1.4 and 1.7), but are even better. When using 1/3 equal volume mix of sulfolane, heptanoic acid and methyl benzoate, relative volatility values of 1.74 after 30 minutes and 2.04 after 80 minutes were obtained. These values also agree with the values obtained in the Othmer still (2.9 and 2.5). The extractive agent mixtures used to separate formic acid/acetic acid/4-methyl-2-pentanone proved to be very effective.

Two different key compounds with different extractive agent mixtures were tested on the formic acid/4-methyl-2-pentanone system. The key components used were dimethylformamide and dimethylacetamide. Due to preference of the extractive agent mixture by the industrial sponsor only dimethylacetamide was examined in the plate column. A 1/3 equal volume mix of DMAA, heptanoic acid and methyl benzoate was tested in the plate column. Relative volatility values of 3.5 after 45 minutes and 2.9 after 90 minutes were obtained. By examining the values obtained, there is a good chance that decomposition of one or more components of the system to be separated occurred, therefore causing the relative volatility to drop to 2.9. Even if the lower value of 2.9 were to be taken, when compared with the values obtained from the Othmer still (2.6 and 2.1) it proves not only to be consistent, but is even better.

Nine different extractive agents, or extractive agent mixtures, were tested on the m-xylene/o-xylene system. Table 18 below shows a comparison between relative volatility values obtained from the plate column and values from the Othmer still regarding each extractive agent and extractive agent mixtures used.

Table 18. Comparison of relative volatility values obtained from the plate column and Othmer still.

Agent	Relative volatility (PC)*	Relative volatility (OS)**
50% Dimethyl adipate, 50% Dimethyl glutarate	1.221	1.28
Dimethyl phthalate	1.277	1.34
Diethyl phthalate	1.231	1.32
50% Diethyl phthalate, 50% Dihexyl phthalate	1.235	1.33
Dibutyl Phthalate	1.236	1.24
Dihexyl phthalate	1.239	1.25
Diisooctyl phthalate	1.215	1.24
Diisononyl phthalate	1.240	1.24
Diisodecyl phthalate	1.253	1.23

* (PC) = Plate Column
** (OS) = Othmer Still

From the table above one can easily obtain the agent used, the relative volatility value obtained from the plate column and the relative volatility value obtained from the Othmer still for the agent used. In each case a mixture of 275 ml. m-xylene and 50 ml. o-xylene was charged to the stillpot and heated. Again, the values obtained from both techniques are consistent.

The effect of increasing concentration of extractive agent in the plate column's stillpot on column operation has been proven by Yeh [8] as to be negligible. Operating the column in a semi-batch manner has also been shown to have negligible effects, as previously mentioned in reference to Szabados ' work [20]. Comparison of the values obtained from the perforated-plate column and the Othmer still in this thesis appear to be consistent. As a result of this observation, it is reasonable to propose that the chosen extractive agents did indeed enhance the separation of the systems examined.

Viscosity Effects on Tray Efficiency

As a result of the experimental work done on the m-xylene/o-xylene system, it was suggested by the industrial sponsor, in this case EXXON, that the viscosity of the mixture found on each tray may have a decreasing effect on the relative volatility of the system.

The study done by EXXON assumed a 50 % reduction in actual trays and shows a correlation between viscosity and relative volatility, when using phthalates as the extractive agent. Increased viscosity reduces the plate efficiency so that for an increased viscosity a larger apparent relative volatility value will be required to be equivalent to a lower relative volatility value obtained at a lower viscosity.

For example, for a viscosity of 0.7 a relative volatility of 1.7 is needed in order to get an equivalent of a relative volatility of 1.3 at a viscosity of 0.15.

Figure 9 on page 62 shows the separation criteria, as obtained by EXXON, for m-xylene/o-xylene system where phthalates were used as extractive agent.

Polarity Diagrams

The use of Hansen and Hildebrand solubility parameters to obtain polarity diagrams was considered, by previous experimenters, to be a very effective mean of screening potentially effective agents for various azeotropic systems [8]. Even though the technique seems to be efficient for binary mixtures with pure extractive agents, it is not very reliable when multicomponent extractive agents or ternary and greater systems are used [8]. Table 19 on page 63 lists solubility parameters for the azeotropic systems studied and for the key components of the extractive agents used [29].

In Yeh's studies [8], the hydrogen bond parameter, δ_h, was plotted against the polar bond parameter, δ_p, on a two dimensional diagram to predict agent effectiveness. The dispersion parameter, δ_d, was not used because values did not differ appreciably between components and extractive agents. To account for the difference in molar volumes of the azeotrope components, the diagram was split into two regions based on molar volumes. In the method, solubility parameters were plotted for components of the azeotrope and for the pure extractive agents to be tested. A line was drawn between the two azeotrope components and bisected with a perpendicular line to create two line segments whose ratio is the same as the molar volume ratio of the components. Because like molecules readily associate, the side of the perpendicular an extractive agent is plotted on will determine which component of the azeotrope it will bring to the bottom of the column. Figure 10, 11, and 12 represent polarity diagrams for the systems discussed in this thesis. Due to lack of solubility parameters for

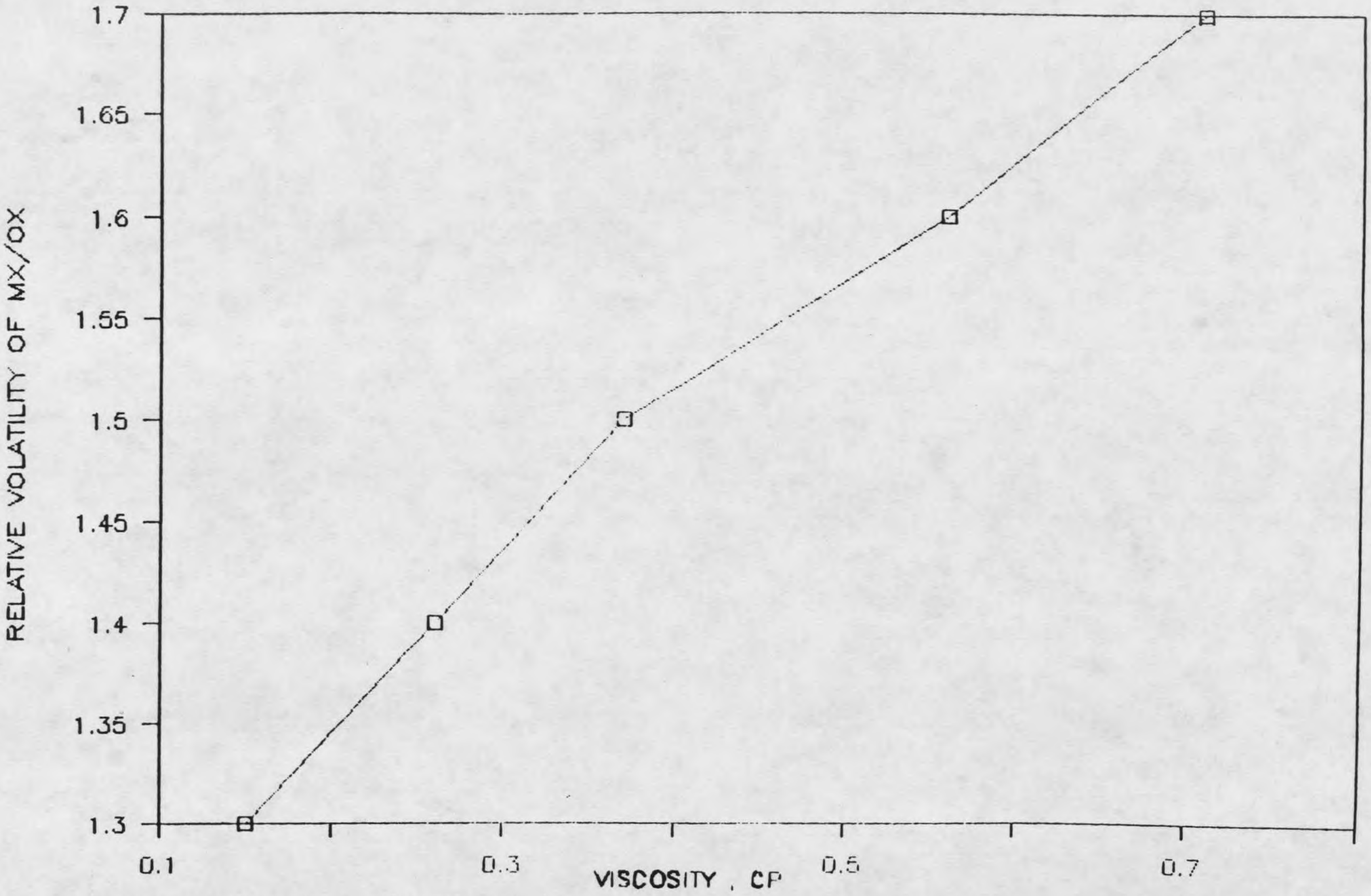


Figure 9. Separation criteria. 50% reduction in actual trays.

sulfolane, polarity diagrams could not be obtained for the systems involving sulfolane. For the systems discussed in this thesis the polarity diagrams proved to be efficient, but alone they are inconclusive when predicting extractive agent effectiveness.

Table 19. Solubility parameters at 25^{0}C [29].

NOTE: $\delta_t = (\delta^2{}_d + \delta^2 p + \delta^2{}_h)^{1/2}$

Compound	δ_t(MPa$^{1/2}$)	δ_d(MPa$^{1/2}$)	δ_p(MPa$^{1/2}$)	δ_h(MPa$^{1/2}$)
Formic acid	24.9	14.3	11.9	16.6
Acetic acid	21.4	14.5	8.0	13.5
DMFA	24.8	17.4	13.7	11.3
DMAA	22.7	16.8	11.5	10.2
DMSO	26.7	18.4	16.4	10.2
3-methyl-2-butanone	18.4	14.6	8.8	7.0
4-methyl-2-pentanone	17.6	14.4	8.1	5.9
m-Xylene	18.2	16.5	7.2	2.4
o-Xylene	18.5	17.0	7.5	0.0
Dimethyl phthalate	22.1	18.6	10.8	4.9
Diethyl phthalate	20.6	17.6	9.6	4.5
Dibutyl phthalate	20.2	15.9	9.5	8.1

Table 19. (Continued)

NOTE: $\delta_t = (\delta^2{}_d + \delta^2 p + \delta^2{}_h)^{/2}$

Compound	$\delta_t(MPa^{/2})$	$\delta_d(MPa^{/2})$	$\delta_p(MPa^{/2})$	$\delta 12h(MPa^{/2})$
Diisodecyl phthalate	18.5	16.5	4.2	7.3

Other experimenters have not had such good success with the polarity diagram method. Some experimenters reported the use of polarity diagrams was deficient in their experiments and others reported extractive agent models which did not conform. Polarity diagrams could not be obtained for the systems involving sulfolane. For opinion of Barton [29] that an expanded set of parameters using dispersion, induction orientation, acid, and base interaction is necessary for reliable quantitative evaluation of behavior in multicomponent systems.

Other models for studying nonideal solutions based on functional group contributions are available. One such model is called the modified separation of cohesive energy density model (MOSCED)[30], another is the UNIFAC method [30]. Although these models are reported to give good results for nonelectrolyte solutions, they only give insight into the outcome of experimentation and do not replace it.

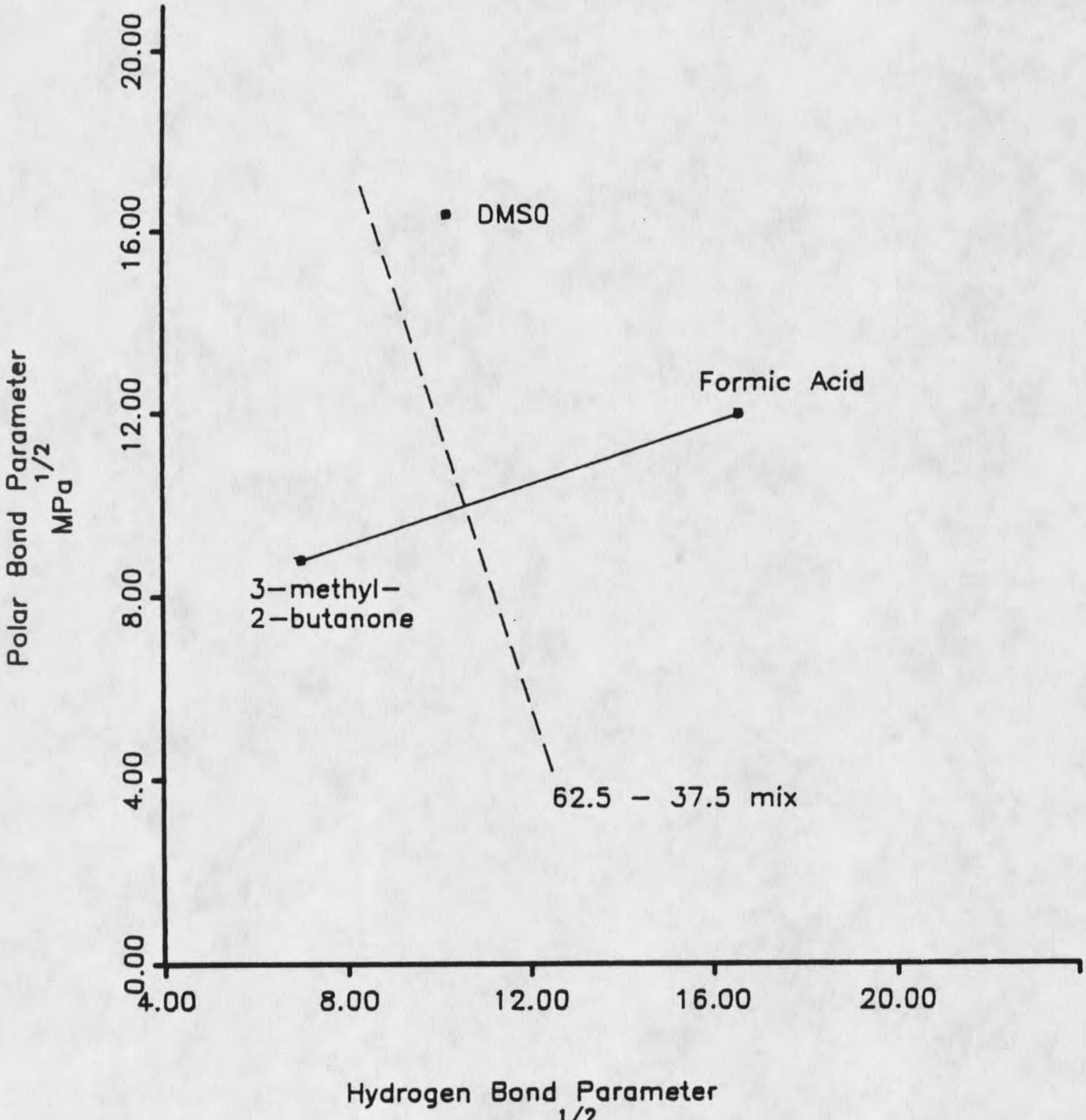


Figure 10. Polarity diagram for formic acid/3-mehtyl-2-butanone.

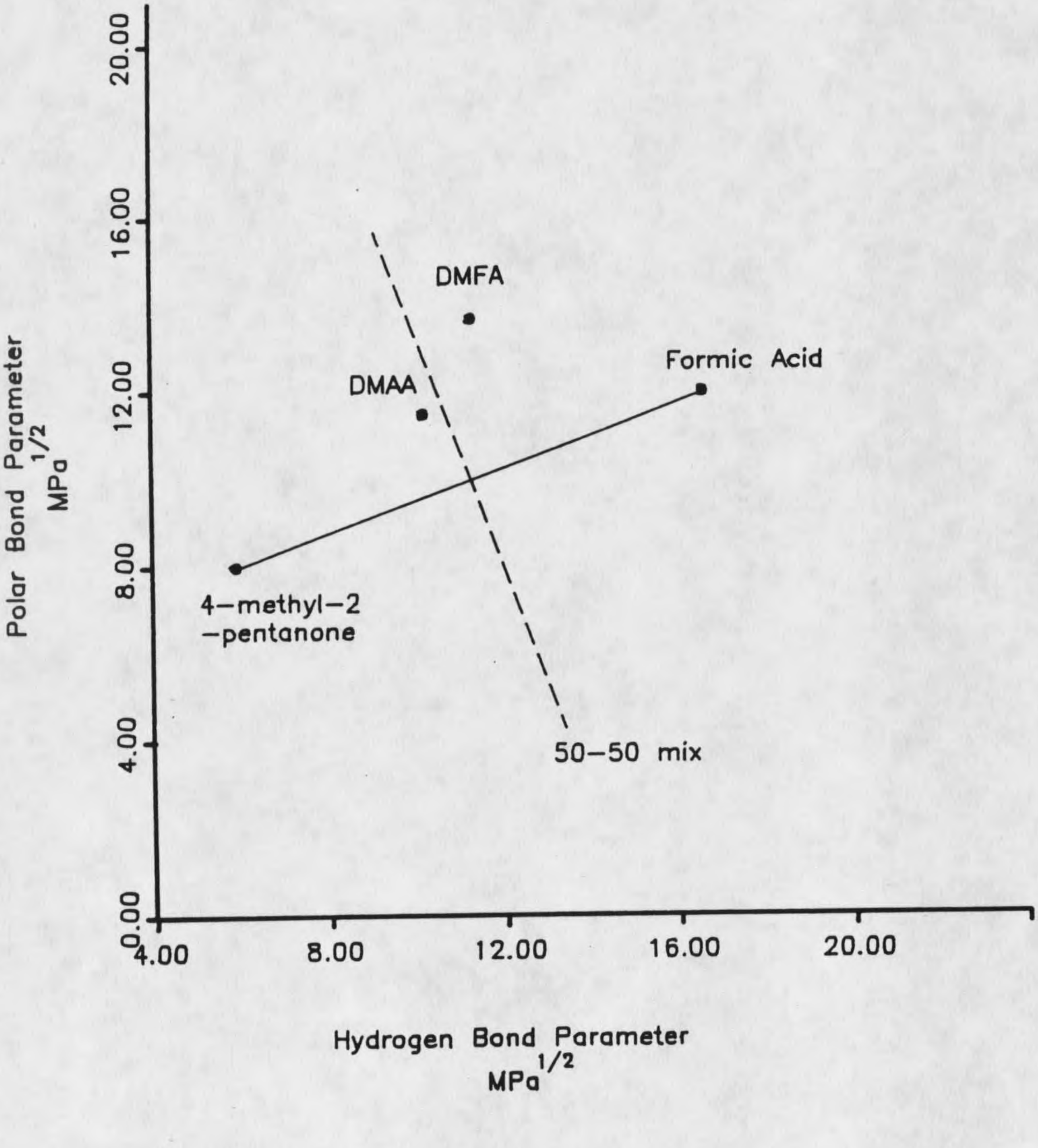


Figure 11. Polarity diagram for formic acid/4-methyl-2-pentanone.

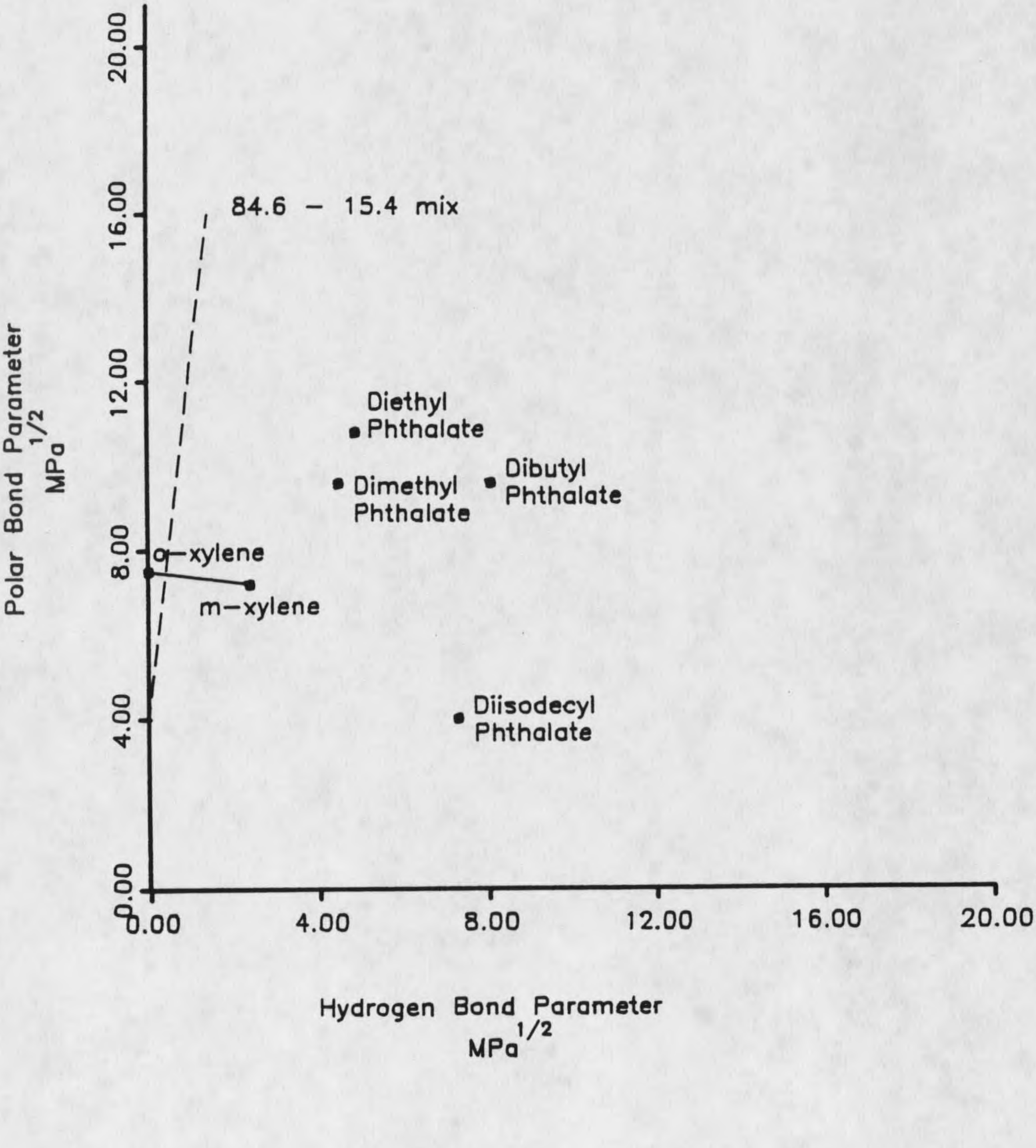


Figure 12. Polarity diagram for m-xylene/o-xylene.

SUMMARY AND CONCLUSIONS

1. Extractive distillation of the azeotropic systems studied in this thesis can successfully be accomplished if the proper extractive agents are chosen. The systems studied in this thesis were:
    - (i) formic acid/3-methyl-2-butanone
    - (ii) formic acid/acetic acid/4-methyl-2-pentanone
    - (iii) formic acid/4-methyl-2-pentanone
    - (iv) m-xylene/o-xylene
2. The perforated-plate column provided the most reliable data for determining the effectiveness of extractive agents.
3. The data obtained from the Othmer still provides a good method for screening potential extractive agents, but is unsuitable for use in design.
4. The polarity diagram can be used to compare the affinity of an agent for key components in binary mixtures. Thus the key component which will be the bottoms product can be predicted.

RECOMMENDATIONS FOR FUTURE RESEARCH

Through the use of polarity diagrams and data obtained from the Othmer still, it is probable that extractive agents can be found to negate most azeotropes. Polarity diagrams should only be used as a comparison technique and most emphasis should be put on the data obtained from the Othmer still. Although these preliminary steps are important in extractive distillation, they can be misleading. For reliable data one should always test the system and the extractive agent(s) in the plate column. The data obtained in the plate column should be the determining and most deciding step in choosing a suitable extractive agent.

As outlined in the discussion section, a study of the effects of viscosity on the plate efficiency showed that an increase in viscosity decreases plate efficiency. Since the study was available only for the m-xylene/o-xylene system, it is my recommendation that future research explore the correlation more in depth and also for different systems. This method could be found very useful in screening potential extractive agents for a particular system.

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