



Separation of acetic acid/4-methyl-2-pentanone, formic acid/4-methyl-2-pentanone and vinyl acetate/ethyl acetate by extractive distillation  
by Marc Wayne Paffhausen

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

Extractive distillation of the acetic acid/4-methyl-2-pentanone, formic acid/4-methyl-2-pentanone and vinyl acetate/ethyl acetate close boiling systems was investigated. Initial screening of potential extractive agents was carried out for each system in an Othmer vapor-liquid equilibrium still. Well over one hundred extractive agents, either alone or in combination with other compounds, were investigated overall. Subsequent testing of selected agents was carried out in a perforated-plate column which has been calibrated to have the equivalent of 5.3 theoretical plates. Relative volatilities for extractive distillation trial runs made in the perforated-plate column were calculated using the Fenske equation. All three systems investigated were successfully separated using chosen extractive agents. The use of polarity diagrams as an additional initial screening device was found to be a simple and effective technique for determining potential extractive agents as well.

Decomposition of acetic acid during one of the test runs in the perforated-plate column was believed to have led to the discovery of ketene gas, which is both difficult to obtain and uniquely useful industrially.

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**APPROVAL**

of a thesis submitted by

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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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## TABLE OF CONTENTS

	Page
BACKGROUND . . . . .	1
Extractive and Azeotropic Distillation . . . . .	3
Selection of Extractive Agents . . . . .	6
THEORETICAL ASPECTS . . . . .	8
Thermodynamics of Vapor-Liquid Equilibrium . . . . .	8
Relative Volatility . . . . .	10
The Fenske Total-Reflux Equation . . . . .	11
Altering Relative Volatility . . . . .	15
Selectivity . . . . .	15
Factors Affecting Selectivity . . . . .	16
Use of Solubility Parameters and Polarity Diagrams . . . . .	18
Other Methods to Predict Nonideal Solution Behavior . . . . .	19
RESEARCH OBJECTIVES . . . . .	20
SYSTEMS TO BE SEPARATED . . . . .	21
In General . . . . .	21
Acetic Acid/4-Methyl-2-Pentanone . . . . .	21
Formic Acid/4-Methyl-2-Pentanone . . . . .	22
Vinyl Acetate/Ethyl Acetate . . . . .	23
EXPERIMENTAL AND ANALYTICAL EQUIPMENT . . . . .	26
Othmer Vapor-Liquid Equilibrium Still . . . . .	26
The Perforated-Plate Column . . . . .	28
Extractive Agent Recovery . . . . .	31
The Gas Chromatograph . . . . .	31

TABLE OF CONTENTS—Continued

EXPERIMENTAL PROCEDURE . . . . .	33
Operation of the Othmer Still . . . . .	33
Calibration of the Perforated-Plate Column . . . . .	33
Extractive Distillation in the Perforated-Plate Column . . . . .	34
RESULTS . . . . .	37
Vinyl Acetate/Ethyl Acetate . . . . .	37
Acetic Acid/4-Methyl-2-Pentanone . . . . .	40
Formic Acid/4-Methyl-2-Pentanone . . . . .	47
DISCUSSION . . . . .	50
The Othmer Still as a Screening Device . . . . .	50
Polarity Diagrams as a Screening Device . . . . .	50
Data from the Perforated-Plate Column . . . . .	56
SUMMARY AND CONCLUSIONS . . . . .	59
RECOMMENDATIONS FOR FUTURE RESEARCH . . . . .	60
REFERENCES CITED . . . . .	61

## LIST OF TABLES

Table	Page
1. Favorable Characteristics of an Extractive Agent . . . . .	7
2. Relative Volatility-vs.-Theoretical Plates-vs.-Column Cost . . . . .	14
3. Effective agents for vinyl acetate/ethyl acetate . . . . .	37
4. Column results for vinyl acetate/ethyl acetate . . . . .	38
5. Ineffective agents for vinyl acetate/ethyl acetate . . . . .	39
6. Effective agents for acetic acid/4-methyl-2-pentanone using DMSO . . .	40
7. Effective agents for acetic acid/4-methyl-2-pentanone using DMFA . . .	43
8. Ineffective agents for acetic acid/4-methyl-2-pentanone using DMFA . . .	44
9. Column results for acetic acid/4-methyl-2-pentanone using DMSO . . .	45
10. Column results for acetic acid/4-methyl-2-pentanone using DMFA . . .	45
11. Results of decomposition in acetic acid/4-methyl-2-pentanone system .	46
12. Effective agents for formic acid/4-methyl-2-pentanone using DMSO . . .	47
13. Column results for formic acid/4-methyl-2-pentanone using DMSO . . .	49
14. Ineffective agents for formic acid/4-methyl-2-pentanone using DMSO .	49
15. Solubility parameters at 25° C . . . . .	51

## LIST OF FIGURES

Figure	Page
1. Fractional distillation column . . . . .	2
2. Extractive distillation column . . . . .	5
3. Number of theoretical plates as a function of relative volatility . . . . .	13
4. Structures and physical data for system components . . . . .	24
5. Structures and physical data for key extractive agents . . . . .	25
6. Othmer vapor-liquid equilibrium still . . . . .	27
7. Batch-wise extractive distillation column . . . . .	29
8. Agent recovery by simple distillation . . . . .	32
9. Polarity diagram for acetic acid/4-methyl-2-pentanone . . . . .	53
10. Polarity diagram for formic acid/4-methyl-2-pentanone . . . . .	54
11. Polarity diagram for vinyl acetate/ethyl acetate . . . . .	55

## ABSTRACT

Extractive distillation of the acetic acid/4-methyl-2-pentanone, formic acid/4-methyl-2-pentanone and vinyl acetate/ethyl acetate close boiling systems was investigated. Initial screening of potential extractive agents was carried out for each system in an Othmer vapor-liquid equilibrium still. Well over one hundred extractive agents, either alone or in combination with other compounds, were investigated overall. Subsequent testing of selected agents was carried out in a perforated-plate column which has been calibrated to have the equivalent of 5.3 theoretical plates. Relative volatilities for extractive distillation trial runs made in the perforated-plate column were calculated using the Fenske equation. All three systems investigated were successfully separated using chosen extractive agents. The use of polarity diagrams as an additional initial screening device was found to be a simple and effective technique for determining potential extractive agents as well.

Decomposition of acetic acid during one of the test runs in the perforated-plate column was believed to have led to the discovery of ketene gas, which is both difficult to obtain and uniquely useful industrially.

## BACKGROUND

Distillation is a mass-transfer operation which separates the components of liquid mixtures containing miscible and volatile substances by vaporization into individual components or, in some cases, into groups of components. The separation of a mixture of alcohol and water into its components; of liquid air into nitrogen, oxygen and argon; and of crude petroleum into gasoline, kerosene, fuel oil, and lubricating stock are examples of distillations [1].

It is believed that distillation was first used around 1500 B.C. thus making it the oldest method for effecting liquid separations [2]. It is also the most widely used technique today mainly due to the ease with which scale-up from the laboratory to an industrial size process can be conducted but also because of its extreme commercial value to the chemical industry [3,4].

Simple fractional distillation is applicable when the liquid feed mixture to be separated forms no azeotrope(s) and the difference in the volatilities of its components is significant, i.e., usually meaning relative volatility values of 1.05 or greater. The components must be capable of vaporizing at feasible temperature and pressure. Also, no reaction can occur between components nor can decomposition or polymerization of one or more of the components occur [5].

Figure 1 on page 2 illustrates a typical fractional distillation column [6]. Feed enters the column at or near a stage which has approximately the same liquid composition as the feed. The "plate" where the feed enters the column is referred to as the feed plate. All plates below and including the feed plate constitute the stripping section of the column. Plates above the feed plate constitute the rectification section. Liquid from the feed plate travels downward through the

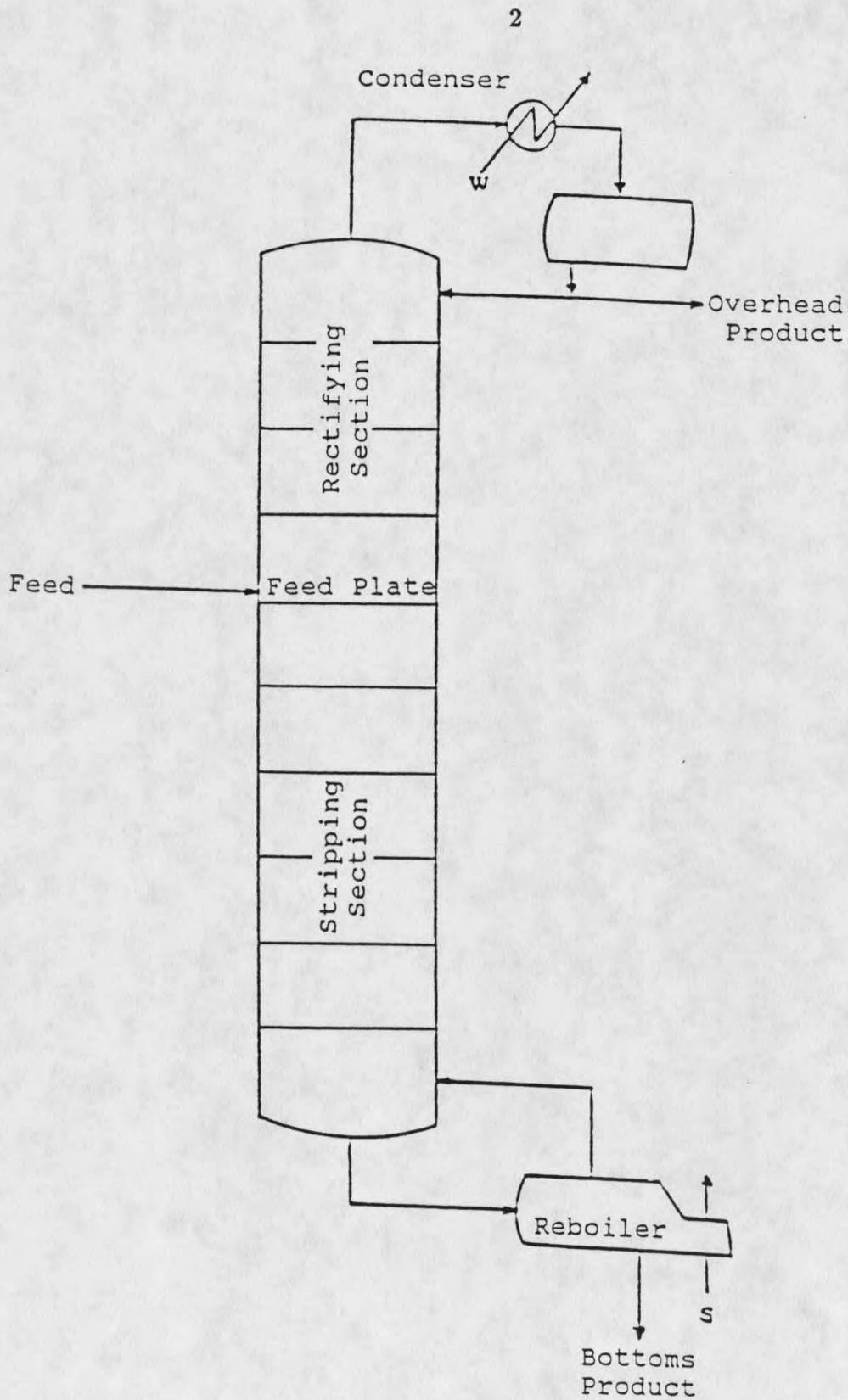


Figure 1. Fractional distillation column.

column and is intimately contacted by rising vapor at each plate. By trading latent heat of vaporization between the high and low boiling components, the vapor deposits its high boiling component in the liquid phase and removes low boiling component from the liquid as vapor to be carried to the overhead condenser. There it is either completely or totally condensed, part is taken off as product, and the rest returned to travel down the column as liquid. Without this liquid returned to the column no rectification would occur in the rectification section. This liquid serves to wash the high boiling component from the vapor as it ascends through the top portion of the column. In this manner, liquids that are separable may be brought to any desired purity at the top and bottom of the column.

In some cases distillation techniques other than simple fractional distillation must be used due to its ineffectiveness. Those cases are (i) when two or more of the components to be separated have only a slight, if any, difference in volatility, i.e., relative volatility is approximately equal to unity; (ii) two or more of the components form homogeneous azeotrope(s) which are not pressure sensitive or which are pressure sensitive but will not provide sufficient relative volatility change; and (iii) where one or more of the components will decompose or change chemically at temperature and pressure well within economic distillation ranges [7]. Fortunately, the technology of distillation has developed two modified forms which are now available for use. They are azeotropic and extractive distillation techniques.

#### Extractive and Azeotropic Distillation

Both azeotropic and extractive distillation are extremely effective techniques of separation involving the introduction of an additional component to the mixture to be separated. This additional component is referred to as a solvent or an agent.

The purpose of the agent is to change the way the components in the mixture chemically relate to one another. Specifically, the agent alters the relationship between the vapor pressures of the components in the mixture.

Benedict and Rubin have defined extractive and azeotropic distillation [8]. Extractive distillation is carried out in the presence of an agent which is relatively non-volatile compared to the components to be separated. This agent is charged continuously near the top of the column so that an appreciable concentration is maintained on all the plates of the column. The first extractive distillation process was patented by Emile and Guillaume in 1908 for the separation of fusel oil from fermentation alcohol [9]. Azeotropic distillation involves formation of a minimum boiling azeotrope between the agent and one of the components to be separated. The term "azeotrope" means a constant-boiling mixture. It is a very specific mixture of two or more components that boil at a specific temperature and which cannot be readily separated by ordinary distillation.

Figure 2 on page 5 illustrates a typical extractive distillation scheme. Distillation proceeds as described previously in the first column with the exception of the addition of the extractive agent near its top. The extractive agent is usually added a plate or two below the top so as to avoid carryover into the overhead product. The second column is used to recover the extractive agent from the bottoms product which is usually a simple task when the extractive agent being recovered is relatively non-volatile.

Extractive distillation has an advantage over azeotropic distillation in that a larger number of possibilities for successful agents exist and lower energies are required since vaporization of the agent is not necessary. Another advantage of extractive distillation is that the agent is usually easily recoverable. Extractive

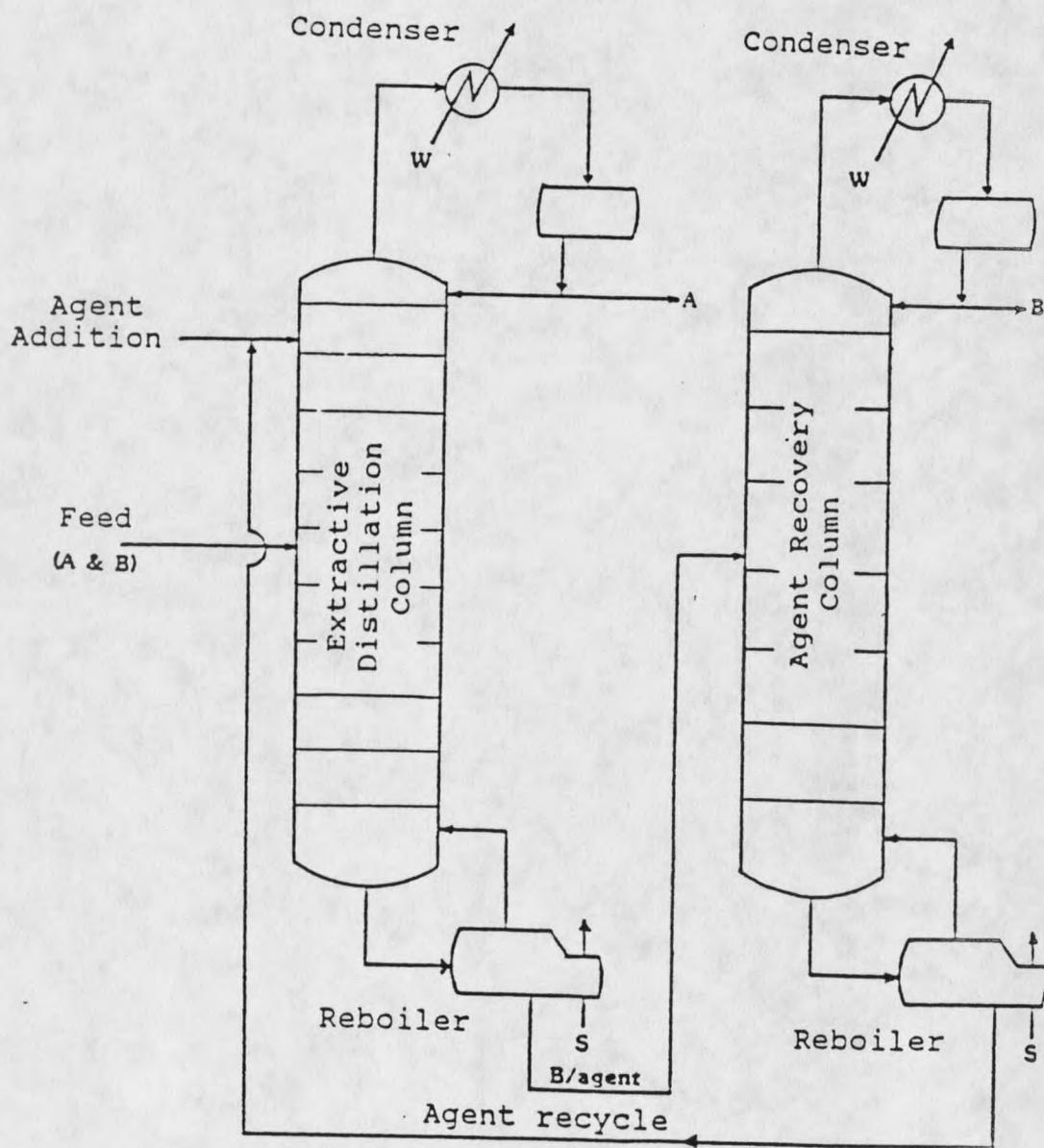


Figure 2. Extractive distillation column.

distillation is, however, not entirely without shortcomings. The additional volume of liquid on each plate added by the agent requires that columns have larger plates to process the same amount of material. Also, recovery of the agent usually requires an additional column and some additional energy inputs. Still, because of the variety of agents and lower heat requirements, extractive distillation seems to be preferred by industry.

Azeotropic distillation also has a couple of drawbacks. First, this separation technique relies on the formation of an acceptable azeotrope. This greatly reduces the possibility of finding a suitable agent. Secondly, there may still be the difficulty of separating the newly formed azeotrope so that the agent may be reused and the original component made useful.

#### Selection of Extractive Agents

The final selection of an extractive agent will be affected by many variables such as effectiveness, economics, chemical compatibility and company preference. Table 1 on page 7 contains a modified list of criteria reported by Rall [10] which have been previously suggested by Berg [11] and Yeh [12]. It is apparent after one reviews this list that the task of selecting the right extractive agent is not an easy one. In some instances a company will choose an agent with which it is already familiar or that it is already producing rather than choose the agent with the most favorable characteristics [13]. Fortunately, it is not unusual to have a number of effective agents from which to compare and choose.

Table 1. Favorable Characteristics of an Extractive Agent.

---

1. It should have a high boiling point, at least 20 degrees centigrade 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 agent may be used. This results in lower recycle rates for the agent, smaller column plates, 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.
  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.
-

## THEORETICAL ASPECTS

### Thermodynamics of Vapor-Liquid Equilibrium

The most common liquid mixture separation technique used by chemical process industries is distillation, a diffusional operation [14]. 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. For this reason, experimental data are a must for designs utilizing extractive distillation.

The distillation process is dependent upon a departure from 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 originally 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) [14]:

$$f_i^{\ell} = f_i^v \quad (\text{for all components } i = 1, 2, \dots, n) \quad (1)$$

where  $f_i$  is the fugacity of component  $i$  at the temperature, pressure, and composition of the system,  $v$  is the vapor phase, and  $\ell$  is the liquid phase. It is important to note that fugacity is a function of temperature, pressure, and composition only. 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 [14,15]. For the vapor phase:

$$\phi_i = \frac{f_i^v}{y_i P} \quad (2)$$

where  $\phi_i$  is the vapor phase fugacity coefficient of  $i$  in the mixture,  $P$  is total pressure of the system, and  $f_i$  is the fugacity of  $i$  in the mixture. For the liquid phase:

$$\gamma_i = \frac{a_i}{x_i} = \frac{f_i^l}{x_i f_i^o} \quad (3)$$

where  $\gamma_i$  is the liquid phase activity coefficient,  $a_i$  is activity of component  $i$ , and  $f_i^o$  is the standard state fugacity of component  $i$  at the system temperature and at some arbitrary pressure and composition chosen for convenience.

However, it is at this point that the typical thermodynamic development as described by Rall [10] becomes no longer applicable. Although the above development can be valid if used correctly for our extractive distillation scenario, a more simplified view of nonideal mixtures was preferred. What is being done when relative 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 get 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 or an extractive agent mixture 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 then be obtained at many different compositions and temperatures. Reduction of this data, i.e., by using Barker's method along with an optimization technique such as the Complex Method of Box [16,17], is done in order to fit the data to an equation for the activity coefficient. For instance, 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 [18]:

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

where  $\Lambda$  is the symbol for a Wilson parameter. Note that  $\Lambda_{ij} = 1$  for  $i = j$  and so on and also that 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  $\Lambda_{12}, \Lambda_{21}; \Lambda_{13}, \Lambda_{31};$  and  $\Lambda_{23}, \Lambda_{32}$ . From this an actual activity coefficient,  $\gamma_i$ , for ternary systems or higher is obtained. It was beyond the scope of this thesis project, however, to follow the rigorous analysis. The "empirical" results obtained on the extractive agent free basis were considered sufficient for the goals of this thesis.

### Relative Volatility

The single most useful measure of separation for a distillation process is relative volatility. 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 [1]:

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

where  $\alpha_{ij}$  is the relative volatility of component  $i$  in  $j$ ,  $y_i, y_j$  are vapor mole fractions at equilibrium, and  $x_i, x_j$  are liquid mole fractions at equilibrium. By

convention, the value of  $\alpha_{i,j}$  is taken such that the volatility of component  $j$  is always less than that of  $i$ , i.e.,  $\alpha_{i,j}$  is greater than or equal to unity. Although the relative volatility, given by  $\alpha$ , 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 discussion to be undertaken later, 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:

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

and

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

where  $P$  is the total pressure of the system,  $P_{vpi}$  is the vapor pressure of component  $i$ ,  $P_{vpj}$  is the vapor pressure of the component  $j$ ,  $y_i$  and  $y_j$  are vapor mole fractions at equilibrium, and  $x_i$  and  $x_j$  are liquid mole fractions at equilibrium. Substitution of these values in equation (5) yields the following expression for relative volatility which is also valid:

$$\alpha_{ij} = \frac{\gamma_i P_{vpi}}{\gamma_j P_{vpj}} \quad (8)$$

#### The Fenske Total-Reflux Equation

Under conditions of total reflux, the minimum number of theoretical plates required to effect a separation is given by the Fenske total-reflux equation [19]:

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

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

to that in the bottoms, and  $N_m$  is the minimum number of plates required. It should be noted that the relative volatility in equation (9) must either be constant or represented by the geometric mean to be strictly valid. A good representation of the geometric mean for relative volatility is given by [19]:

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

where top, middle, and bottom refer to column position.

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

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

For use of this equation the number of theoretical plates must be estimated by calibration of the column (see Calibration of the Perforated-Plate Column). Also, when used in this form the relative volatility is not the geometric mean across the column but is the overall average across the column.

Figure 3 on page 13 depicts the number of theoretical plates needed to separate a binary mixture into 99% products as a function of relative volatility. The number of theoretical plates approaches infinity as the relative volatility approaches unity. The number of plates required decreases rapidly when the relative volatility value is in the area of 1.25 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 shown in Table 2 on page 14 [12].

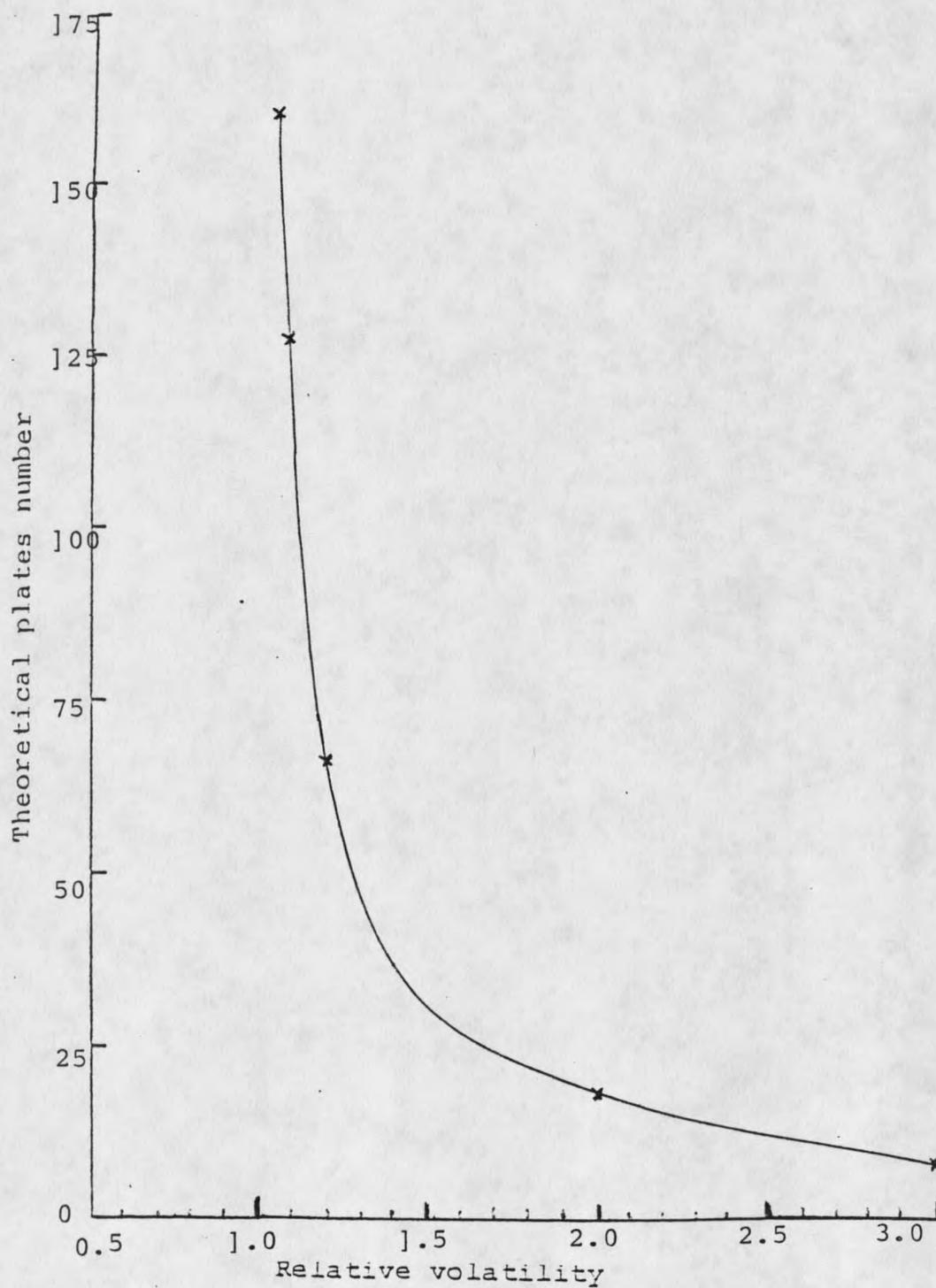


Figure 3. Number of theoretical plates as a function of relative volatility. In a separation of a binary mixture, the overhead and bottoms products are specified 99%.

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	100.00
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 value of 1.05.

The column cost is a relative value which is based on a value of relative volatility of 1.05. Using the Fenske equation with geometric mean relative volatilities, the number of theoretical plates required to achieve 99% pure distillate and bottoms products have been calculated. When interpreting Table 2 it is important to understand 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. In practice, mixtures with a relative volatility less than 1.1 are considered extremely difficult to separate and the process is usually uneconomical.

### Altering Relative Volatility

By looking at the Fenske equation it is apparent that the key to separating an azeotropic mixture, or one having a very low relative volatility such as in a close boiling mixture, is to increase its separation factor, or its relative volatility. There are three possible means by which this might be accomplished. First, one could alter the correction factors for the components, given by  $\gamma_i$  and  $\phi_i$ , used to obtain equations (6) and (7). However, these values are very close to unity at moderate pressure and do not appreciably affect the relative volatility. By examination of equation (8) the last two alternatives become apparent. One might choose to alter the ratio of the pure component vapor pressures. For instance, as operating temperature of the column is reduced, i.e., reduced column pressure, this ratio will increase which will, in turn, enhance the separation. Unfortunately, this change is usually not appreciable enough to significantly affect the separation [20]. The final 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 relative volatility. The latter case provides a basis for extractive distillation.

### Selectivity

An important characteristic of an extractive agent based on its relative volatility is one called selectivity. It is defined as the ability of an agent to preferentially enhance the volatility of one component in a mixture over that of another. One

expression used to define selectivity is given by Anderson and Prausnitz [20]:

$$S_{ij} = [\alpha_{ij}]_P / [\alpha_{ij}]_A \quad (12)$$

where  $S_{ij}$  is the selectivity of agent on component  $i$  relative to component  $j$ ,  $[\alpha_{ij}]_P$  is relative volatility in the presence of agent, and  $[\alpha_{ij}]_A$  is relative volatility in the absence of agent. It is desirable for the agent to increase the volatility of one component while decreasing the volatility of the other in order to maximize selectivity.

#### Factors Affecting Selectivity

The selectivity an extractive agent exhibits toward other components is the result of molecular interaction. Work done by Hildebrand and others has resulted in the development of two broad classifications of these interactive forces which are generally recognized to be (i) physical and (ii) chemical forces [21,22]. Physical forces, sometimes called van der Waals forces, are broken into three groups:

- (1) Dispersion forces. This is the cause of 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 is primarily what 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 and of these two, the hydrogen bonding is the most important. Liquids have been classified according to the strength and number of hydrogen bonds that their molecules may form [23]. 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 [24]:

- (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 might be able to identify groups of compounds that might also be used successfully as extractive agents for similar chemical systems.

Two other important effects on agent selectivity are (i) temperature and (ii) fraction of extractive agent present. Higher temperatures tend to disrupt the process of chemical complexing, thus lower temperatures are preferred. This would imply the use of vacuum distillation, the implementation of which would depend upon economics. Increasing the volume fraction of agent in the mixture to be separated also improves selectivity. However, this effect may lead to immiscibility within the system if carried to an extreme. 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. Because the force of repulsion becomes very small as two molecules are separated by distance, 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: (i) molecular interactions between components of the feed mixture, (ii) molecular interactions between the extractive agent and one of the feed components, and (iii) 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 [12] reported considerable success in predicting the degree of attraction between extractive agents and mixture components using solubility parameters. In his studies, the dispersion force,  $\delta_d$ , hydrogen bonding,  $\delta_h$ , and polarity,  $\delta_p$ , solubility parameters were used in conjunction with specific volumes of liquids to explore the degree of attractive molecular interactions. However, he found that differences in the dispersion force parameters were negligible and unsuitable for investigation. The remaining factors,  $\delta_h$  and  $\delta_p$ , can be plotted on polarity diagrams for the preliminary screening of agents (see Polarity Diagrams as a Screening Device).

### Other Methods to Predict Nonideal Solution Behavior

The use of Barker's method and CMBOX as a data reduction technique, as previously mentioned, is not the only way to reduce data to fit an equation like Wilson's. Also, other correlation equations exist [15,25] besides the Wilson equation. These methods were chosen for discussion because of the author's undergraduate and graduate work which utilized these techniques for evaluation of vapor-liquid equilibrium data and also because other methods may have been too time consuming or not as effective.

One such method of predicting nonideal solution behavior is the purely theoretical UNIFAC method. In this method, reduction of experimentally determined activity coefficient data into parameters characterizing structural groups is used to predict activity coefficients for systems not studied experimentally [25]. Two major drawbacks of the UNIFAC method are its inability to be used in electrolyte systems and its lack of accuracy for systems which are very nonideal. Another is the MOSCED model which stands for modified separation of cohesive energy density. It also has been reported to give good results for nonelectrolyte systems.

## RESEARCH OBJECTIVES

The objective of this research is to find extractive agents which will effectively separate the following close boiling systems: acetic acid/4-methyl-2-pentanone, formic acid/4-methyl-2-pentanone, and vinyl acetate/ethyl acetate. The agents used could be either pure compounds or mixtures of compounds. They should be chemically as well as thermally stable, easily reclaimable and reusable, and should not react with or cause decomposition of the mixtures to be separated.

It is a further objective of this study to determine whether polarity diagrams are useful in initial screening of potential extractive agents in each of the above mentioned systems when they are considered along with data obtained from the Othmer vapor-liquid equilibrium still for each system.

## SYSTEMS TO BE SEPARATED

### In General

Figures 4 and 5, which follow the descriptions of the three systems to be separated, are shown on pages 24 and 25, respectively. The chemical structures of the components in all three systems as well as structures for the principle extractive agents used are illustrated for convenience of reference [13,26]. The mixtures were obtained from Hoechst Celanese. The company oxidizes n-butane to obtain both acetic and formic acids. However during this partial oxidation reaction all kinds of other impurities get into the desired product, three of which were studied in this thesis: 4-methyl-2-pentanone, vinyl acetate and ethyl acetate. The ketone and acetates pass through the typical distillation process without being separated. This causes a problem because upon standing, the acids now discolor due to the impurities present. Only clear acids are commercially desirable and so it only makes sense that the company which can do this will control the market.

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

Acetic acid has a molecular weight of 60.05 and a boiling point of 117.9° 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. It currently sells for between 29¢ and 31¢ per pound. Hoechst Celanese's two plants in Clear Lake and Pampa, Texas supply nearly half of the 3.7 billion pounds that are produced annually [13].

4-methyl-2-pentanone has a molecular weight of 100.16 and a boiling point of 117°C. Over 80% of the total compound produced annually is used as a general solvent in coating processes (paints, varnishes, lacquers, etc.) and processes for making adhesives, pesticides and rubber processing chemicals. Fourteen percent is exported annually. Its current value is around 38¢ per pound. The largest producer is Union Carbide in Institute, West Virginia which supplies 65 million pounds per year [13].

Acetic acid and 4-methyl-2-pentanone boil only 0.9°C apart thus having a relative volatility extremely close to 1.0. This is almost as difficult to separate as an azeotrope which suggests that distillation would be nearly impossible without the use of an extractive agent [31].

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

Formic acid has a molecular weight of 46.03 and a boiling point of 100.8°C. It has about the same strength as sulfuric acid and may cause severe burns if improperly handled. Industrial uses are in textile dyeing and finishing (21%), pharmaceuticals (20%), rubber intermediates (16%), leather and tanning treatment (15%), and catalysts (12%). It currently sells for 36.5¢ per pound and is provided mainly by Hoechst Celanese's Pampa, Texas plant producing 25 million pounds annually. The 4-methyl-2-pentanone was already discussed [13].

The two components boil 16.2°C apart, however they do form a close boiling mixture. Separation is achieved by distillation with any one of a number of extractive agents being used. The formic acid in this system was unpure due to a water content of about 5%. Some extractive agents caused decomposition to occur in this system [34].

Vinyl Acetate/Ethyl Acetate

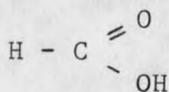
Vinyl acetate has a molecular weight of 86.09 and boils at 72° C. Over 60% of its industrial use is in polyvinyl acetate emulsions and resins (40%), polyvinyl alcohols (15%) and polyvinyl butyrals (8%). Export estimates are at 27%. It currently sells for 39 to 40¢ per pound. Hoechst Celanese's Bay City and Clear Lake, Texas plants produce 1.1 billion pounds of the 2.7 billion produced yearly [13].

Ethyl acetate has a molecular weight of 88.11 and boils at 76.5° C. 60% of its industrial use is in coatings solvent (40%), miscellaneous solvents (12%), and plastics (8%), and approximately 38% is exported. It currently sells for 41 to 42.5¢ per pound. The annual supply of 210 million pounds is equally produced by Eastman, Celanese and Monsanto [13].

The two components boil only 4.5° C apart and thus have a relative volatility of nearly 1.0. Both effective and ineffective extractive agents were observed during investigations of this system [30].

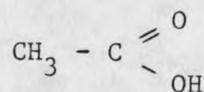
B.P. = 100.8°C

MW = 46.03

Formic Acid

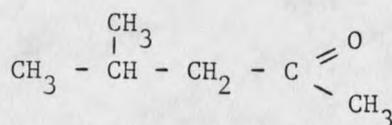
B.P. = 117.9°C

MW = 60.05

Acetic Acid

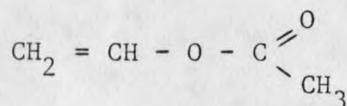
B.P. = 117°C

MW = 100.16

4-Methyl-2-Pentanone

B.P. = 72°C

MW = 86.09

Vinyl Acetate

B.P. = 76.5°C

MW = 88.11

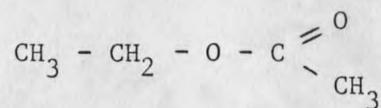
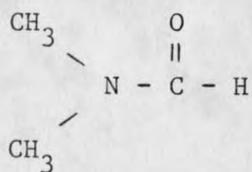
Ethyl Acetate

Figure 4. Structures and physical data for system components [13,26].

B.P. = 153°C

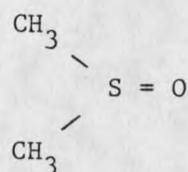
MW = 73.10



Dimethylformamide  
(DMFA)

B.P. = 189°C

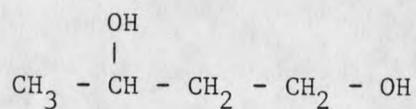
MW = 78.13



Dimethylsulfoxide  
(DMSO)

B.P. = 203°C

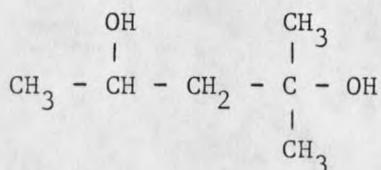
MW = 90.12



1,3-Butanediol

B.P. = 197°C

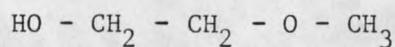
MW = 118.18



2-Methyl-2,4-Pentanediol  
(Hexylene Glycol)

B.P. = 124°C

MW = 76.10



Ethylene Glycol Methyl Ether  
(Methyl Cellosolve)

Figure 5. Structures and physical data for key extractive agents [13,26].

## EXPERIMENTAL AND ANALYTICAL EQUIPMENT

### Othmer Vapor-Liquid Equilibrium Still

The Othmer vapor-liquid equilibrium still was used as an initial screening device to find potentially successful extractive agents for all three systems. It should be pointed out here that the data obtained at this level merely suggests that these agents may work on a larger scale. When the time comes to decide which agents to try in the perforated-plate column, the following constraints are considered: (i) values for relative volatility obtained from the Othmer still, (ii) which agents there are enough of for use in larger scale runs, (iii) which agents will be safe in the laboratory, and (iv) which agents will be most cost efficient on a larger scale for use and reuse [13]. Figure 6 on page 27 illustrates the Othmer vapor-liquid equilibrium still used for preliminary investigations. A discussion of the system follows.

The mixture to be separated is introduced to the still along with a known volume fraction of agent to be tested. Although the total volume introduced to the still is relatively unimportant, the amount must be sufficient to maintain a liquid level between points A and B during operation. Heat for vaporization of the liquid is supplied to the bottom of the still by means of a heating coil. The outside of the still is covered with insulation to prevent condensation of the vapor leaving the still before it reaches the primary condenser. The condensing vapor continuously flushes the vapor sampling tube and returns to the stillpot by means of an overflow tube. To insure that atmospheric pressure is maintained in the still,

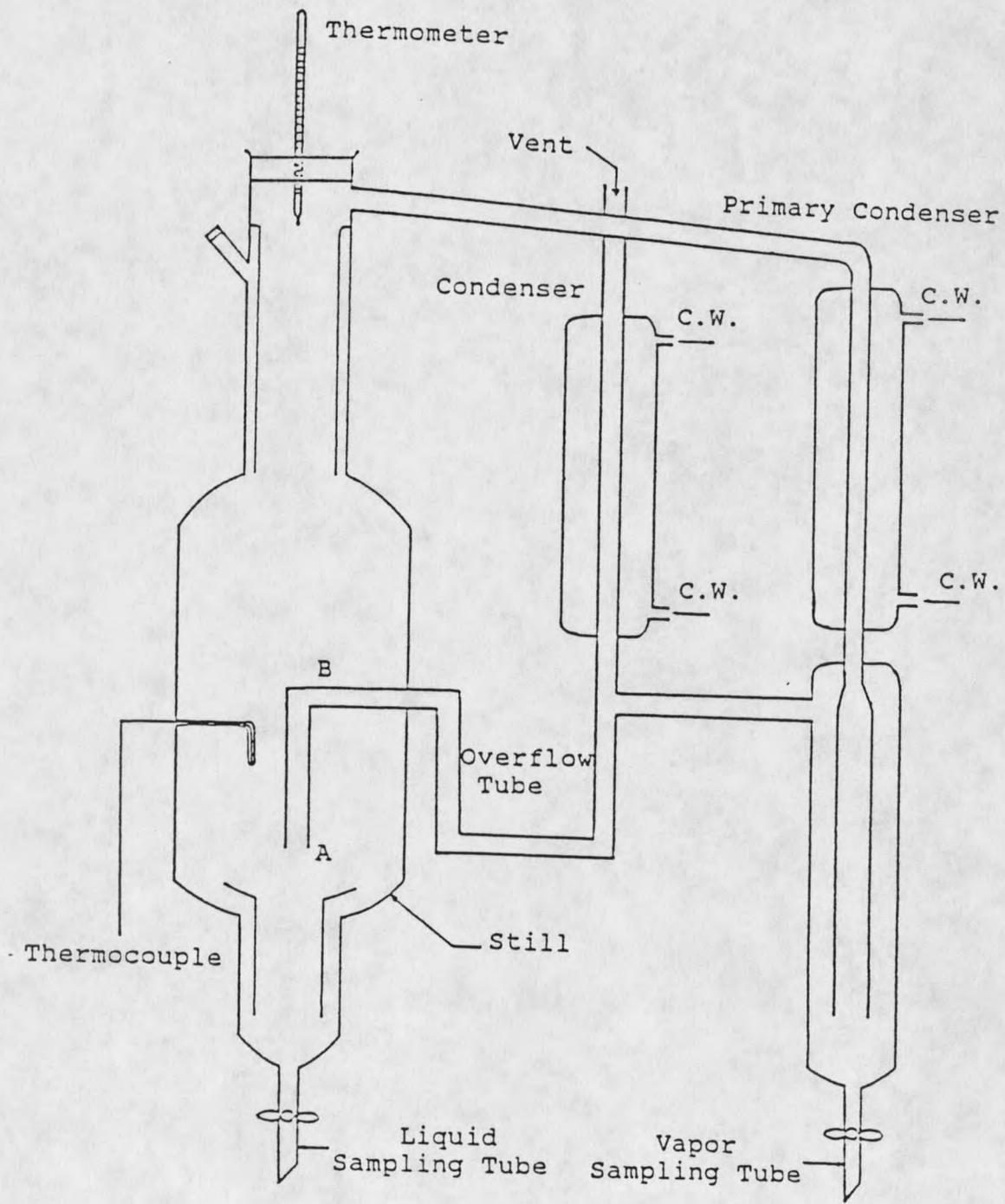


Figure 6. Othmer vapor-liquid equilibrium still.

it is equipped with a vent on the overflow tube. This vent is equipped with an additional condenser so that no material is lost from the system to the atmosphere.

Vapor-liquid 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 ports for analysis on the gas chromatograph. The Othmer still in effect represents one equilibrium stage or one theoretical plate. By analyzing the vapor and liquid samples on the gas chromatograph, the relative volatility of the components for one equilibrium stage may be determined. As a further aid in the analysis of the data, a thermometer and thermocouple are available for measurement of vapor and liquid temperatures, respectively.

### The Perforated-Plate Column

From the list of successful extractive agents obtained from the Othmer still, a few of them which had the characteristics mentioned previously were tested in the perforated-plate column. Figure 7 on page 29 illustrates the column features. Szabados [27] showed that semi-batch operation of the perforated-plate column, for reasons of simplicity as well as for conservation of chemical materials, did not significantly affect experimental results.

The column is mainly a stripping column with a rectification section above the extractive agent feedpoint. The main components of the column and a brief description, as reported by Rall [10], 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

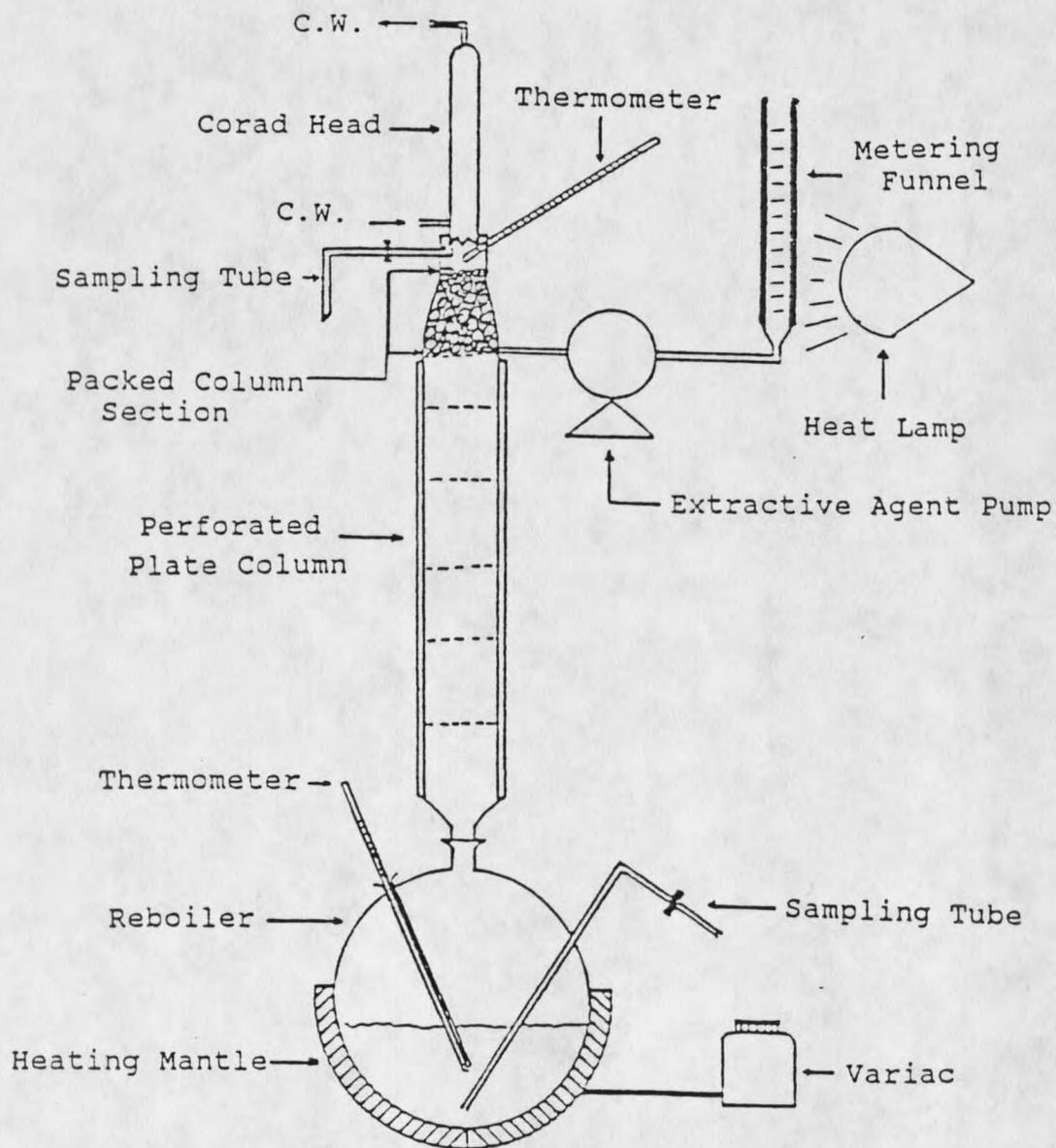


Figure 7. Batch-wise extractive distillation column.

point to the overhead sample 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, 5:1, 3:1, and 2:1. The head is also fitted with a thermometer port for overhead temperature measurement.

- (2) Section of packed column. Four inches of insulated packed column separate the Corad head from the perforated-plate section of column. The packing is  $3/8'' \times 1/4''$  bits of glass tubing. Its function is to prevent dynamic carryover of the extractive agent into the overhead product.
- (3) Perforated-plate column. An Oldershaw perforated-plate column comprised the contacting portion of the column. It is silvered and vacuum jacketed to minimize heat loss. The column is 20 inches long containing 8 actual plates with a 1.5 inch separation between plates. Liquid height on each of the plates is  $3/8$  inch.
- (4) 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.
- (5) Extractive agent pump. Preheated extractive agent is supplied to an adjustable micro-bellows metering pump by means of a calibrated 200 ml. glass funnel. The extractive agent enters the column between the packed column and perforated-plate column sections. 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 temperatures. It is also advantageous to have a stop watch on hand to aid in measuring flow rates.

#### Extractive Agent Recovery

Extractive agents may be easily recovered when necessary by a simple distillation process like the one pictured in Figure 8 on page 32. 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.

Following an extractive distillation column run, the resulting bottoms mixture is 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.

#### The Gas Chromatograph

The bottoms and overhead products from experimental runs in both the Othmer vapor-liquid equilibrium still and perforated-plate column were analyzed using a gas chromatograph. The gas chromatograph used was a Varian Aerograph model 1400 which utilizes a six foot column containing standard Poropak QS packing. Data was output to a Welch-Sargent model SRG recorder in the form of peak heights. Peak height 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 column.

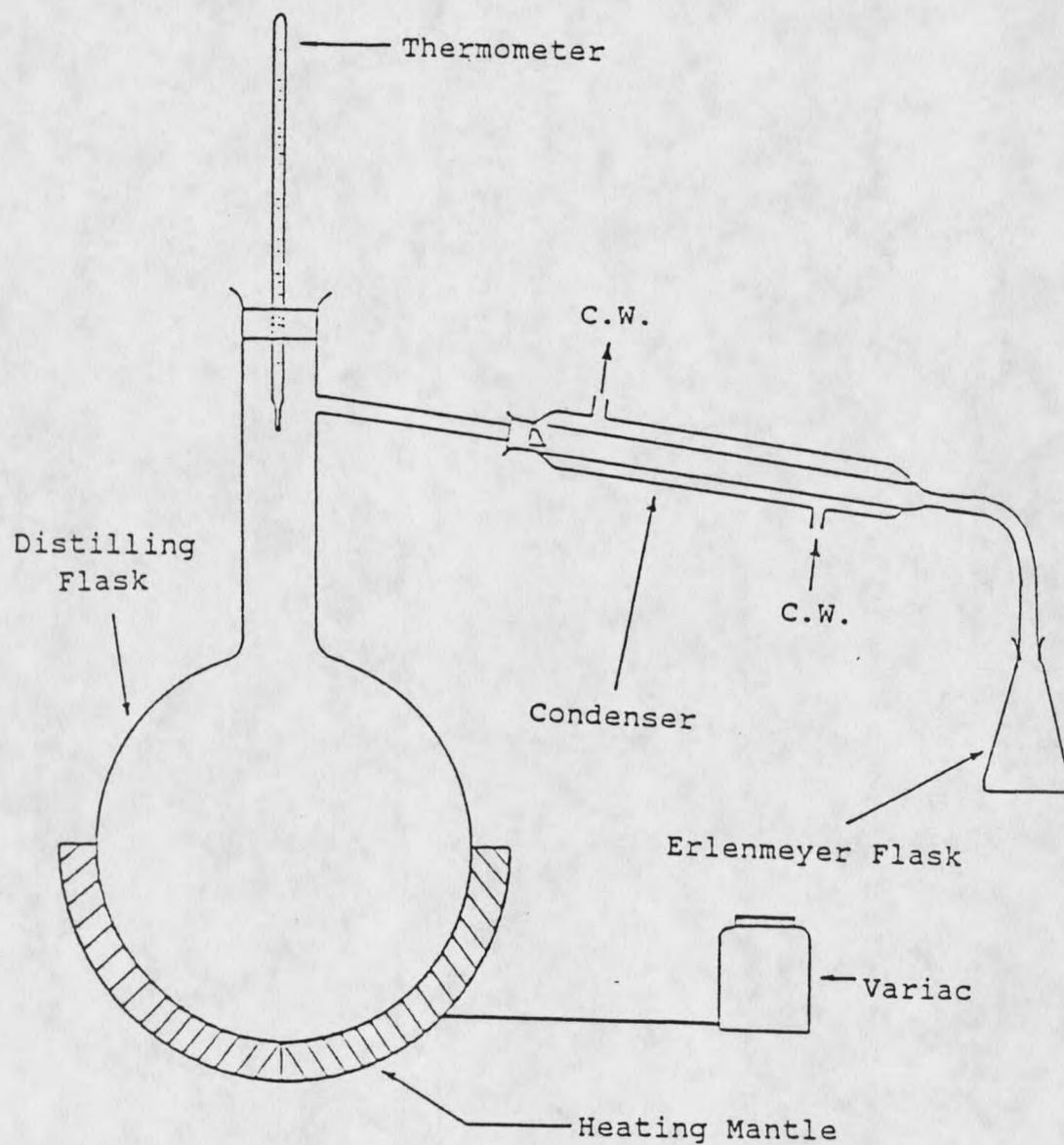


Figure 8. Agent recovery by simple distillation.

## EXPERIMENTAL PROCEDURE

### Operation of the Othmer Still

Fifty grams of the mixture to be studied is charged to the Othmer vapor-liquid equilibrium still along with fifty grams of pure extractive agent or extractive agent mixture. This charge is then allowed to reflux in the still for at least six hours to assure that a state of equilibrium has been reached. Samples are taken for analysis from the condensed overhead vapor and from the bottoms product. The still is flushed with acetone and blown dry with compressed air at the conclusion of a run in order to prepare it for the next charge.

Analysis of the samples on the gas chromatograph gives an indication of the extractive agent's potential effectiveness, and also discloses the amount, if any, of decomposition in the system.

### Calibration of the Perforated-Plate Column

Ratanapuech [28], Vosburgh [29], Yeh [12], and Szabados [27] have all conducted calibration experiments on the perforated-plate column that was utilized in this thesis. Their calibrations used a variety of ideal test mixtures with known relative volatilities, and Yeh's work included calibration with extractive agents present. It was their unanimous conclusion that the number of theoretical plates in the column was a calibrated value of 4.5.

For the experiments of this thesis, however, the value reported by Rall [10] of 5.3 was used. Rall decided the column was not plumb and it was therefore causing the liquid level to vary across the surface of the perforated-plates in the column.

After proper plumbing, column calibration was carried out using a mixture of known relative volatility as described below.

A mixture of 100 grams of toluene (110.6°C) and methylcyclohexane (100.9°C) was charged to the Othmer still and refluxed for 4 hours. Analysis of the overhead and bottoms products revealed 73.1% toluene and 26.9% methylcyclohexane in the vapor, 80% toluene and 20% methylcyclohexane in the liquid. This gives a relative volatility of 1.47 and compares favorably with the known value of 1.5 [10].

A charge of 134 grams of toluene and 16 grams of methylcyclohexane was then charged to the perforated-plate column. The column was operated at total reflux for 2 hours with a boil-up rate of 60 ml. per minute. Product samples were taken and analysis revealed 24% methylcyclohexane and 76% toluene in the vapor, 4% methylcyclohexane and 96% toluene in the liquid. Using the Fenske equation, the number of theoretical plates in the column was found to be 5.3.

It should be noted that the value of 5.3 is probably accurate for the system used to do the calibration but it may or may not be a fair assumption for the systems in this thesis. Previous researchers have used the calibrated column value in their system calculations. The author realizes that this method of column calibration has its shortcomings. However, in light of the fact that no better method can be found in the literature, it can be considered reasonable.

#### 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 close boiling mixture is introduced as an initial charge, but extractive agent is added continuously throughout the operation.

Approximately 200 grams of the close boiling mixture was charged to the stillpot in the beginning. 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 to achieve operating conditions.

In the meantime, the extractive agent mixture was being heated to about 100° C for use on the acetic acid/4-methyl-2-pentanone and formic acid/4-methyl-2-pentanone systems and to about 70° C for use on the vinyl acetate/ethyl acetate system. These warming temperatures were picked somewhere close to the boiling points present in each mixture so that upon addition, the efficiency of the column would not decrease because of having to compensate for a cooler temperature [13]. 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. Overhead and bottoms samples were taken at half-hour intervals from the time at which agent addition began until equilibrium in the column was established. Extractive agent was fed above the top plate in the column at a rate of approximately 16 ml. per minute. The rate of extractive agent was easily verified since the flask from which the micro-bellows pump fed was calibrated. Heat to the column was adjusted to achieve a boil-up rate of between 48 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 accomplished 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 boiling extractive agents or with higher extractive agent addition rates were avoided.

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

## RESULTS

Vinyl Acetate/Ethyl Acetate

The vinyl acetate/ethyl acetate system was initially separated using various extractive agents in the Othmer still. Single agents and mixtures of agents that appear to be effective on this system are listed below in Table 3 [30].

Table 3. Effective agents for vinyl acetate/ethyl acetate.

Compounds	Ratios	Relative Volatility
2-Methyl-2, 4-pentanediol	2	1.25
2-Methyl-2, 4-pentanediol, Ethylene glycol methyl ether	1:1	1.28
2-Methyl-2, 4-pentanediol, Diethylene glycol ethyl ether	1:1	1.20
2-Methyl-2, 4-pentanediol, Butoxypropanol	1:1	1.15
1,3-Butanediol	2	1.19
1,3-Butanediol, Ethylene glycol methyl ether	1:1	1.23
Butoxypropanol	2	1.17
Ethylene glycol methyl ether	2	1.20
Diethylene glycol ethyl ether	2	1.19
Ethylene glycol methyl ether, Diethanol amine	1:1	1.22

The ratios and relative volatility values are easy to obtain from this table. For example, 2 parts 1,3-butanediol added to 1 part vinyl acetate/ethyl acetate yielded a relative volatility value of 1.19 and 1 part 1,3-butanediol plus 1 part ethylene glycol methyl ether added to 1 part vinyl acetate/ethyl acetate yielded a value of 1.23.

After the initial screening, two of the effective extractive agent mixtures were chosen for runs in the perforated-plate column. In the first run, a mixture of 50 wt.% 2-methyl-2,4-pentanediol (Hexylene glycol) and 50 wt.% ethylene glycol methyl ether (Methyl Cellosolve) was used. In the second run, the latter compound above was mixed with 50 wt.% 1,3-butanediol to form the extractive agent. The results of these runs are listed in Table 4 below. Please note that in this table and also in those to follow, under the heading "Column", O represents overhead and B represents bottoms products.

Table 4. Column results for vinyl acetate/ethyl acetate.

Agent	Column	Time, hrs.	Weight % Vinyl Acetate	Weight % Ethyl Acetate	Relative Volatility
2-Methyl-2,4-pentanediol - Ethylene glycol methyl ether	O	0.5	66.0	34.0	1.17
	B		45.3	54.7	
"	O	1	66.4	33.6	1.18
	B		46.0	54.0	
"	O	1.5	65.4	34.6	1.21
	B		40.5	59.5	
1,3-Butanediol - Ethylene glycol methyl ether	O	0.5	68.4	31.6	1.21
	B		43.8	56.2	
"	O	1	66.0	34.0	1.18
	B		44.6	55.4	

Although several glycol and glycol ether mixtures were effective in separating the vinyl acetate/ethyl acetate system, some agents that might have been expected to be successful were not effective. Table 5 on page 39 lists these deficient agents. Typically, an agent is considered not to be effective when either decomposition occurs or a relative volatility value of less than 1.0 is obtained.

Table 5. Ineffective agents for vinyl acetate/ethyl acetate.

---

1,4-Butanediol
1,5-Pentanediol
1,6-Hexanediol
Diethylene glycol
Dipropylene glycol
Butoxypropanol
Ethylene glycol ethyl ether
Ethylene glycol hexyl ether
Ethylene glycol phenyl ether
Ethylene glycol diacetate
Diethylene glycol methyl ether
Diethylene glycol ethyl ether
Propylene glycol methyl ether
Propylene glycol propyl ether
Propylene glycol isobutyl ether
Dipropylene glycol methyl ether
Glycerol triacetate
Triethylene glycol
Tripropylene glycol methyl ether
1,3-Butanediol - Diethylene glycol ethyl ether
1,4-Butanediol - Diethylene glycol methyl ether
1,4-Butanediol - Diethylene glycol diethyl ether
Ethylene glycol methyl ether - Triethylene glycol
Ethylene glycol methyl ether - Dimethyl isopropanol amine
Diethylene glycol ethyl ether - Diethyl ethanol amine

---

Acetic Acid/4-Methyl-2-Pentanone

Preliminary data for the acetic acid/4-methyl-2-pentanone system was gathered from the Othmer still in the same manner described for vinyl acetate/ethyl acetate. Table 6 below and on the following pages lists compounds that were used with the key component of dimethylsulfoxide to form extractive agent mixtures which were successful at increasing the relative volatility in the Othmer still. Table 7 which follows contains similar data except the key component in the extractive agent mixtures is dimethylformamide [31,32].

Table 6. Effective agents for acetic acid/4-methyl-2-pentanone using DMSO [31].

Compounds	Ratios		Relative Volatilities	
Dimethylsulfoxide (DMSO)	2	12/5	2.2	2.2
DMSO, Acetyl salicylic acid	$(1/2)^2$	$(3/5)^2$	2.3	3.3
DMSO, Adipic acid	"	"	4.4	4.0
DMSO, Azelaic acid	"	"	3.4	2.6
DMSO, Benzoic acid	"	"	2.5	2.6
DMSO, 2-Benzoylbenzoic acid	"	"	3.8	3.0
DMSO, p-tertiary Butyl benzoic acid	"	"	2.9	3.4
DMSO, Cinnamic acid	"	"	2.9	2.5
DMSO, Decanoic acid	"	"	5.4	3.5
DMSO, Dodecanedioic acid	"	"	2.2	2.8
DMSO, Glutaric acid	"	"	3.1	2.6
DMSO, Heptanoic acid	"	"	2.9	3.4
DMSO, Hexanoic acid	"	"	2.1	3.2
DMSO, 4-Hydroxybenzoic acid	"	"	2.2	2.2
DMSO, Itaconic acid	"	"	3.2	3.3
DMSO, Malic acid	"	"	3.5	2.8
DMSO, Methyl isoamyl ketone	"	"	1.6	1.6
DMSO, Myristic acid	"	"	2.7	2.0
DMSO, Neodecanoic acid	"	"	3.9	4.4
DMSO, Neopentanoic acid	"	"	2.0	2.5
DMSO, m-Nitrobenzoic acid	"	"	2.2	2.6
DMSO, p-Nitrobenzoic acid	"	"	1.4	2.5

Table 6 - continued

Compounds	Ratios		Relative Volatilities	
DMSO, Octanoic acid	$(1/2)^2$	$(3/5)^2$	3.1	2.5
DMSO, Oxalic acid	"	"	4.1	4.6
DMSO, Diethylene glycol diethyl ether	"	"	1.2	1.2
DMSO, Salicylic acid	"	"	2.1	2.6
DMSO, Sebacic acid	"	"	2.3	2.3
DMSO, Succinic acid	"	"	2.5	2.7
DMSO, o-Toluic acid	"	"	2.6	2.6
DMSO, m-Toluic acid	"	"	2.6	3.0
DMSO, p-Toluic acid	"	"	2.1	2.5
DMSO, 3,4,5-Trimethoxybenzoic acid	"	"	3.5	3.2
DMSO, Undecanoic acid	"	"	2.2	2.1
DMSO, Acetyl salicylic acid, Acetophenone	$(1/3)^3$	$(2/5)^3$	1.9	2.7
DMSO, Adipic acid, Adiponitrile	"	"	3.2	3.3
DMSO, Azelaic acid, Diisobutyl ketone	"	"	2.0	2.2
DMSO, Benzoic acid, Anisole	"	"	1.7	1.7
DMSO, 2-Benzoylbenzoic acid, Glycerol triacetate	"	"	2.1	1.3
DMSO, p-tert. Butyl benzoic acid, Methyl salicylate	"	"	1.7	1.5
DMSO, Cinnamic acid, Butyl ether	"	"	1.6	1.8
DMSO, Decanoic acid, Cyclohexanone	"	"	2.8	2.5
DMSO, Dodecanedioic acid, Diisobutyl ketone	"	"	2.0	2.0
DMSO, Glutaric acid, Methyl isoamyl ketone	"	"	1.7	1.4
DMSO, Heptanoic acid, Ethyl benzoate	"	"	2.6	2.3
DMSO, Hexanoic acid, Methyl benzoate	"	"	1.8	1.9
DMSO, 4-Hydroxybenzoic acid, Ethylene glycol diacetate	"	"	1.9	1.9

Table 6 – continued

Compounds	Ratios		Relative Volatilities	
DMSO, Itaconic acid, 2-Octanone	$(1/3)^3$	$(2/5)^3$	2.2	2.2
DMSO, Malic acid, Diethylene glycol dibenzoate	"	"	2.8	2.2
DMSO, Myristic acid, Hexyl acetate	"	"	2.2	2.6
DMSO, Neodecanoic acid, Isophorone	"	"	3.1	3.9
DMSO, Neopentanoic acid, 2-Heptanone	"	"	2.0	2.1
DMSO, m-Nitrobenzoic acid, Benzyl acetate	"	"	1.7	1.4
DMSO, p-Nitrobenzoic acid, Isobutyl heptyl ketone	"	"	1.1	1.4
DMSO, Octanoic acid, Butyl benzoate	"	"	2.4	2.0
DMSO, Oxalic acid, 2-Octanone	"	"	2.1	3.1
DMSO, Undecanoic acid, Benzyl benzoate	"	"	2.9	2.5
DMSO, Salicylic acid, Ethyl salicylate	"	"	1.9	1.6
DMSO, Sebacic acid, Ethyl butyl ketone	"	"	1.8	1.9
DMSO, Succinic acid, 2-Undecanone	"	"	1.7	1.8
DMSO, o-Toluic acid, Diethylene glycol dimethyl ether	"	"	1.9	2.2
DMSO, m-Toluic acid, Diethylene glycol diethyl ether	"	"	1.6	2.0
DMSO, p-Toluic acid, Dipropylene glycol dibenzoate	"	"	2.1	1.2
DMSO, 3,4,5-Trimethoxybenzoic acid, Ethyl phenyl acetate	"	"	3.6	2.6
DMSO, Undecanoic acid, Diethyl maleate	"	"	1.7	1.1

The two relative volatility values shown in Table 6 are for the two different ratios of extractive agent mixtures that were investigated. For example, 1/2 part of dimethylsulfoxide plus 1/2 part acetyl salicylic acid with one part acetic acid/4-methyl-2-pentanone gives a relative volatility of 2.3 whereas 3/5 part DMSO plus 3/5 part acetyl salicylic acid with one part acetic acid/4-methyl-2-pentanone gives

a relative volatility of 3.3. In both cases, the superscript 2 means there are 2 components present in the extractive agent mixture. The following table is interpreted in the same way however dimethylformamide is the key component of the extractive agent mixtures in this case.

Table 7. Effective agents for acetic acid/4-methyl-2-pentanone using DMFA [32].

Compounds	Ratios		Relative Volatilities	
Dimethylformamide (DMFA)	2	12/5	3.2	3.3
DMFA, Adipic acid	$(1/2)^2$	$(3/5)^2$	2.0	2.3
DMFA, Acetyl salicylic acid	"	"	1.3	1.9
DMFA, Cinnamic acid	"	"	1.9	1.6
DMFA, Decanoic acid	"	"	1.1	1.2
DMFA, Glutaric acid	"	"	1.2	1.3
DMFA, Heptanoic acid	"	"	1.5	1.7
DMFA, Hexanoic acid	"	"	1.7	1.3
DMFA, Pelargonic acid	"	"	1.5	1.4
DMFA, Neodecanoic acid	"	"	2.3	1.9
DMFA, Octanoic acid	"	"	1.1	2.1
DMFA, Salicylic acid	"	"	1.1	1.5
DMFA, Sebacic acid	"	"	1.2	1.5
DMFA, m-Toluic acid	"	"	2.4	1.2
DMFA, p-Toluic acid	"	"	2.3	1.7
DMFA, Adipic acid, Diethyl glycol dibenzoate	$(1/3)^3$	$(2/5)^3$	2.2	2.1
DMFA, Acetyl salicylic acid, Ethylene glycol phenyl ether	"	"	1.1	1.4
DMFA, Azelaic acid, Propiophenone	"	"	2.2	1.1

Table 7 - continued

Compounds	Ratios		Relative Volatilities	
DMFA, Cinnamic acid, Diethyl maleate	(1/3) <sup>3</sup>	(2/5) <sup>3</sup>	2.1	1.3
DMFA, Decanoic acid, Benzyl benzoate	"	"	1.1	1.2
DMFA, Glutaric acid, Diethylene glycol diethyl ether	"	"	2.9	2.2
DMFA, Hexanoic acid, Ethyl benzoate	"	"	3.1	1.2
DMFA, Heptanoic acid, Benzyl ether	"	"	2.4	1.7
DMFA, Pelargonic acid, Methyl benzoate	"	"	1.5	1.6
DMFA, Neodecanoic acid, 2-Octanone	"	"	1.3	1.2
DMFA, Octanoic acid, Cyclohexanone	"	"	1.5	2.4
DMFA, Salicylic acid, Ethyl acetoacetate	"	"	2.8	1.6
DMFA, Sebacic acid, Ethylene glycol methyl ether acetate	"	"	1.7	1.6
DMFA, m-Toluic acid, Isobutyl heptyl ketone	"	"	2.4	1.4

Once again, some agents that might have been expected to be successful on this system but were not are listed for reference in Table 8 below.

Table 8. Ineffective agents for acetic acid/4-methyl-2-pentanone using DMFA.

Dimethylformamide (DMFA), Azelaic acid
DMFA, Itaconic acid
DMFA, Itaconic acid, Ethylene glycol butyl ether acetate
DMFA, p-tert. Butyl benzoic acid
DMFA, p-tert. Butyl benzoic acid, Ethylene glycol ethyl ether acetate
DMFA, Benzoic acid
DMFA, Benzoic acid, Butyl ether
DMFA, o-Toluic acid
DMFA, o-Toluic acid, Ethyl phenyl ether

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 9 contains the results obtained using the agent chosen from Table 6 which was a 50-50 volume % mixture of DMSO and methyl isoamyl ketone. Similarly, Table 10 contains the results obtained using the agent chosen from Table 7 which was a one-third equal volume mixture of DMFA, pelargonic acid and methyl benzoate.

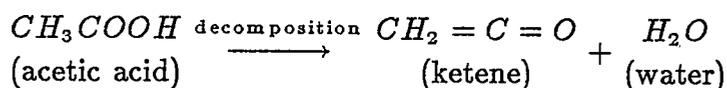
Table 9. Column results for acetic acid/4-methyl-2-pentanone using DMSO [31].

Agent	Column	Time, hrs.	Weight % 4-Me-2-Pt	Weight % Acetic Acid	Relative Volatility
50% DMSO, 50% Methyl isoamyl ketone	O	0.5	23.9	76.1	1.25
	B		8.8	91.2	
50% DMSO, 50% Methyl isoamyl ketone	O	1	47.4	52.6	1.25
	B		21.7	78.3	

Table 10. Column results for acetic acid/4-methyl-2-pentanone using DMFA [32].

Agent	Column	Time, hrs.	Weight % Ketone	Weight % Acetic acid	Relative Volatility
33% DMFA, 33% Pelargonic acid, 33% Methyl benzoate	O	0.5	84.6	15.4	1.57
	B		33.3	66.7	
33% DMFA, 33% Pelargonic acid, 33% Methyl benzoate	O	1	92.3	7.7	1.64
	B		46.2	53.8	

Not all extractive agents tested were successful on the acetic acid/4-methyl-2-pentanone system when using DMSO. When a 50-50 volume % extractive agent mixture of dimethylsulfoxide and pelargonic acid was added to the column during distillation of the above system, the acetic acid was believed to have decomposed exclusively to water and ketene [13].



If this was the case, the water would form a two-phase azeotrope with the 4-methyl-2-pentanone which would come off in the overhead in the liquid phase. This then would form two liquid layers which could be separated by simple decantation. Ketene is a gas with a fairly dangerous toxicity level comparable to that of phosgene gas which was used in World War II. It has a MW of 42.04 ( $CH_2 = C = O$ ) and a normal boiling point of  $-56^\circ C$ . If indeed this gas is present in the overhead, care should be taken when considering its recovery. The DMSO-pelargonic acid mixture, then, could be recovered as a bottoms product from the stillpot. Table 11 shows the results of this run if indeed the unknown peak observed on the gas chromatograph represented ketene [33].

Table 11. Results of decomposition in acetic acid/4-methyl-2-pentanone system.

Column	Time, hr.	Percent Ketene	Percent Water	Percent Acetic acid	Percent 4-Me-2-Pt
O	1/2	37	55.6	0.7	6.7
B		10	11.6	68.4	10.0

Formic Acid/4-Methyl-2-Pentanone

Preliminary data for the formic acid/4-methyl-2-pentanone system was gathered in the same manner as previously described. Table 12 below lists the compounds that were used with the key component of dimethylsulfoxide to form extractive agent mixtures which were successful at separating this close boiling mixture in the Othmer still [34].

Table 12. Effective agents for formic acid/4-methyl-2-pentanone using DMSO.

Compounds	Ratios		Relative Volatilities	
Dimethylsulfoxide (DMSO), Adipic acid	$(1/2)^2$	$(3/5)^2$	5.5	4.8
DMSO, Acetyl salicylic acid	"	"	2.9	3.0
DMSO, Azelaic acid	"	"	4.6	2.4
DMSO, Benzoic acid	"	"	2.4	2.4
DMSO, p-tert. Butyl benzoic acid	"	"	3.7	2.5
DMSO, Cinnamic acid	"	"	2.7	3.5
DMSO, Decanoic acid	"	"	1.1	2.1
DMSO, Glutaric acid	"	"	4.1	5.5
DMSO, Heptanoic acid	"	"	2.0	4.1
DMSO, Hexanoic acid	"	"	1.6	3.3
DMSO, Itaconic acid	"	"	2.9	3.7
DMSO, Neodecanoic acid	"	"	2.8	2.5
DMSO, Octanoic acid	"	"	3.3	2.4
DMSO, Pelargonic acid	"	"	3.4	1.3
DMSO, Salicylic acid	"	"	2.5	3.5
DMSO, Sebacic acid	"	"	3.2	1.3
DMSO, o-Toluic acid	"	"	3.3	5.3
DMSO, m-Toluic acid	"	"	3.8	4.1
DMSO, p-Toluic acid	"	"	5.7	3.6

Table 12 - continued

Compounds	Ratios		Relative Volatilities	
DMSO, Adipic acid, Dipropylene glycol dibenzoate	$(1/3)^3$	$(2/5)^3$	2.4	1.4
DMSO, Acetyl salicylic acid, 2-Undecanone	"	"	2.3	2.3
DMSO, Azelaic acid, Methyl salicylate	"	"	1.8	1.8
DMSO, Cinnamic acid, Benzonitrile	"	"	1.4	1.7
DMSO, Decanoic acid, 2-Methoxyethyl ether	"	"	1.7	2.1
DMSO, Heptanoic acid, Benzyl benzoate	"	"	2.2	1.7
DMSO, Hexanoic acid, Methyl benzoate	"	"	2.1	2.0
DMSO, Itaconic acid, Dipropylene glycol methyl ether acetate	"	"	4.9	2.3
DMSO, Neodecanoic acid, Ethylene glycol diacetate	"	"	2.1	1.8
DMSO, Octanoic acid, Isophorone	"	"	2.8	1.4
DMSO, Pelargonic acid, Acetophenone	"	"	1.5	2.8
DMSO, Sebacic acid, Hexyl acetate	"	"	2.4	2.6
DMSO, o-Toluic acid, Ethyl phenyl acetate	"	"	1.3	1.4
DMSO, m-Toluic acid, Isobutyl heptyl ketone	"	"	3.2	1.7
DMSO, p-Toluic acid, Diphenyl ether	"	"	1.7	1.9

The values in this table are to be interpreted as previously described on pages 42-43. The extractive agent that was chosen for testing in the perforated-plate column was not an exact mixture used in the Othmer still for screening so it does

not appear in Table 12. However, it is very similar to two of the extractive agent mixtures that were initially screened. One would predict that the results would compare favorably with those shown for the agents DMSO-heptanoic acid-benzyl benzoate and DMSO-hexanoic acid-methyl benzoate. Table 13 contains the results obtained in the perforated-plate column using a one-third equal volume mix of DMSO, heptanoic acid and methyl benzoate as the chosen extractive agent.

Table 13. Column results for formic acid/4-methyl-2-pentanone using DMSO.

Agent	Column	Time, hrs.	Weight % Ketone	Weight % Formic acid	Relative Volatility
33% DMSO, 33% Heptanoic acid, 33% Methyl benzoate	O B	0.5	80.0 9.6	20.0 90.4	1.98
33% DMSO, 33% Heptanoic acid, 33% Methyl benzoate	O B	1	76.8 7.5	23.2 92.5	2.02

Table 14 lists some potentially effective agents that were ineffective in the experimentation conducted for this system.

Table 14. Ineffective agents for formic acid/4-methyl-2-pentanone using DMSO.

Dimethylsulfoxide (DMSO), Glutaric acid, Benzyl cyanide

DMSO, Salicylic acid, Diethyl succinate

DMSO, p-tert. Butyl benzoic acid, 4-Methoxy-4-methyl pentanone-2

## DISCUSSION

### The Othmer Still as a Screening Device

From Tables 3, 6, 7 and 12 it is apparent that there are many potentially effective extractive agents for separating the three close boiling systems examined in this thesis. Two different concentrations of agent were tested for most potential extractive agents examined. In some cases the lower concentration appears to give the lowest value for relative volatility and other times the opposite is true. Small, medium, and large gains in relative volatility between low and high concentrations of the same agent can be seen. There are many possible reasons for these occurrences, i.e., (i) temporary upset in operation of the Othmer still, (ii) decomposition, and (iii) an increasingly negative effect by one of the agents in the extractive agent mixture. However, these and others are only proposed ideas.

The only point which may be made from the above discussion is that data taken from the Othmer still is inconclusive. Relative volatility values calculated from data obtained from the still should not be used in design or in any way be misrepresented as being rigorously determined. These values only show results of the initial screening of extractive agents which were shown to enhance the relative volatility. They may or may not be suitable for further investigation.

### Polarity Diagrams as a Screening Device

The use of Hansen and Hildebrand solubility parameters to obtain polarity diagrams is considered to be the current state-of-the-art as a means for screening potentially effective extractive agents to be used on the close boiling mixtures [12]. This technique seems to work very well for binary systems with pure extractive

agents. However, results are questionable when multicomponent extractive agents are used or when ternary or greater systems are considered. The solubility parameters for the close boiling systems studied in this thesis as well as for the key components of the extractive agents utilized are listed in Table 15 below [35].

Table 15. Solubility parameters at 25°C [35].

$$\text{Note that } \delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}.$$

Compound	$\delta_t(MPa^{1/2})$	$\delta_d(MPa^{1/2})$	$\delta_p(MPa^{1/2})$	$\delta_h(MPa^{1/2})$
Formic acid	24.9	14.3	11.9	16.6
Acetic acid	21.4	14.5	8.0	13.5
Ethyl acetate	18.1	15.8	5.3	7.2
Vinyl acetate	18.5	12.9	10.0	8.7
4-methyl- 2-pentanone	17.6	14.4	8.1	5.9
DMSO	26.7	18.4	16.4	10.2
DMFA	24.8	17.4	13.7	11.3
1,3-butanediol	28.9	16.6	10.0	21.5
Hexylene glycol	23.1	12.5	11.4	16.8
Methyl cellosolve	23.9	13.0	10.0	17.4

In Yeh's studies [12], the hydrogen bond parameter,  $\delta_h$ , was plotted against the polar bond parameter,  $\delta_p$ , on a two dimensional diagram to predict agent effectiveness. The dispersion parameter,  $\delta_d$ , was not used because values did not differ appreciably between components and extractive agents. To account for the difference in molar volumes of the close boiling components, the diagram was split into two regions based on molar volumes. In the method, solubility parameters were plotted for components of the close boiling compounds and for the pure extractive agents to be tested. A line was drawn between the two close boiling 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 in the initial mixture.

Figures 9 and 10 on the next two pages show polarity diagrams for acetic acid/4-methyl-2-pentanone and formic acid/4-methyl-2-pentanone systems, respectively. In both cases the extractive agents are shown to be more compatible with the acids rather than the ketone. This is a conclusion based on which side of the perpendicular bisector the extractive agents appear. Similarly, from Figure 11 on page 55 one can see that the extractive agents are more compatible with the vinyl acetate.

Other experimenters have not had such good success with the polarity diagram method. Szabados [27] reported that the use of polarity diagrams was deficient in his experiments. Yeh [12] also had extractive agent models which did not conform. It is the opinion of Barton [35] that an expanded set of parameters using dispersion, induction, orientation, acid, and base interactions is necessary for reliable quantitative evaluation of behavior in multicomponent systems. However, the simplicity with which a polarity diagram may be obtained does seem to present an easy way to initially screen potential extractive agents.

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) [14], another is the UNIFAC method [14]. 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.

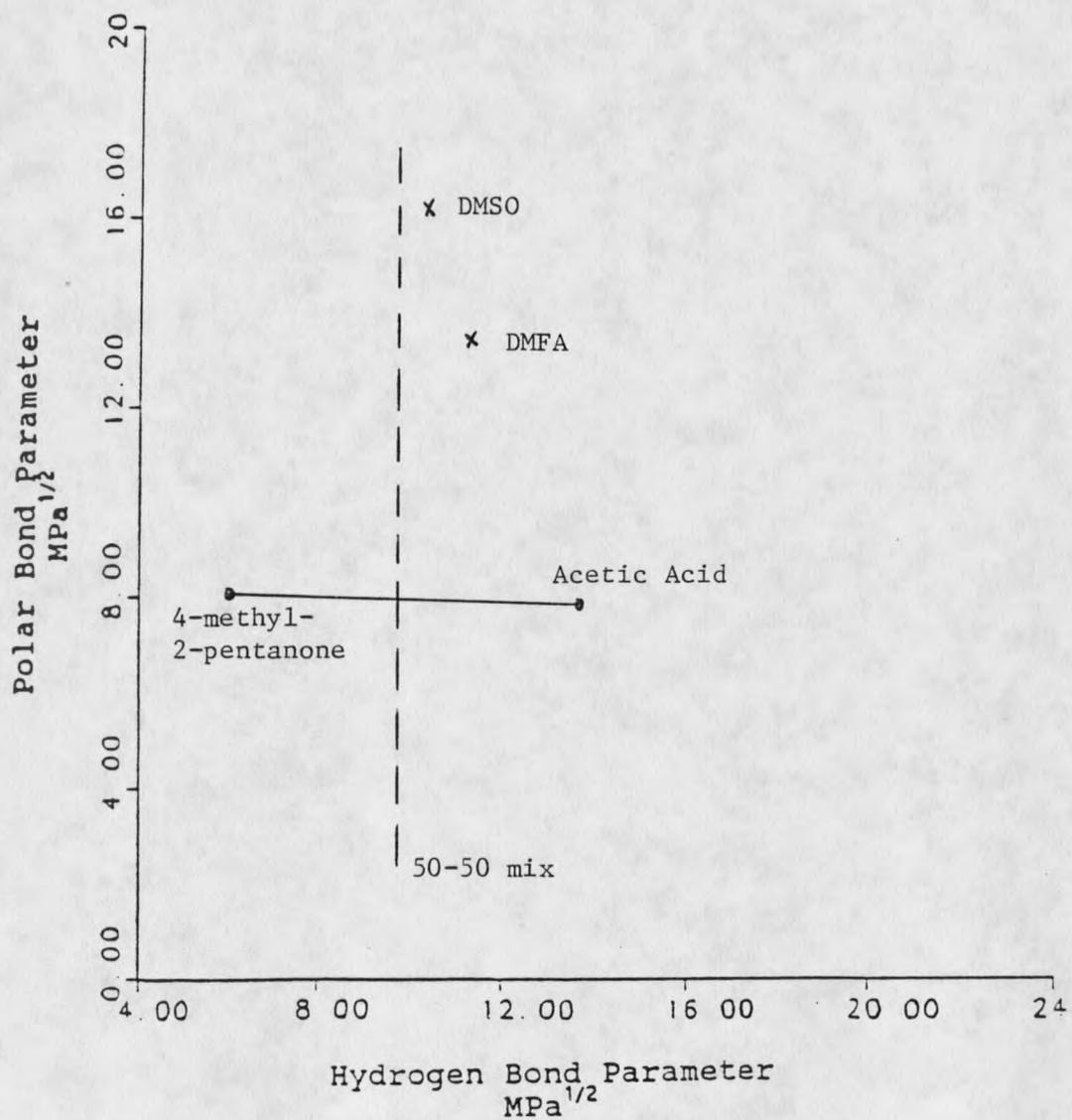


Figure 9. Polarity diagram for acetic acid/4-methyl-2-pentanone.

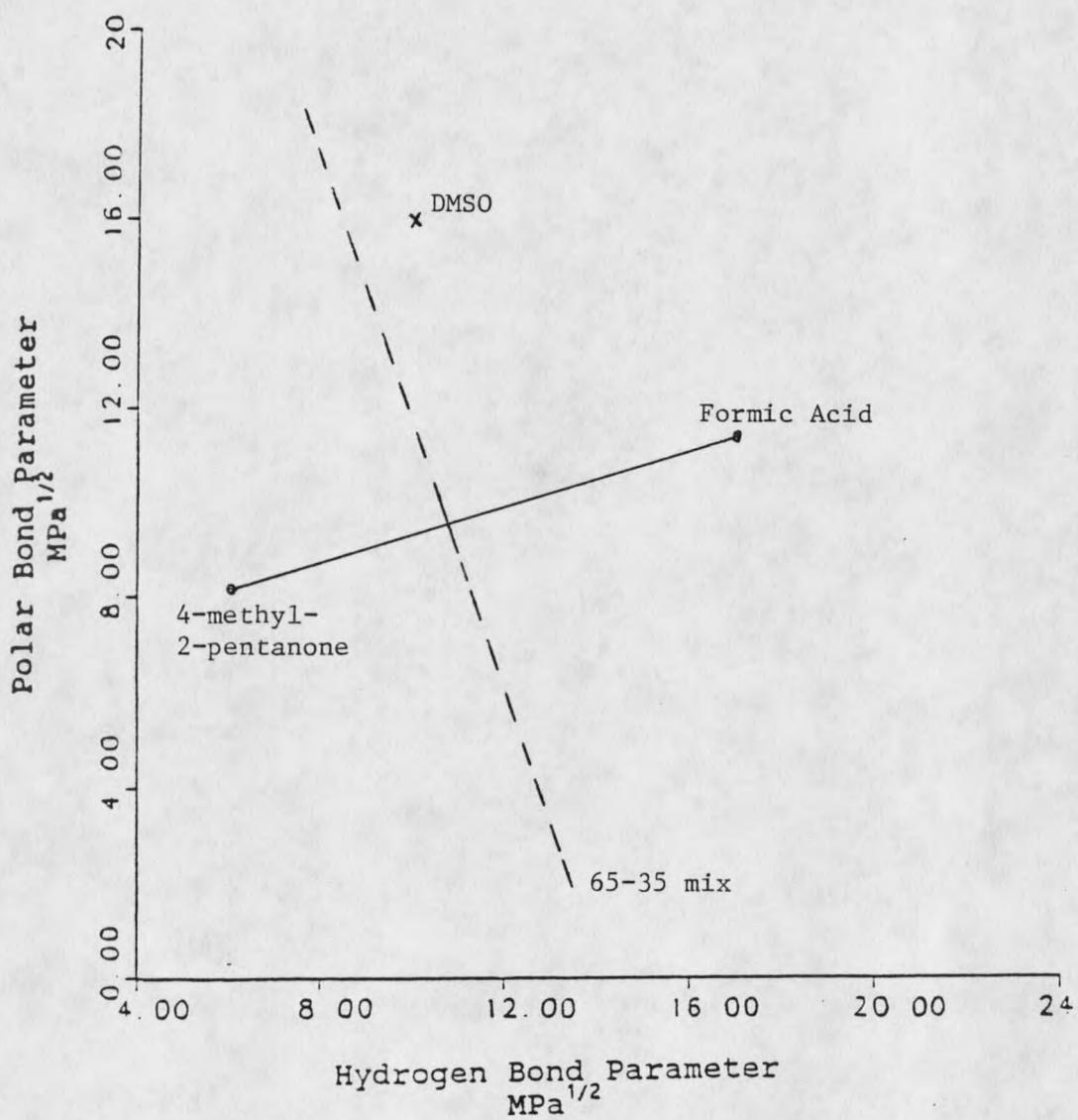


Figure 10. Polarity diagram for formic acid/4-methyl-2-pentanone.

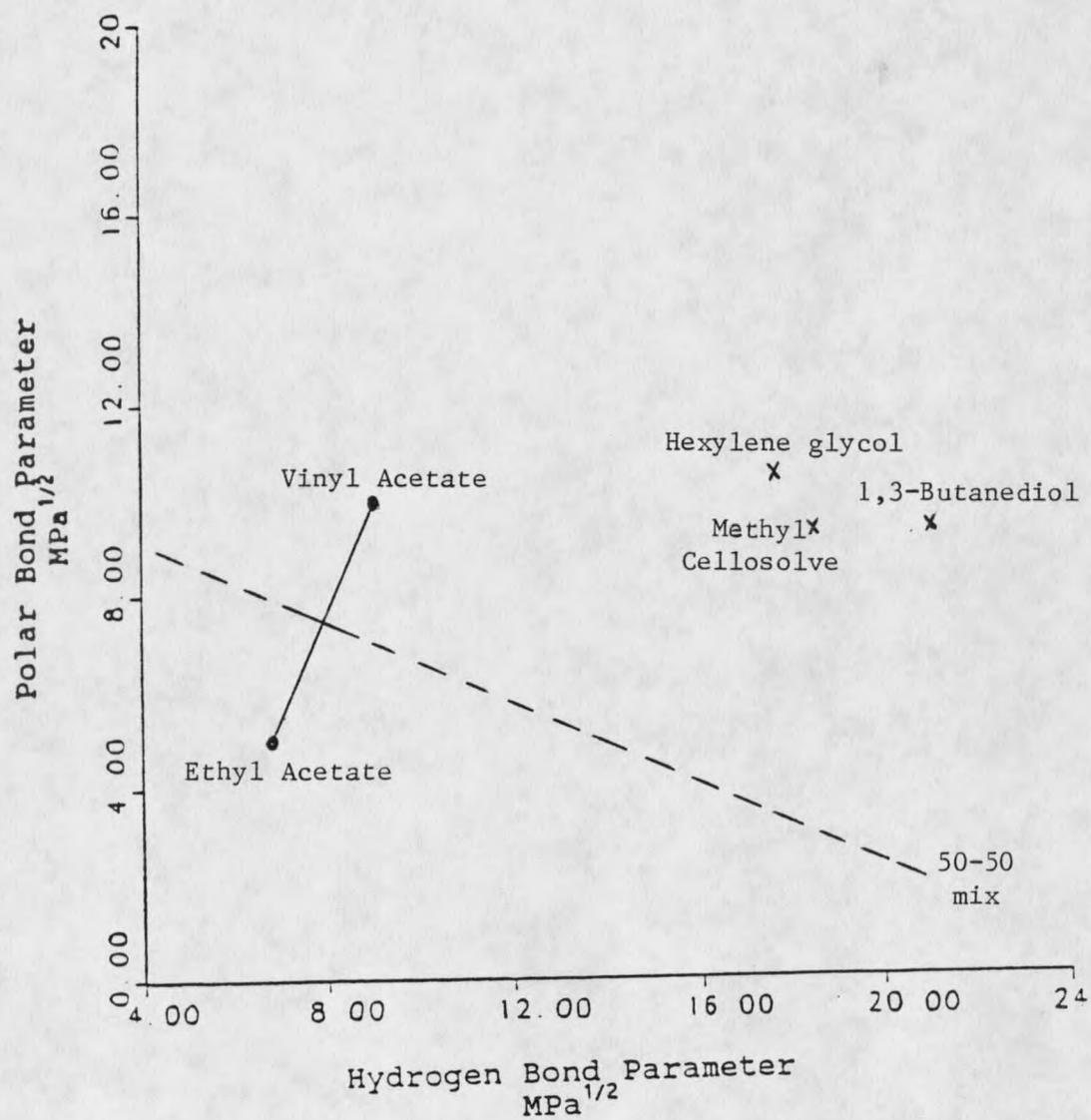


Figure 11. Polarity diagram for vinyl acetate/ethyl acetate.

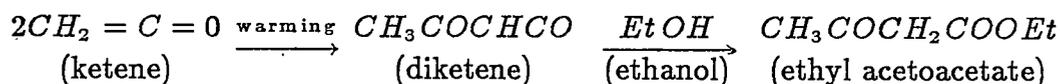
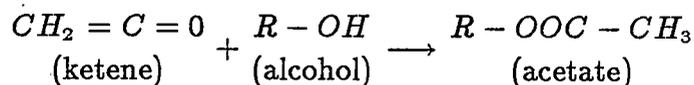
### Data from the Perforated-Plate Column

Data taken from the perforated-plate column is believed to be more accurate than data taken from the Othmer still. Equilibrium is achieved in a shorter period of time in the perforated-plate column thus reducing the possibility of decomposition. Because of the 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 5.3 equilibrium stages instead of one stage.

Two different extractive agent mixtures were tested on the vinyl acetate/ethyl acetate system. First, using a 50-50 weight % mixture of 2-methyl-2,4-pentanediol and ethylene glycol methyl ether as an extractive agent, average relative volatility values of 1.17 after 30 minutes, 1.18 after 1 hour, and 1.21 after 90 minutes were obtained. These values are fairly consistent with the 1.28 value obtained in the Othmer still. The second extractive agent mixture was composed of 50-50 weight % 1,3-butanediol and ethylene glycol methyl ether. Average relative volatility values of 1.21 after 30 minutes and 1.18 after 1 hour were obtained for the perforated-plate column. Again good consistency with the Othmer still value of 1.23 [30] is observed.

The acetic acid/4-methyl-2-pentanone system was tested with three different extractive agent mixtures. The first agent examined, a 50-50 volume % mix of DMSO and pelargonic acid, was believed to have caused decomposition of the acetic acid to ketene gas and water as described earlier. A patent was filed for the recovery of the gas from the overhead which also had a provision for the recovery of pure 4-methyl-2-pentanone. This was done not only because processes for making ketene gas are scarce but also because the compound is useful in making other chemicals in a very efficient manner, i.e., the formation of acetates from alcohols

and the formation of ethyl acetoacetate which has a flowery or fruity odor and is used in industry in artificial essences [32,13]:



The second agent examined consisted of a 50-50 volume % mix of DMSO and methyl isoamyl ketone. Average relative volatility values after 30 minutes and 1 hour in the perforated-plate column were identical, 1.25. In the Othmer still, a value of 1.6 was obtained for two different concentrations of extractive agent. These values have good consistency [31]. The final agent examined was a 1/3 equal volume mix of DMFA, pelargonic acid and methyl benzoate. In the Othmer still, values of 1.5 and 1.6 were obtained at the two different concentration levels. Testing conducted in the perforated-plate column yielded average relative volatility values of 1.57 after 30 minutes and 1.64 after 1 hour had elapsed. Again, the values obtained from both techniques are consistent [32].

The formic acid/4-methyl-2-pentanone system was tested with a 1/3 equal volume mix of DMSO, heptanoic acid and methyl benzoate. Average relative volatility values of 1.98 after 30 minutes and 2.02 after 1 hour were obtained in the perforated-plate column. This exact extractive agent mixture was not tested in the Othmer still, however, two similar mixtures were tested and because they are both very similar in composition, those values will be used for comparison. For a 1/3 equal volume mix of DMSO, heptanoic acid and benzyl benzoate, a relative volatility value of 2.2 was obtained. For a 1/3 equal volume mix of DMSO, hexanoic acid and methyl benzoate, a relative volatility value of 2.1 was obtained.

By comparison, the values obtained from the perforated-plate column appear to be consistent.

Yeh and others [36,37] have shown that as the concentration of extractive agent in the perforated-plate column stillpot increases, it has a negligible effect on column operation. Operating the column in a semi-batch manner has also been shown to have negligible effects, as previously mentioned in reference to Szabados' work [27]. Comparison of the values obtained from the perforated-plate column and the Othmer still in this thesis appear to be consistent. In light of this observation, it is reasonable to propose that the chosen extractive agents did indeed enhance the separation of the three close boiling mixtures examined.

## SUMMARY AND CONCLUSIONS

1. Extractive distillation of three close boiling systems positively enhanced their components' separation when proper extractive agents were chosen. The systems examined were:
  - (i) acetic acid/4-methyl-2-pentanone
  - (ii) formic acid/4-methyl-2-pentanone
  - (iii) vinyl acetate/ethyl acetate
2. The most reliable data for determining the effectiveness of extractive agents was obtained from the perforated-plate column.
3. Data obtained from the Othmer still screening device provided the best correlation for potential effectiveness of extractive agents.
4. The use of polarity diagrams as a preliminary screening device was shown to be both effective and practical in this thesis. However, the diagrams should only be used in conjunction with the Othmer still screening device because alone they are inconclusive when predicting extractive agent effectiveness.

## RECOMMENDATIONS FOR FUTURE RESEARCH

Through the use of initial screening devices, such as polarity diagrams and the Othmer vapor-liquid equilibrium still, and occasionally a little trial and error, it is highly probable that an extractive agent can be found to separate most azeotropic and close boiling systems. For the purpose of this thesis, relative volatility values produced between the two components present in the initial close boiling systems were desired. It is recognized that these are only empirical values. In a more rigorous thermodynamic evaluation one would need to obtain vapor-liquid equilibrium data for all the possible binary interactions that could occur after addition of the extractive agent or the extractive agent mixture. Along these lines, it would have been necessary to look at all the possible combinations for systems of as many as five components in this thesis. This fact makes it apparent why only the more simplified approach used in this thesis was applicable. It is the author's recommendation that future research explore a well-behaved ternary or higher system more in depth, as indicated above and outlined in the theoretical section, for the purpose of comparison with values previously obtained by the more simplified approach.

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