



Separation of ethyl acetate and ethanol from methyl ethyl ketone and water, and ethyl acetate from ethanol and water by extractive distillation  
by Pisant Ratanapuech

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

A number of extractive distillation agents were investigated to separate ethyl acetate and ethanol from methyl ethyl ketone and water in an ethyl acetate-ethanol-methyl ethyl ketone-water mixture, and ethyl acetate from ethanol and water in an ethyl acetate-ethanol-water mixture by means of extractive distillation. A measure of separation is the relative volatility, which was calculated by the Fenske equation. The method of analyzing samples from the distillate and bottoms was gas chromatography. Packed columns as well as the vacuum jacketed perforated plate column were employed. The results showed that it is possible to separate the components from these two mixtures by extractive distillation with a distillation column containing relatively few theoretical plates. It was found that the proper extractive distillation agent completely eliminated azeotrope formation among the components in the mixtures investigated. Packed columns can be used in extractive distillation even though they are not quite as efficient as perforated plate columns.

For the separation of ethyl acetate and ethanol from methyl ethyl ketone and water one of the more attractive extractive agents is comprised of 25.0 wt.% hydroquinone, 25.0 wt.% ortho-tert-butylphenol, 25.0 wt.% catechol and 25.0 wt.% dimethylformamide, and the relative volatilities of ethanol to methyl ethyl ketone obtained was 1.51 and ethyl acetate to methyl ethyl ketone was 1.69. For the separation of ethyl acetate from ethanol and water a typical attractive extractive agent is comprised of 33.33 wt.% glycerol, 33.33 wt.% ethylene glycol and 33.33 wt.% triethylene glycol, and the relative volatility of ethyl acetate to ethanol obtained was 3.93.

SEPARATION OF ETHYL ACETATE AND ETHANOL FROM METHYL ETHYL  
KETONE AND WATER, AND ETHYL ACETATE FROM ETHANOL  
AND WATER BY EXTRACTIVE DISTILLATION

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APPROVAL

of a thesis submitted by

Pisant Ratanapuech

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

A number of extractive distillation agents were investigated to separate ethyl acetate and ethanol from methyl ethyl ketone and water in an ethyl acetate-ethanol-methyl ethyl ketone-water mixture, and ethyl acetate from ethanol and water in an ethyl acetate-ethanol-water mixture by means of extractive distillation. A measure of separation is the relative volatility, which was calculated by the Fenske equation. The method of analyzing samples from the distillate and bottoms was gas chromatography. Packed columns as well as the vacuum jacketed perforated plate column were employed. The results showed that it is possible to separate the components from these two mixtures by extractive distillation with a distillation column containing relatively few theoretical plates. It was found that the proper extractive distillation agent completely eliminated azeotrope formation among the components in the mixtures investigated. Packed columns can be used in extractive distillation even though they are not quite as efficient as perforated plate columns.

For the separation of ethyl acetate and ethanol from methyl ethyl ketone and water one of the more attractive extractive agents is comprised of 25.0 wt.% hydroquinone, 25.0 wt.% ortho-tert-butylphenol, 25.0 wt.% catechol and 25.0 wt.% dimethylformamide, and the relative volatilities of ethanol to methyl ethyl ketone obtained was 1.51 and ethyl acetate to methyl ethyl ketone was 1.69. For the separation of ethyl acetate from ethanol and water a typical attractive extractive agent is comprised of 33.33 wt.% glycerol, 33.33 wt.% ethylene glycol and 33.33 wt.% triethylene glycol, and the relative volatility of ethyl acetate to ethanol obtained was 3.93.

## INTRODUCTION

In order to separate two or more components occurring in a mixture, fractional distillation is one of the methods which is simple. Distillation is defined as the separation of two or more liquids of different volatility (1). Separation here refers to a division into parts, each of different composition, as the result of relative differences in volatility of the components of the mixture being separated. The method is particularly applicable when the components to be separated differ considerably in volatility. It frequently happens that the components to be separated boil close together or form an azeotrope. The components are then entirely incapable of separation by simple distillation. In these instances, extractive distillation, azeotropic distillation or a two-column distillation which changes the conditions of the distillation process is essential if the components are to be separated by a distillation process. However, extractive distillation is more flexible than the other types of distillation processes listed above in that a wider variety of conditions may be run in a given tower or a wider variety of towers may be designed for the separation of a given mixture. Extractive distillation is defined as

distillation in the presence of a substance which is relatively non-volatile compared to the components to be separated. The column, therefore, is charged continuously near the top so that an appreciable concentration is maintained on all the plates of the column (2). In other words, extractive distillation is fractional distillation in the presence of a solvent.

In extractive distillation, separation of two components is effected by the addition of a third component. This third component is usually called the extractive agent or solvent. The extractive agent usually is of low volatility, is added at or near the top of the column, is present throughout the tower, washes the ascending vapors and absorbs one of the components preferentially, and exits with the bottoms. The solvent must be subsequently separable from the original component(s) by some method (often distillation). The temperature of the system is such that the liquid and vapor phases coexist. The partial pressure of one component is lowered, thus raising the relative volatility of the two-component mixture to be separated (3). This process can be applied to multicomponent mixtures as well as binaries.

The most convenient measure of the difficulty of separation of two liquids is the relative volatility. The relative volatility is defined as the ratio of the

compositions of the two components in the vapor phase to their ratio in the liquid phase. The relative volatility of components 1 and 2 is represented by  $\alpha_{12}$  :

$$\alpha_{12} = \frac{y_1}{y_2} / \frac{x_1}{x_2}$$

where:  $y_1$  and  $y_2$  = mole fraction of the two components in the vapor, and  $x_1$  and  $x_2$  = mole fraction of the two components in the liquid. If  $\alpha_{12} > 1$ , substance 1 is more volatile. The greater the value of relative volatility, the easier the separation (4). The number of theoretical plates or stages required in distillation is a direct function of the value of relative volatility. Colburn and Schoenborn (5) offered the approximate generalization that the number of theoretical plates required for a separation of a binary mixture to yield products each of 99.9% purity, varied as the ratio  $4/(\alpha-1)$ . The larger the number of plates, the higher the capital investment cost. In general, the relative volatility does not remain constant because vapor pressures do not change proportionally between two components. Often the change is small and average relative volatilities are used. The purpose of extractive agents is to increase the relative volatility from values close to 1.0 or even 1.0 (an azeotrope) to values of 1.5 and higher.

In this work, a number of extractive agents were investigated to separate ethyl acetate and ethanol from methyl ethyl ketone and water as well as ethyl acetate from

ethanol and water by means of extractive distillation. These components have boiling points close together and can form binary and ternary minimum-boiling azeotropes as shown in Table 1. Ethyl acetate is used as a general solvent in coatings and plastics, organic synthesis, smokeless powders, and pharmaceuticals. Methyl ethyl ketone is used as a solvent in nitrocellulose coatings and vinyl films, Glyptal resins, paint removers, cements and adhesives, organic synthesis, the manufacture of smokeless powder, cleaning fluids, printing inks, catalyst carrier, lube oil dewaxing, and acrylic coatings. Ethanol is used as a solvent for resins, fats, oils, fatty acids, hydrocarbons, alkali hydroxides, an extractive medium, in the manufacture of intermediates, organic derivatives especially acetaldehyde, dyes, synthetic drugs, esters, elastomers, detergents, cleaning solutions, surface coatings, cosmetics, pharmaceuticals, explosives, antifreeze, beverages, antiseptics, medicine, gasoline additives, and yeast-growth mediums (10).

The controlled oxidation of butane generally results in a mixture of ethyl acetate, ethanol, methyl ethyl ketone, water, and trace impurities such as methanol, formic acid, methyl propionate, etc. Ethyl acetate is also obtained by heating acetic acid and ethanol in the presence

Table 1. Boiling point and azeotropic data at 1 atm  
(101325 Pa).

Component(s)	Boiling point, °C	Composition, wt. %	Reference
EtAc	77.1		6
EtOH	78.3		6
MEK	79.6		7
H <sub>2</sub> O	100.0		6
EtAc/H <sub>2</sub> O	70.38	91.53/8.47	8
EtAc/EtOH	71.8	69.2/30.8	9
MEK/H <sub>2</sub> O	73.3	88.4/11.6	7
MEK/EtOH	74.8	66/34	6
MEK/EtAc	77.05	11.8/88.2	6
EtOH/H <sub>2</sub> O	78.1	95.5/4.5	9
EtAc/EtOH/H <sub>2</sub> O	70.23	82.6/8.4/9.0	6
MEK/EtOH/H <sub>2</sub> O	73.2	75/14/11	7

EtAc = ethyl acetate

EtOH = ethanol

MEK = methyl ethyl ketone

H<sub>2</sub>O = water

of sulfuric acid and distilling off the resulting ternary minimum-boiling azeotrope of ethyl acetate, ethanol and water.

## BACKGROUND

Extractive distillation is the method of separating close boiling components or azeotropes by carrying out the distillation in a multiplate rectification column in the presence of an added pure liquid or liquid mixture having a boiling point higher than the components being separated. The extractive agent is introduced at or near the top of the column and flows downward until it reaches the still-pot or reboiler. Its presence on each plate of the rectification column alters the relative volatility of the key components in a direction to make the separation on each plate greater and thus either requires fewer plates to effect the same separation or makes possible a greater degree of separation with the same number of plates. When the components to be separated normally form an azeotrope, the proper extractive agents will cause them to vaporize separately during extractive distillation and thus make possible a separation in a rectification column that can not be done at all when no extractive agent is present. The extractive agent should boil considerably higher than any of the components in the mixture being separated and not form azeotropes with them. Usually the extractive agent is introduced a few plates from the top of the column in

order to insure that none of the extractive agent is carried over with the lowest boiling component. This usually requires that the extractive agent boils twenty Celsius degrees or more higher than the lowest boiling component.

At the bottom of a continuous column, the less volatile components of the close boiling mixtures and the extractive agent are continuously removed from the column. The usual methods of separation of these two components are the use of another rectification column, cooling and phase separation, or solvent extraction. The typical flow pattern for an extractive distillation process is shown in Figure 1.

The amount of solvent used is an important variable in effecting a separation. A common rule of thumb is: 1 to 4 mole of solvent per mole of feed, but this is only a rough generalization (4). Each system has its own range which can be determined by experiment. The extractive distillation agent should be heated to about the same temperature as the plate into which it is introduced. Thus extractive distillation imposes an additional heat requirement on the column as well as somewhat larger diameter plates for the same production output. To be economically attractive, the extractive distillation system must save more in the reduction of the number of theoretical plates and the height of the column than it adds in the cost of larger

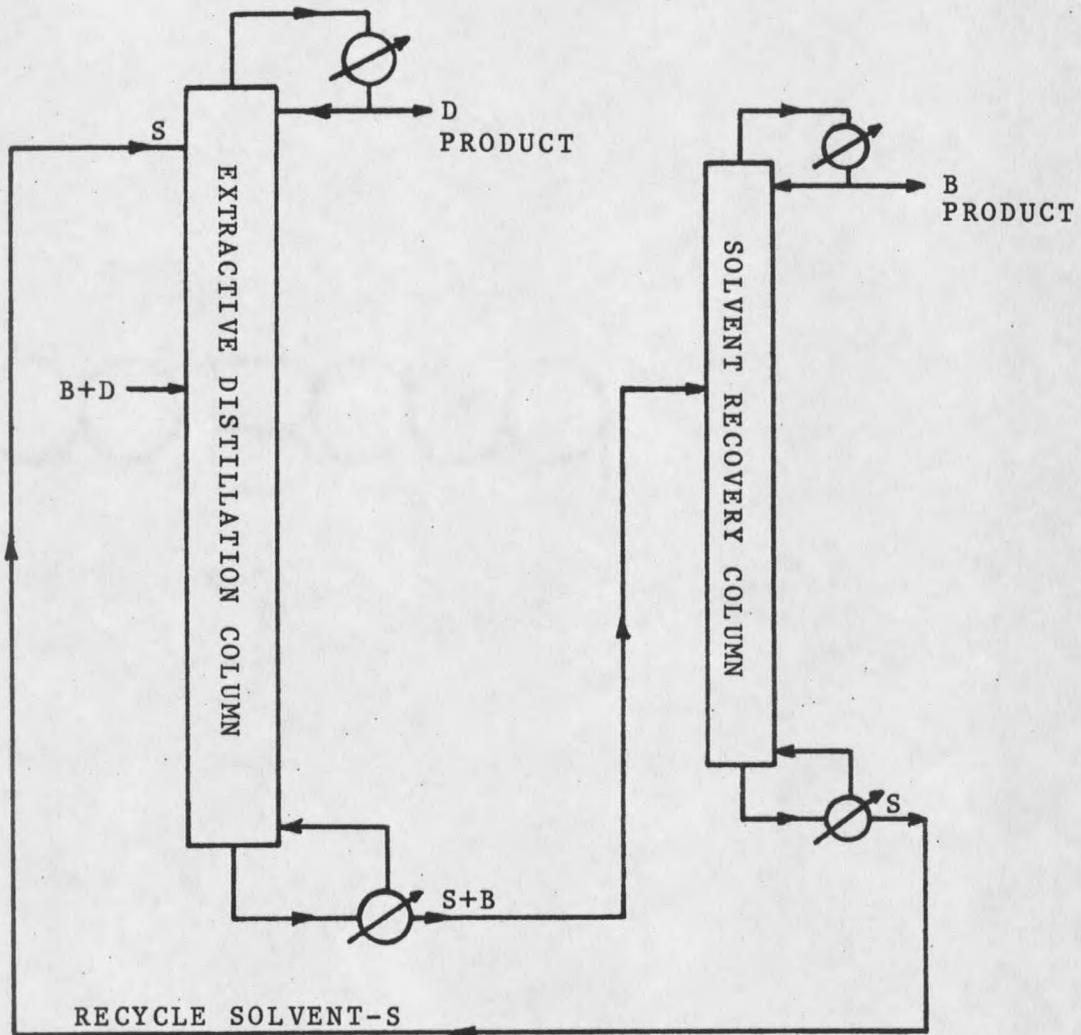


Figure 1. Extractive distillation with solvent recovery by fractionation.

plates and additional heat requirement. This will vary depending on the difficulty of the separation and the cost of heat.

In extractive distillation the extractive agent or solvent which is added must induce a difference in the partial pressures of the components in the mixture to be separated at a given concentration. Thus the basic phenomenon upon which this process depends is the difference in the deviations from ideality which is manifested by nonideal solutions.

From the general criterion of vapor-liquid equilibrium of a multicomponent system of  $N$  nonreacting chemical species (11) :

$$\hat{f}_i^v = \hat{f}_i^l \quad (i = 1, 2, \dots, N) \quad (A)$$

where  $\hat{f}_i$  is the fugacity of component  $i$  and the superscripts  $v$  and  $l$  denote the vapor and liquid phases.

The defining expression for the fugacity coefficient is written for each phase :

Vapor :

$$\hat{f}_i^v = \hat{\phi}_i^v y_i P \quad (B)$$

Liquid :

$$\hat{f}_i^l = \hat{\phi}_i^l x_i P \quad (C)$$

where  $\hat{\phi}_i$  = fugacity coefficient of component  $i$  in solution

$y_i$  = mole fraction of component  $i$  in the vapor phase

$x_i$  = mole fraction of component  $i$  in the liquid phase

$P$  = total pressure

Thus

$$y_i \hat{\phi}_i^V = x_i \hat{\phi}_i^L \quad (D)$$

The simplest result is obtained when the major assumptions are that the vapor phase is an ideal gas and the liquid phase is an ideal solution :

1. When the vapor phase is an ideal gas,

$$\hat{\phi}_i^V = 1 \quad (E)$$

2. When the liquid phase is an ideal solution in the sense of the Lewis-Randall rule,

$$\hat{\phi}_i^L = \frac{\hat{f}_i^L}{x_i P} = \frac{x_i f_i^L}{x_i P} = \frac{f_i^L}{P} \quad (F)$$

where  $f_i^L$  is the fugacity of pure liquid  $i$  at the temperature and pressure of the system.

3. It is also necessary to assume that the fugacity of pure liquid  $i$  is insensitive to pressure.

Then we can write

$$f_i^L = f_i^{\text{sat}} \quad (G)$$

where  $f_i^{\text{sat}}$  is evaluated at the temperature of the system but at  $P_i^{\text{sat}}$ .

The defining fugacity coefficient for either saturated liquid or vapor :

$$\phi_i^{\text{sat}} = \frac{f_i^{\text{sat}}}{P_i^{\text{sat}}}$$

Since the vapor phase is assumed to be an ideal gas,  
 $\phi_i^{\text{sat}} = 1$ . Thus,

$$f_i^{\text{sat}} = p_i^{\text{sat}}$$

Thus Eq.(G) may be written :

$$f_i^l = p_i^{\text{sat}}$$

where  $p_i^{\text{sat}}$  is the vapor pressure of pure  $i$  at the system temperature.

Combining this result with Eq.(F) gives

$$\hat{\phi}_i^l = \frac{p_i^{\text{sat}}}{P} \quad (\text{H})$$

Substitution of Eqs.(E) and (H) into Eq.(D) yields

$$y_i P = x_i p_i^{\text{sat}} \quad (\text{I})$$

This is known as Raoult's law and solutions which do not obey this law are called nonideal.

From the definition of the activity  $\hat{a}_i$  of component  $i$  in solution,

$$\hat{a}_i = \frac{\hat{f}_i}{f_i^0}$$

where  $f_i^0$  is the standard-state fugacity.

From the definition of the activity coefficient  $\gamma_i$  of component  $i$  in solution,

$$\gamma_i = \frac{\hat{a}_i}{x_i}$$

Thus

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i^0} \quad (\text{J})$$

For a component in a liquid solution Eq. (J) becomes

$$\hat{f}_i^l = x_i \gamma_i f_i^0 \quad (K)$$

Substitution of Eqs. (B) and (K) into Eq. (A) yields

$$y_i \hat{\phi}_i^P = x_i \gamma_i f_i^0 \quad (i = 1, 2, \dots, N) \quad (L)$$

Superscripts  $v$  and  $l$  need not be used here if it is understood that  $\hat{\phi}_i$  refers to the vapor phase and that  $\gamma_i$  and  $f_i^0$  are liquid-phase properties.

If the standard-state fugacity is taken in the sense of the Lewis-Randall rule, then  $f_i^0$  becomes  $f_i$ , the fugacity of pure liquid  $i$  at the temperature and pressure of the system. Then we may write the identity

$$f_i^0 = f_i = p_i^{\text{sat}} \left( \frac{f_i^{\text{sat}}}{p_i^{\text{sat}}} \right) \left( \frac{f_i}{f_i^{\text{sat}}} \right)$$

At low to moderate pressures it can be assumed that the liquid-phase properties  $\gamma_i$  and  $f_i^0$  are independent of pressure.

Therefore,  $f_i/f_i^{\text{sat}}$  is equal to unity. Thus,

$$f_i^0 = f_i = p_i^{\text{sat}} \phi_i^{\text{sat}}$$

and Eq. (L) becomes

$$y_i \hat{\phi}_i^P = x_i \gamma_i p_i^{\text{sat}} \phi_i^{\text{sat}} \quad (i = 1, 2, \dots, N) \quad (M)$$

At pressures of 1 atm (101325 Pa) and less, the assumption of ideal gases introduces little error. When this assumption is made, Eq. (M) becomes

$$y_i^P = x_i \gamma_i p_i^{\text{sat}} \quad (i = 1, 2, \dots, N)$$

The product  $y_i^P$  is the partial pressure  $p_i$  of component  $i$  in the gas mixture.

Thus

$$P_1 = x_1 \gamma_1 P_1^{\text{sat}}$$

$$P_2 = x_2 \gamma_2 P_2^{\text{sat}}$$

where  $p_1$  and  $p_2$  are the partial pressures of components 1 and 2 which are to be separated, and  $P_1$  and  $P_2$  are the vapor pressures of components 1 and 2. The superscript sat need not be used here if it is understood that  $P_1$  and  $P_2$  are the same as  $P_1^{\text{sat}}$  and  $P_2^{\text{sat}}$ , respectively.

Their relative volatility from solution is the ratio of their partial pressures divided by the ratio of their concentrations in the liquid. And it can be shown that :

$$\alpha_{12} = \frac{\gamma_1 P_1^{\text{sat}}}{\gamma_2 P_2^{\text{sat}}}$$

This equation illustrates some important principles about extractive distillation. The purpose of any solvent is to give as great a relative volatility as possible and, in that case, the solvent must allow the lower boiling component to pass overhead so that advantage will be taken of the  $P_1/P_2$  ratio in addition to the ratio of the activity coefficients. Obviously if a solvent gives a greater activity coefficient for the higher boiling component of the mixture, the difference in the activity coefficients is partly neutralized by the ratio of the vapor pressures, whereas in the opposite case, the relative volatility is augmented by the ratio of the vapor pressures. Since the ratio  $P_1/P_2$  is essentially constant for small temperature

changes, the only way that the relative volatility is affected is by introducing a solvent which changes the ratio  $\gamma_1/\gamma_2$ . This ratio, in the presence of the solvent, is called selectivity,  $S_{12}$  :

$$S_{12} = \{\gamma_1/\gamma_2\}_{\text{solvent}}$$

As an example of the effectiveness of extractive distillation, Benedict and Rubin (2) reported the separation of a mixture of paraffins and toluene using phenol as a solvent. Without the solvent,  $\alpha = 1$ , giving no separation. On the addition of phenol, the  $\alpha$  increases to 3.7, corresponding to a usual difference in boiling point of 44 °C.

Dicks and Carlson (12) compared directly one instance of extractive distillation and ordinary fractional distillation by using the same column as a batch-enriching fractional distillation column and as an extractive distillation column. When a mixture consisting of 10 mole per cent methylcyclohexane and 90 mole per cent toluene was distilled in the column studied, an average of 17.8 theoretical plates was obtained, giving a distillate consisting of 84-89 per cent methylcyclohexane. When the same column was used as an extractive distillation column, using aniline as a solvent, 100 per cent methylcyclohexane was recovered in the distillate. A study of the vapor pressure curve of the system toluene-methylcyclohexane

shows that a separation to give more than 92 per cent methylcyclohexane in the distillate is extremely difficult. Therefore this is a case in which extractive distillation accomplishes very easily what would be impractical by ordinary fractional distillation.

The same authors used the same column to compare the separation of n-heptane-methylcyclohexane by the two techniques. With fractional distillation a value of 13.1 theoretical plates was obtained. The relative volatility, reported previously, is 1.074 for the mixture. When n-heptane-methylcyclohexane was extractively distilled, using aniline as the solvent, a separation equivalent to that which would be obtained in a fractional distillation column of 51.9 theoretical plates was obtained. On the basis of the separation reported in a column of 13.1 theoretical plates, the relative volatility was raised from 1.074 to 1.30. Using a different concentration of aniline, Griswold, et al. (13) reported an increase of  $\alpha$  from 1.074 to 1.47 for the same system.

This method was also applied to the separation of the cyclohexane-benzene azeotrope. Using aniline, the azeotrope of 47 mole per cent cyclohexane was broken so as to give 100 per cent cyclohexane as distillate.

Buell and Boatright (14) studied the separation of butadiene from a number of hydrocarbons, using furfural as the solvent. The relative volatility of the mixture of

butadiene with the second component is given for normal distillation and for extractive distillation in Table 2.

Table 2. Comparison of relative volatilities of butadiene and hydrocarbons, and the number of theoretical plates required for the same separation with and without the extractive agent.

Butadiene with	Normal		With furfural	
	Rel. vol.	Plates required	Rel. vol.	Plates required
isobutane	1.209	48.4	2.614	9.6
isobutylene	1.070	135.7	1.666	18.0
1-butene	1.046	204.4	1.718	17.0
n-butane	0.871	66.6	2.020	13.1

In Table 2 the plates required for the separation of the given mixture, both with and without the addition of furfural, are calculated by the Fenske equation based on 99 mole per cent of the more volatile component in the distillate and one per cent of the more volatile component in the residue.

Berg (15) studied the separation of ethylbenzene from para-xylene. Without the solvent,  $\alpha = 1.06$ . For 99% purity of the products 157 theoretical plates are required at total reflux, somewhat more under a finite reflux ratio. When ethylbenzene-para-xylene was extractively distilled, using m-nitro acetophenone as the solvent, the  $\alpha$  increases to 1.25 and 41 theoretical plates are required for the same purity of the products.

When producing methyl ethyl ketone from the controlled oxidation of butane, not only methyl ethyl ketone but also ethyl acetate, ethanol, water and trace impurities such as methanol, formic acid, methyl propionate, etc. are obtained. The principal method of manufacturing ethyl acetate is to react acetic acid with ethanol in the presence of a catalyst such as hydrochloric acid or sulfuric acid. An excess of ethanol is used, thus converting all of the acetic acid to ethyl acetate and water. However, when the mixture is subjected to rectification, a ternary minimum-boiling azeotrope at 70.23 °C and comprising 82.6 wt.% ethyl acetate, 8.4 wt.% ethanol and 9.0 wt.% water comes off. The flow diagram of the present methods to separate the components from these two mixtures is shown in Figure 2.

The purpose of this work is to investigate as many extractive agents as possible to separate ethyl acetate and ethanol from methyl ethyl ketone and water as well as ethyl acetate from ethanol and water by extractive distillation. The purpose of separating ethyl acetate and ethanol from ethyl acetate-ethanol-methyl ethyl ketone-water mixture is to find a substitute for the present method which is represented by the two blocks, ethyl acetate hydrolysis and separation of methyl ethyl ketone from ethanol by extraction, in Figure 2.













































































































































































