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**Separation of Non-ideal Quaternary Mixtures with Novel Hybrid  
Processes Based on  
Extractive Heterogeneous-Azeotropic Distillation**

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by

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## ABSTRACT

Distillation has been of a paramount importance, even today, in the separation processes. Therefore, its investigation is an important part of chemical engineering since its development is always an actual industrial problem. Today, the separation of the highly non-ideal mixtures is the most researched area largely due to the fact that important industrial problems emphasize it. A less investigated area is the separation of the non-ideal quaternary mixtures containing azeotropes. The main object of this thesis is the investigation of a possible separation methods for the separation of highly non-ideal quaternary mixtures produced by industrial processes, e.g. in pharmaceutical companies, in printing companies, etc.

The first step in order to design a suitable separation method is the exhaustive study of the vapour-liquid-liquid equilibrium (VLLE) of the quaternary mixtures. The azeotropes formed by the components of the mixtures investigated are always minimum boiling, both heterogeneous and homogeneous azeotropes. In my studies ten quaternary mixtures has been selected in such a systematic way that the mixtures can be classified into four groups according to their VLLE.

The first part of this study is the exhaustive investigation of the VLLE of the mixtures, the visualisation and classification of their VLLE in two and three dimensional tetrahedron, the characterisation and categorisation of the nodes of the mixtures. Seven rules are determined for the change of the types of the nodes if one of the components of the quaternary mixtures is present or missing according to the steps of a possible separation process. This new approach leads to determine specific rules for the classification of quaternary mixtures, including ternary sub-mixtures.

After the study and the classification of mixtures according to the increasing complexity, the investigation and design of possible separation structures is needed. For the quaternary mixtures investigated a novel hybrid distillation technique, the extractive heterogeneous-azeotropic distillation (EHAD) is elaborated. This new distillation technique combines the advantages of the extractive and the heterogeneous azeotropic distillation and works with autoentrainer/extractive agent that is the water always present in the mixtures investigated.

For each group of mixtures a novel uniform separation scheme based on EHAD is designed and applied with success. The important part of the separation schemes are verified with experiments. Finally, a design strategy is suggested for the groups of quaternary mixtures containing minimum boiling either homogeneous or heterogeneous azeotropes. The strategy is based on the proper position of the EHAD within the separation train.

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**TABLE OF CONTENTS**

1. Introduction .....	6
1.1 Motivation of the work, industrial importance.....	6
1.2 The aims of the work.....	7
1.3 Applied tools .....	8
1.4 Thesis overview.....	8
2. Classification of mixtures according to their VLLE.....	10
2.1 Ideal mixtures.....	10
2.2 Non-ideal mixtures.....	11
2.2.1 Azeotropy, and non-ideality.....	12
2.2.2 Ternary mixtures .....	13
2.2.2.1 Residue curve map.....	13
2.2.2.2 Serafimov's classification of ternary mixtures .....	16
2.2.3 Multicomponent mixture - quaternary mixture.....	20
3. Separation of non-ideal mixtures .....	22
3.1 Pressure-swing distillation .....	23
3.2 Membrane-distillation hybrids, pervaporation.....	23
3.3 Entrainer-addition distillation methods.....	25
3.3.1 Entrainers.....	25
3.3.2 Heteroazeotropic distillation .....	27
3.3.3 Extractive distillation .....	28
3.3.4 Heteroextractive distillation.....	28
3.4 Feasibility study .....	30
4. The mixtures selected for investigation .....	31
4.1 Classification of the quaternary mixtures according to their VLLE .....	34
4.1.1 Group 1.....	35

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4.1.2	Group 2.....	38
4.1.3	Group 3.....	39
4.1.4	Group 4.....	40
4.1.5	Conclusions .....	41
5.	Extractive heterogeneous-azeotropic distillation .....	43
5.1	Feasibility study of the EHAD .....	45
5.2	Comparison of EHAD and the heteroextractive distillation .....	47
6.	Study of separation of mixtures .....	48
6.1	Group 1.....	48
6.1.1	Separation schemes for mixtures 1a and 1b .....	51
6.1.2	Separation schemes for mixtures 2a and 2b .....	55
6.2	Group 2.....	61
6.2.3	Separation structures .....	62
6.2.4	Comparison of energy consumption.....	66
6.3	Group 3.....	67
6.3.1	Separation method .....	68
6.4	Group 4.....	71
6.4.1	Separation schemes for Group 4 .....	72
6.5	Experimental verification.....	76
6.6	Strategy for the separation of highly non-ideal quaternary mixtures.....	79
7.	Major scientific results .....	81
8.	List of major publications.....	87
9.	References .....	91
	Abbreviations .....	98

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# 1. Introduction

## 1.1 Motivation of the work, industrial importance

The separation of liquid mixtures is an exhaustively investigated old area of the different engineering sciences. A basic unit operation considered for such processes is distillation and its different alternatives. The distillation based separation of ideal or almost ideal mixtures has been comprehensively studied. Also, several design/synthesis strategies have been recommended in the last decades by several authors.

The separation of the non-ideal mixtures is newer areas of the chemical engineering sciences, but several significant contributions have been done up till now which are listed in the literature survey part. In spite of the several hundreds of publications and books about the separation of these non-ideal mixtures, the topic is still not exhausted and new problems and areas are arising everyday. There are several incentives for the researchers to determine any synthesis/design strategy for the separation of the non-ideal mixtures containing azeotropes. It is a quite difficult task since the vapour-liquid-liquid equilibrium of the non-ideal mixtures are usually quite complex and unique, it is difficult to give general classification, like in the case of the ideal mixtures

Due to this fact, the research works and books try to handle this problem step by step, proceeding from simpler problems towards the more and more complex mixtures. The elaboration of a synthesis strategy for the separation of a non-ideal, azeotrope-forming mixture badly needs a comprehensive visualisation. Due to this fact, the separation of binary and ternary mixtures has been studied where the separation can be represented easily. For the sake of simplicity, the investigation of the separation of such non-ideal mixtures is favoured where only homogeneous azeotropes are formed. Kiva *et al.* [6] have classified the ternary azeotropic mixtures on the basis of Serafimov's work, but they have not considered the heterogeneous azeotropes.

There are only a few attempts to exhaustively investigate and classify the quaternary non-ideal mixtures and their separation, especially if heterogeneous azeotropes are also present.

Therefore, this work investigates of the vapour-liquid-liquid equilibrium of quaternary mixtures and on the behalf of this investigation, the development of separation solutions which can be successfully applied for the separation of quaternary mixtures. For this research

work such quaternary mixtures are selected which form both homogeneous and heterogeneous minimum boiling azeotropes.

The importance of this research work can also be explained with the significant industrial needs for the efficient solution of solvent recovery problems, e.g. printing companies, medicine factories. Since the waste streams of the solvent mixtures arise usually in quantities of several (ten) thousand tons per year, continuous recovery methods are considered. The proper solution of the solvent recovery problems is, on the other hand, a contribution to sustainable development and consumption.

It is also an aim of this research work to find a strategy for the design of separation schemes for the separation of the quaternary mixtures selected.

## **1.2 The aims of the work**

This thesis is based on studying the vapour-liquid-liquid equilibrium and the separation problems of the highly non-ideal quaternary mixtures arising as waste streams in different process industries. The different quaternary mixtures are classified into four groups according to their vapour-liquid-liquid equilibrium.

This work consists of the following steps:

- detailed study of the highly non-ideal quaternary mixtures according to their VLLE data;
- classification of the quaternary mixtures based on the Serafimov's classification for ternary mixtures; establishing the rules for the new approach of the classification for the quaternary mixtures;
- sorting the highly non-ideal quaternary mixtures into four groups according to their VLLE features (number of binary and ternary azeotropes);
- design of uniform novel continuous separation strategies for the mixtures of the four groups considering the proper position of the novel separation method - the extractive heterogeneous-azeotropic distillation - within the separation train;

- feasibility investigations of the extractive heterogeneous-azeotropic distillation method;
- design strategy for the separation alternatives for highly non-ideal quaternary mixtures.

### **1.3 Applied tools**

The work in this thesis is significantly based on computer simulations using the ASPEN PLUS and ASPEN SPLIT 12.1 software packages. The results are verified with experiments that give confidence for the calculated results.

Rigorous steady state simulations are carried out and used for evaluation. A user added subroutine is developed for the calculation of cost features of the design alternatives.

The experiments are carried out in laboratory scale distillation column.

### **1.4 Thesis overview**

To develop the above mentioned objectives, this thesis work is divided into 7 chapters, covering the following aspects:

Chapter 1 gives an introduction to the dissertation, including motivation and aims of the work.

Chapter 2 comprises the classification of mixtures according to their vapour-liquid-liquid equilibrium data. This part of the work contains the classification of the ternary mixtures established by Serafimov. This classification gives a background to the new approach of the classification of the quaternary mixtures.

Chapter 3 outlines the well-known methods for the separation of the highly non-ideal mixtures. The important part of this chapter describes the entrainer-addition distillation method.

Chapter 4 covers classification of the investigated quaternary mixtures. This part of the dissertation has a great importance in the new approach of the classification of the highly non-ideal quaternary mixtures.

Chapter 5 discusses the novel hybrid separation process, the extractive heterogeneous-azeotropic distillation, and the feasibility study of this separation method.

Chapter 6 discusses the possible separation schemes for the mixtures sorting to the four groups. The first part of this chapter describes the characteristics and separation alternatives of the four mixtures of group 1. The mixtures offer also the possibility to study the validity of the “easy split first” heuristic for highly non-ideal mixtures. The next part shows the study of the separation mixtures of group 2 and involves a comparison of their energy consumptions. The separation alternatives for the mixtures of group 3 describe the next part of this chapter. The separation train for the most complicated mixtures sorting to the group 4 contains the final part of this chapter. This part of the work contains the results of the experimental investigation of the mixtures in each group. Comparisons with the calculated results are also presented. The conclusion of this chapter is the strategy for the separation structures based on the proper positioning of the extractive heterogeneous-azeotropic distillation within the separation train. The strategy can be recommended for the mixtures classified into the four groups according to the increasing complexity of their vapour-liquid-liquid equilibrium.

Chapter 7 summarizes the major scientific results of this thesis.

## Literature review

### 2. Classification of mixtures according to their VLLE

The distillation and the distillation-based processes are significantly influenced by the vapour-liquid equilibrium of the mixture to be separated. In the chemical engineering practice, there are several ways for the classifications for these mixtures according to their vapour-liquid equilibrium and one frequently applied alternative is whether the mixtures show “ideal” or “non-ideal” behaviour.

#### 2.1 Ideal mixtures

The components have similar physiochemical properties. The intermolecular forces between identical and different molecules are equal. The vapour-liquid phase equilibrium for a multicomponent mixture may be expressed as:

$$y_i P = x_i \gamma_i(T, x) P_i^{SAT}(T) \quad i=1, 2, 3, \dots, n \quad (1)$$

where:

$x_i, y_i$  - the vapour and liquid compositions of component  $i$

$P, T$  - the system pressure and temperature

$P_i^{SAT}$  - saturated vapour pressure of component  $i$

$\gamma_i$  - activity coefficient of component  $i$  in the liquid phase.

The activity coefficient is a measure of the non-ideality of a mixture and changes both with temperature and composition. In the case of ideal mixtures the value of activity coefficient is  $\gamma_i = 1$ .

Ideal or nearly ideal behaviour is encountered in mixtures formed by closely related chemical substances like several hydrocarbons e.g. heptane and hexane.

However, even among the hydrocarbons, which are believed to be typical ideal mixtures, they can exhibit non-ideal behaviour. If there is a point in the composition space, where the vapour pressures of the two components are equal at a given temperature, this may correspond to an azeotropic point which is called a Bancroft point, illustrated in Figure 2.1.

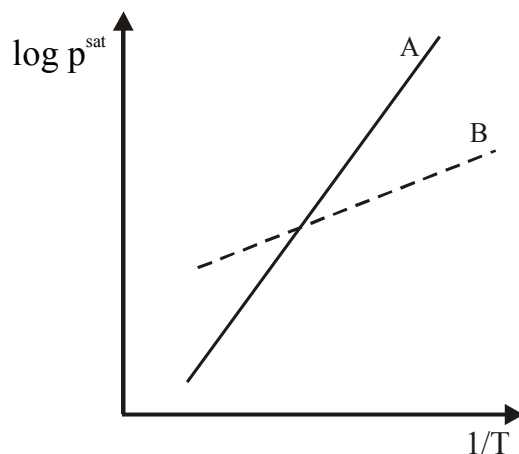


Figure 2.1. Bancroft point (intersection of the vapour pressure curve of the pure components A and B at a given temperature)

This is referred to as Bancroft's rule (Malesinski, 1965). The intermolecular forces in the mixture may be similar, but the mixture still exhibits an azeotropic behaviour. An example of such an azeotrope-forming mixture of nonpolar substances is the mixture of benzene and cyclohexane. Out of 972 examined mixtures, 489 (50 %) have a Bancroft point, but only 377 (40 %) form azeotropes (Malesinski, 1965). Bancroft's rule is neither a necessary nor a sufficient condition for the formation of an azeotrope, and, does not play an important role in determining whether a mixture forms azeotropes or not.

## 2.2 Non-ideal mixtures

The non-ideal mixtures can be classified into the following two groups:

1. The group of mixtures, where there non-ideality is presented but there are no azeotropes.
2. The group of mixtures, where there is presented non-ideality and there are azeotropes

In the case of the non-ideal mixtures, the liquid activity coefficient is usually not equal to one, hence, significantly influencing the vapour-liquid equilibrium. Another factor is the fugacity, which is not considered here.

The tendency of a mixture to form an azeotrope depends on two factors:

- the difference in the pure component boiling points, and
- the degree of non-ideality (Horsley, 1973; King, 1980).

### 2.2.1 Azeotropy, and non-ideality

The term *azeotrope* means “no boiling by any means” (Greek: *a* - non, *zeo* - boil, *tropos* - way/mean), and denotes a mixture of two or more components where the equilibrium vapour and liquid compositions are equal at a given pressure and temperature. The vapour has the same composition as the liquid and the mixture boils at a temperature other than that of the pure components’ boiling points. For an azeotrope, a variation in pressure changes not only the boiling temperature, but also the composition of the mixture, and this easily distinguishes it from a pure component.

If at the equilibrium temperature the liquid mixture is homogeneous, the azeotrope is a homogeneous azeotrope. If the vapour phase coexists with two liquid phases, it is a heterogeneous azeotrope. A brief history of the first observations of azeotropy is given in, for example, Horsley, 1973; Gmehling *et al.* (1994).

Azeotropes are formed due to the differences in intermolecular forces of attraction among the mixture components (hydrogen bonding and others). The particular deviation from ideality is determined by the balance between the physiochemical forces between identical and different components.

The non-ideal mixtures can be classified into the following groups:

1. The group of mixtures, where is presented non-ideality, but there are no azeotropes.

2. *Minimum boiling azeotropes - Positive deviation from Raoult’s law:*

The attraction between identical molecules is stronger than between different molecules. In this case the liquid activity coefficient  $\gamma_i > 1$ . If the positive deviations are sufficiently large ( $\gamma_i > 4$ ), phase splitting may occur and form a heterogeneous azeotrope where the vapour phase is in equilibrium with two liquid phases. In the heteroazeotropic point the overall liquid composition is equal to the vapour composition and the vapour and liquid temperature surfaces are tangential with zero slopes, but the three coexisting phases have different compositions.

3. *Maximum boiling azeotropes - Negative deviation from Raoult’s law:*

The attraction between different molecules is the strongest. In this case the activity coefficient  $\gamma_i < 1$ . To form two liquid phases it is generally required that the activity coefficients are strongly positive. That is why maximum boiling azeotropes are never heterogeneous.

For simplicity, the above explanation is given for binary mixtures. The main difference for ternary and multicomponent mixtures is that an azeotropic point is not necessarily an absolute extreme (minimum or maximum point) of the boiling temperature at isobaric condition, but it may be a local extreme (saddle).

Generally, it can be said that the closer the boiling points of the pure components are and the less ideal the mixture is the greater the probability of an azeotrope. A heuristic rule is given in Perry (1997) that azeotropes occur infrequently between compounds whose boiling points differ by more than about 30 °C. An important exception to this rule is heteroazeotropic mixtures where the components may have a large difference in the boiling points of the pure components, and still exhibit strong non-ideality and immiscibility regions. In heterogeneous mixtures the different components may even repel each other. This is why only minimum-boiling heteroazeotropes occur in nature.

Swietoslawski (1963) pointed out that most mixtures of organic compounds form non-ideal systems. The presence of some specific groups, especially polar groups (oxygen, nitrogen, chlorine and fluorine), often results in the formation of azeotropes. Roughly half of the 18 800 binary systems collected in Horsley (1973), Gmehling *et al.* (1994) are azeotropic. More than 90 % of the known azeotropes show positive azeotropy, that is, minimum-boiling azeotropes in the binary case (Gmehling *et al.*, 1994). Further, more than 80 % of these are homoazeotrope.

## 2.2.2 Ternary mixtures

### 2.2.2.1 Residue curve map

In case of ternary mixtures it is typically the so called “residue curve” map which indicate the behaviour of the ternary mixture. To determine the residue curve map open evaporation is applied. Open evaporation, also known as simple distillation or Rayleigh distillation, is batch distillation with one equilibrium stage where the vapour formed is continuously removed so that the vapour at any instant is in equilibrium with the still-pot liquid (residue). Schreinemakers (1901) considered the instantaneous mass balance equation of this process:

$$d(Lx_i) = - y_i dV \quad (2)$$

or reformulated

$$Ldx_i = -dV(y_i - x_i) \quad (3)$$

where:  $L$  [mol] is the amount of the residue liquid in the still-pot,

$dV$  [mol] is the amount vapour evaporated,

$x_i, y_i$  are the mole fractions of the component  $i$  in the still-pot liquid and in the vapour.

The vapour composition trajectory during open evaporation can be represented graphically by the "vapour line" (Schreinemakers, 1901), later named a distillate curve by Doherty and Perkins (1978). Each distillate curve is connected to a residue curve and moves along the condensation temperature surface. The distillate curves are going through the vapour ends of the equilibrium vectors that are tangent to the corresponding residue curve. The less the curvature of the residue curve, the less is the gap between it and the corresponding distillate curve. The vapour condensation temperature is equal to the liquid boiling temperature at any instant and increases monotonically during the open equilibrium evaporation process. The system of distillate curves has the same singular points as the system of residue curves, and the singular point type is the same as the type of the corresponding singular point of the residue curves (Haase, (1950); Stononkin, (1967), Fien et al. (1994), Safrit et al. (1997)).

Schreinemakers established that the interior of the composition space is filled in with residue curves. The points of components and azeotropes are the isolated residue curves, and the edges of the composition space between the singular points are residue curves too. He analyzed the relation between the position of the equilibrium vectors at the liquid isotherms and the path of the residue curves. Based on this, the literature is referred to as Schreinemakers' rules:

1. a residue curve always moves along the boiling temperature surface in the direction of increasing temperature and cannot intersect twice with the same liquid isotherm;
2. residue curves cannot intersect each other.

Haase (1949) studied the behaviour (paths) of the residue curves near the vertices of the composition triangle and the azeotropic points. The pure component vertex is an initial or a final point (node) of the residue curves if the liquid boiling temperature increases or decreases (near it) by the movement from the vertex along both close by edges. At other singular points (saddles), the residue curves have a hyperbolic shape in the vicinity of the vertex if the liquid boiling point temperature increases at the movement from the vertex along

one of the edges and decreases at the movement along another edge. These interpretations are known as Haase's rule. In summary, the residue curves originate and end at nodes of the boiling temperature surface and have a hyperbolic path in the vicinity of their saddles. Considering the feasible paths of isotherms and residue curves in the vicinity of nodes and saddles for homogeneous mixtures, several works (Bushmakina and Kish (1957a) and Bushmakina and Molodenko (1957b)) pointed out the correspondence between their trajectories. It was found that residue curves begin or end at a singular point (node) and pass through this singular point (saddle). If all the residue curves terminate in a singular point, then the point is a stable node. If all the residue curves extend from a singular point, then the point is an unstable node. If the residue curves both approach and head off a singular point, then the point is a saddle.

Gurikov (1958) formulated the "Rule of azeotropy" and proposed a classification of ternary mixtures based on their thermodynamic topological structures. Zharov (1967; 1968) gave a more rigorous mathematical foundation of the residue curve map analysis and expanded it to multicomponent mixtures. During the same period, Serafimov (1968a) proposed to use structural information of VLE diagrams to predict feasible separations in continuous distillation.

The ternary may have a locus in the composition space where the relative volatility between a pair of the components is equal to unity without forming any azeotropes. It only means that the relative volatility order of the components changes within the composition space and this is common for non-ideal mixtures. Therefore, the terms "light", "intermediate" and "heavy" indicate the relative volatility order of the pure components and in ternary mixtures they have limited meaning for non-ideal and azeotropic mixtures.

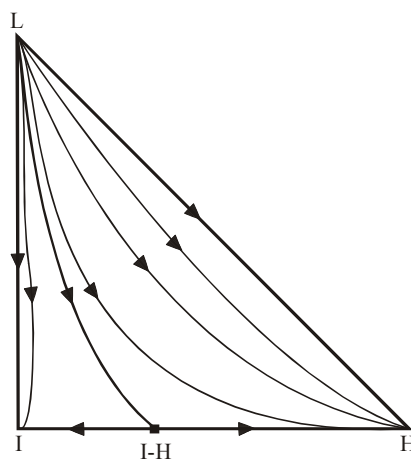


Figure 2.2. Residue curve map of the L, I, and H

A simple distillation region is defined as the union of all residue curves that start at the same unstable node and end at the same stable node. If there exists more than one node of the same kind (stable or unstable), there will be at least as many simple distillation regions as there are nodes of that same kind. The residue curve that separates two simple distillation regions is called a residue curve boundary. The residue curve map shown in Figure 2.2 has two simple distillation regions. The pure component L is the only unstable node where all residue curves initiate. The residue curves either end in pure I or pure H, which are the two stable nodes of this mixture. Thus, there are two simple distillation regions that are separated by the residue curve boundary, which originate from pure L and ends in the I-H azeotrope, the saddle of the system.

### 2.2.2.2 Serafimov's classification of ternary mixtures

This classification was first mentioned by Gurikov (1958). Ternary mixtures were considered with no more than one binary azeotrope for each binary pair of the components and no more than one ternary azeotrope:

$$N_3 + S_3 \leq 1 \quad (4)$$

and

$$N_2 + S_2 \leq 3 \quad (5)$$

where

- N<sub>2</sub> is the number of binary nodes (saddles),
- N<sub>3</sub> is the number of ternary nodes (saddles),
- S<sub>2</sub> is the number of binary saddles,
- S<sub>3</sub> is the number of ternary saddles.

The total number of binary azeotropes as being M can be calculated

$$M = N_2 + S_2 \quad (6)$$

For ternary simple distillation the combination of the singular points of different type always satisfies the rule:

$$2N_3 + N_2 + N_1 = 2S_3 + S_2 + 2 \quad (7)$$

where N<sub>1</sub> is the number of pure component nodes.

---

Substitution (6) into Equation (7) gives:

$$2S_3 + M + 2 = 2N_3 + 2N_2 + N_1 \quad (8)$$

Both  $M$  and  $N_1$  can take the values 0, 1, 2 or 3. From (8) we see that the quantities  $M$  and  $N_1$  are bound to be of equal parity. If  $M$  is an even number (0 or 2), then  $N_1$  is also even. If  $M$  is an odd number (1 or 3), then  $N_1$  is also an odd number. From this analysis Gurikov revealed 22 feasible topological structures of residue curve maps (or boiling temperature surfaces).

Feasible structures of residue curve maps, isotherm maps and vector fields for ternary mixtures are presented by Serafimov (1971). The classification of ternary mixtures may be developed by characteristic between antipodes inside each structure class, based on the reasoning that, minimum- and maximum-boiling azeotropes have different physical nature and different behaviour during distillation (Zharov and Serafimov, 1975). This defined classification includes a total of 49 types of feasible VLE diagrams. This classification and the description can be found in the work by Hilmen (2000).

The literature previews are first introduced the classification of azeotropic mixtures in 113 classes proposed by Matsuyama and Nishimura in 1977, later, as a result of the work done by Foucher (1991), was extended to 125 classes. Serafimov showed that the feasible structures of VLE diagrams for azeotropic mixtures are limited by topological and thermodynamical constraints and classified under 26 topological structures.

All 26 Serafimov's classes are topologically and thermodynamically feasible but their occurrence is determined by the probability of certain combination of molecular interactions. Kiva et al (2003) provided some statistics on the physical occurrence of these 26 classes. It is called "Reshetov statistics". This is based on thermodynamic data for 1609 ternary systems from which 1365 are azeotropic. The database covers data published from 1965 to 1998. The results show that 16 out of the Serafimov's classes were reported in literature. Figure 2.3 shows the 26 classes of the Serafimov's classes, including the value of Reshetov statistics (reprinted from Hilmen (2000)).

Serafimov investigated, however, only homogeneous mixtures. The classification for heterogeneous azeotropic mixtures has not been reported, yet. However, as noted by Kiva et al. (2003) the topology of a residue curve map of a heterogeneous mixture does not differ from that of a homogeneous mixture with the same set of stationary points. The main difference between homogeneous and heterogeneous mixtures is that a heteroazeotrope can only be a minimum boiling one, while a homogeneous azeotrope can be either minimum-boiling or maximum-boiling azeotrope. Thus, a heteroazeotrope can be either unstable node or

saddle and can never be a stable node. Therefore, Serafimov's classification is valid also for heterogeneous mixtures but one should always keep in mind that a maximum-boiling azeotrope could never be a heterogeneous one.

Several articles can be mentioned in this classification and describe the feasibility of separation of some classes, e.g. Skouras (2004).

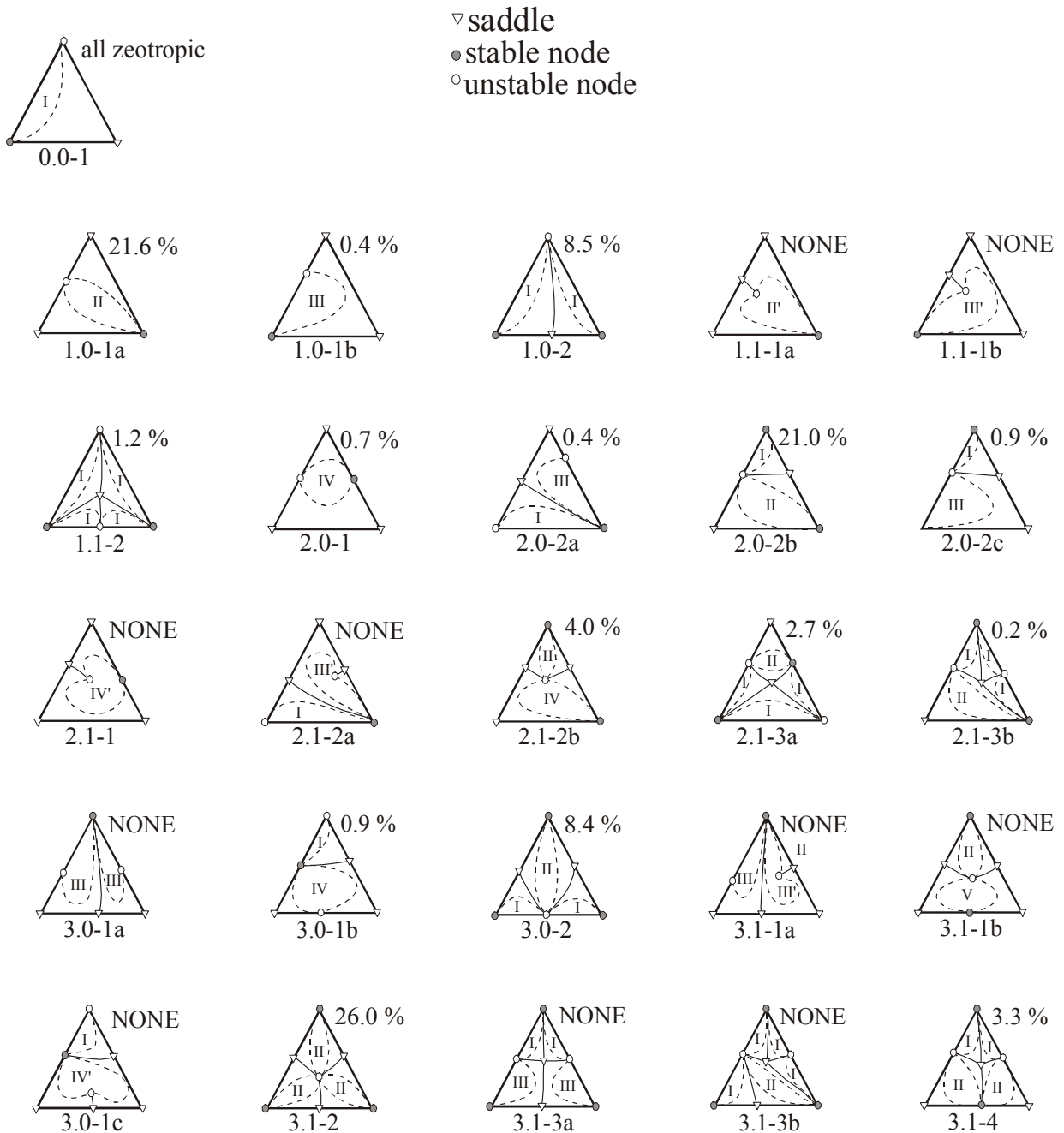


Figure 2.3., Serafimov's classification of the ternary mixtures, including the value of the Reshetov's statistics

In the Serafimov's 26 topological classes there are eight elementary topological cells (denoted I, II, III, IV, II', III', IV' and V) that constitute all the ternary diagrams, where a cell is defined as one residue curve region taken with its boundaries. (Kiva et al. (2003)) From these eight elementary cells all the 26 diagrams can be constructed as shown in Figure 2.3 (reprinted from Hilmen (2000)). Every cell has one unstable and one stable node and some set of saddle points. There are four "primary" diagrams where the composition triangle consists of a single cell (Serafimov's class 0.0-1, 1.0-1a, 1.0-1b and 2.0-1), and these elementary cells (denoted I, II, III, IV) are also reported for naturally occurring mixtures. Cells II', III' and IV' are modifications of the primary cells II, III and IV, respectively (with internal nodes), for which there are no reported physical mixtures. Cell V only occurs as an element in Serafimov's class 3.1-1b. The four primary diagrams and the corresponding elementary cells I, II, III, IV are shown in Figure 2.4.

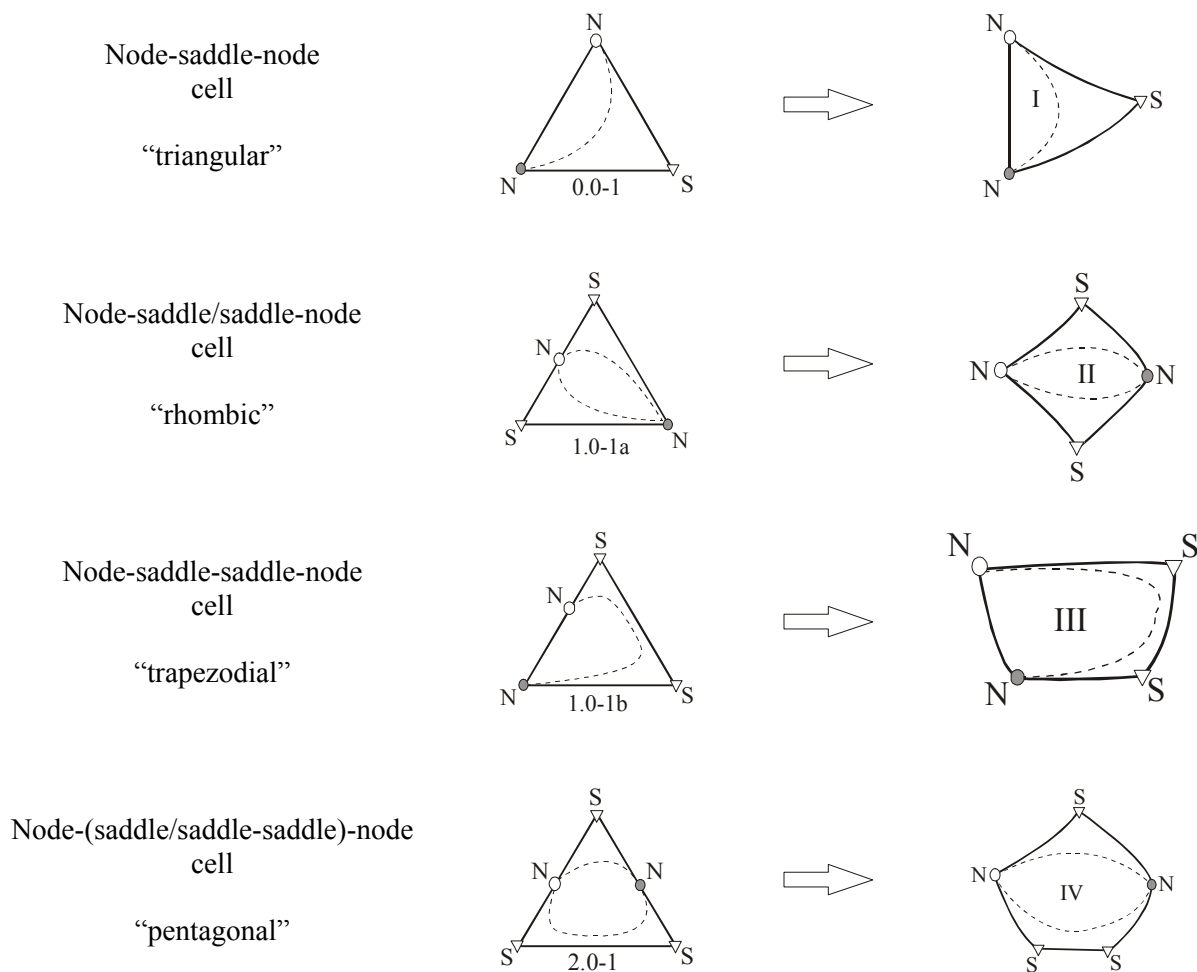


Figure 2.4., The four primary diagram

Each elementary cell is characterized by a certain set and order of the singular points, nodes and saddles. There is an important difference between an elementary cell of the “primary” diagrams, one residue curve region, and an elementary cell incorporated into more complex diagrams. If an elementary cell is a primary diagram, the saddle point is a pure component point. The borders of the cell are the edges of the composition triangle that are linear. The stable and/or unstable nodes are pure component points or points of binary azeotropes. If an elementary cell is a constituent of a complex diagram, at least one of its saddles is a binary or a ternary azeotrope, and, therefore, at least one of the borders of the cell is a residue curve boundary showed by the solid thick lines in Figure 2.4. One of the nodes can be a point of a ternary azeotrope. In general, the composition space is broken into several residue curve regions (cells) if there is more than one unstable node or more than one stable node. Despite these differences, a single elementary cell and an elementary cell included into a complex diagram are topological equivalent.

### **2.2.3 Multicomponent mixture - quaternary mixture**

In the case of multicomponent mixtures, where the number of components ( $n$ ) is higher than three, the composition space is  $(n-1)$ -dimensional and its graphical image is a polyhedron (tetrahedron, pentahedron and so on). In the case of quaternary mixtures, it is possible to graphically represent the VLE or VLLE functions in a composition tetrahedron, but it may be complicated to interpret. If the number of components is more than four, the graphical representation is difficult. However, a multicomponent mixture may be divided into ternary subsystems of components and pseudo-components. The ternary VLE subdiagrams are evaluated as a whole.

The visualization of quaternary mixtures are represented in a 3-dimensional system, where the simple distillation regions are bounded by 2-dimensional surfaces called 2-dimensional separatrixes which are indicated by the 1-dimensional separatrix lines.

The twenty types of singular points for quaternary mixtures that are given by Zharov and Serafimov (1975) are represented in Figure 2.5

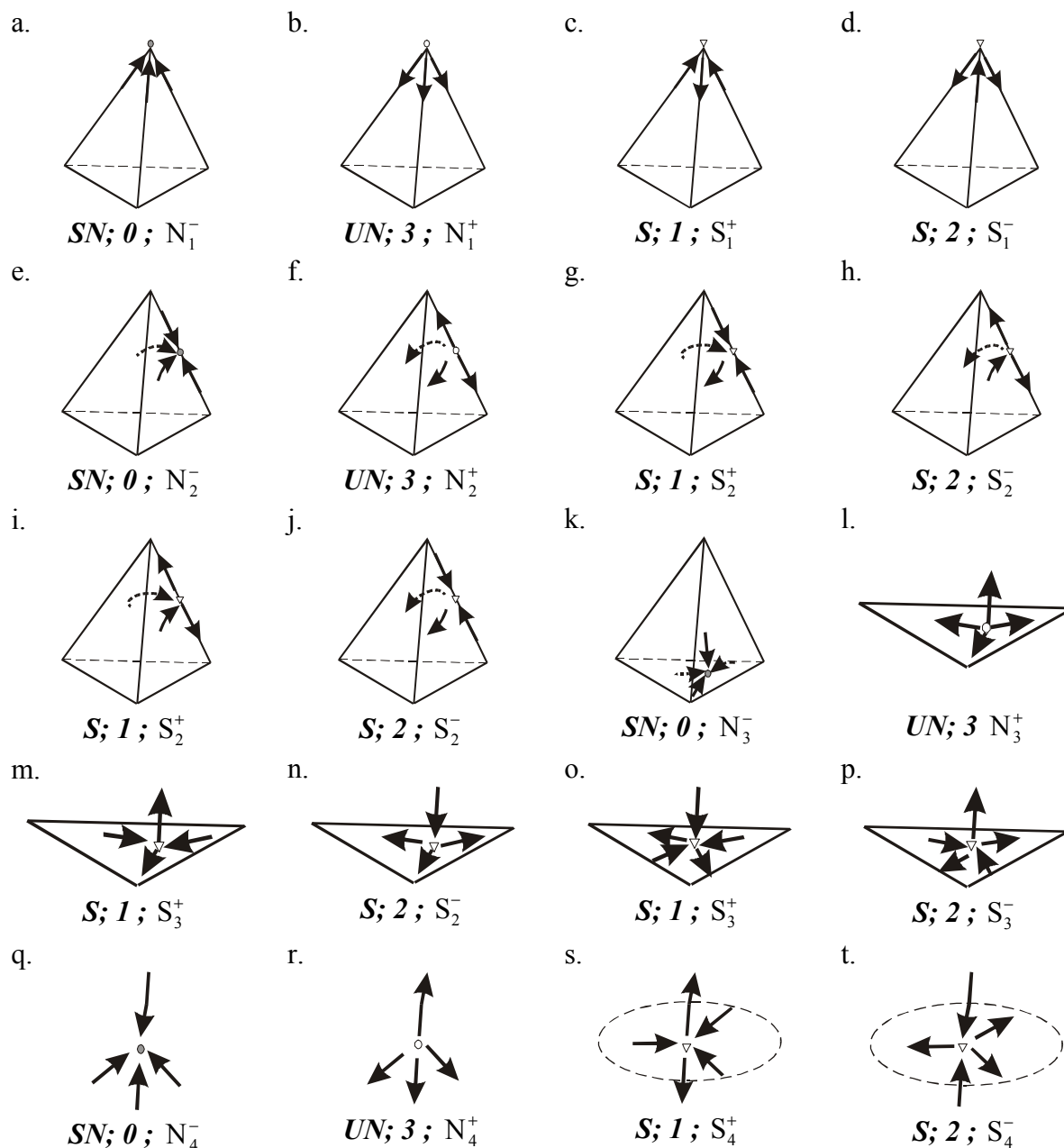


Figure 2.5. Types of singular points for the quaternary diagrams

The idea of the classification is similar to that of ternary ones but the nodes and saddles can be on the nodes, edges, surface of the tetrahedron and also inside them. However, this classification is a combinatorial one including all possible alternatives, and no physical insight is given into the VLLE behaviour of the quaternary mixtures.

### 3. Separation of non-ideal mixtures

There are various methods for the separation of highly non-ideal mixtures. Distillation methods are the oldest and most used, either by pressure variation or the addition of an agent, called entrainer, that may change the phase equilibrium of the mixture. Other alternative separation techniques for azeotropic mixtures, such as membrane separation, are usually combined with distillation resulting in the so called hybrid separation processes. Hybrid separation processes can also be used if distillation is combined with other separation processes e.g. phase separation.

Enhanced distillation is another common term used for distillation systems that utilise mass separating agents other than energy. This term means the use of entrainers, or the use of other separating techniques to complement distillation, and it does not necessarily involve azeotropes (Stichlmair et al., 1989, Westerberg et al., (2000)).

For the prediction of feasible separations by distillation, the analysis of VLE or VLLE equilibrium is the starting point. It allows for determining the thermodynamic possibilities and limitations of the separation due to the character of the mixture. Alternative feasible separation sequences can be synthesized and they should be subject of further investigation and comparison in order to choose the optimal one. Such an approach is called analysis-driven distillation synthesis (Westerberg and Wahnschafft, 1996). The theory of thermodynamic topological analysis or residue curve map analysis also provides a tool for evaluation of these separation techniques. This topological analysis is very useful for the screening of entrainers for heteroazeotropic and extractive distillation. Doherty and Perkins (1978) deduced properties of residue curve maps.

Rev *et al.* (1994) and Mizsey *et al.* (1997) have recommended a framework for designing feasible schemes of multicomponent azeotropic distillation. This procedure recommends studying in detail the vapour-liquid-liquid equilibrium data to explore immiscibility regions, azeotropic points of binary and ternary ones, and separatrices for ternary and quaternary regions. On the behalf of the VLLE data the set of feasible separation structures can be explored.

### 3.1 Pressure-swing distillation

Pressure changes can have a large effect on the vapour-liquid equilibrium compositions of azeotropic mixtures and thereby affect the possibilities to separate the mixture by ordinary distillation. By increasing or decreasing the operating pressure in individual columns distillation boundaries can be moved in the composition space. For some mixtures, a simple change in pressure can result in a significant change in the azeotrope composition and enable a complete separation by pressure-swing distillation as illustrated in Figure 3.1

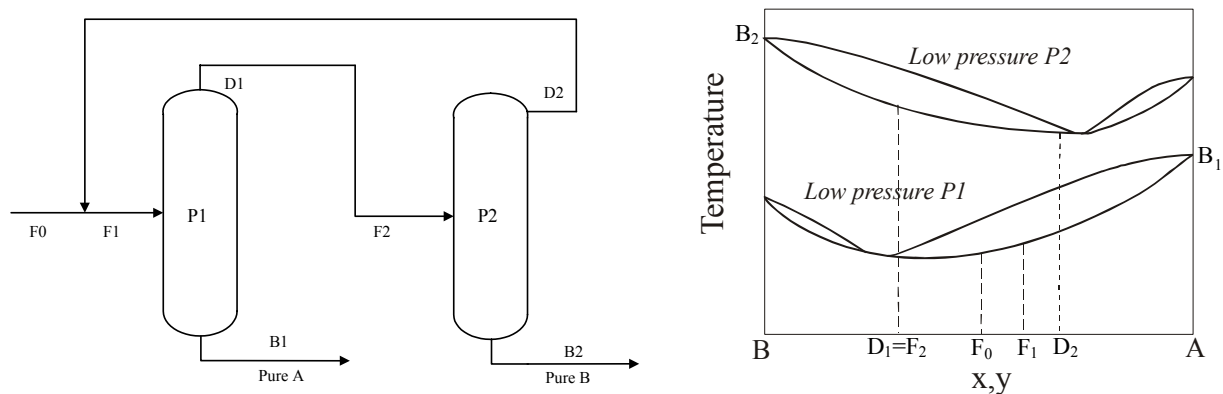


Figure 3.1., Pressure swing distillation

Examples of industrial mixtures that can be separated by pressure-swing distillation are given by Schweitzer (1997). The tetrahydrofuran-water azeotrope may be separated by using two columns operated at 1 atm and 8 atm.

Although changing the vapour-liquid equilibrium (VLE) properties of an azeotropic mixture by purely pressure or temperature changes is an attractive and definite possibility, it cannot be generally applied and such processes are often uneconomical (Van Winkle, 1967).

### 3.2 Membrane-distillation hybrids, pervaporation

The separation of liquid and gas mixtures with membranes as separating agents is an emerging separation technology. Industrial applications were greatly accelerated in the 1980s (Seader and Henley, 1998). The feed mixture is partially separated by means of a semi-permeable barrier, which is the membrane, into a permeate, that part of the feed that does pass

through the membrane and a retentate, that part of the feed that does not pass through the membrane (Seader and Henley, 1998).

The most commonly used membrane technology for liquid azeotropic mixtures is pervaporation with low pressure on the permeate side of the membrane in order to evaporate the permeate (Pettersen and Lien, 1995; Seader and Henley, 1998). Pervaporation is applicable to separations over the entire composition range, but the phase change requires considerably more energy than other pressure driven membrane techniques like reverse osmosis (Goldblatt and Gooding, 1986).

The main industrial applications of pervaporation separation processes include (Seader and Henley, 1998):

- removal of water from organic solvents (e.g., dehydration of alcohols, ketones and esters);
- removal of organics from water, and
- separation of organic-organic azeotropes (e.g., benzene-cyclohexane).

There are many alternatives for membrane-distillation hybrid separation processes. The key to an efficient and economic separation process is the membrane. It must have good permeability (high mass-transfer flux), high selectivity, stability, freedom from fouling (defect-free), and a long life (two or more years) (Seader and Henley, 1998). An illustration of a hybrid industrial separation process for dehydration of ethanol using membrane pervaporation in combination with a continuous distillation column is given in Figure 3.2.

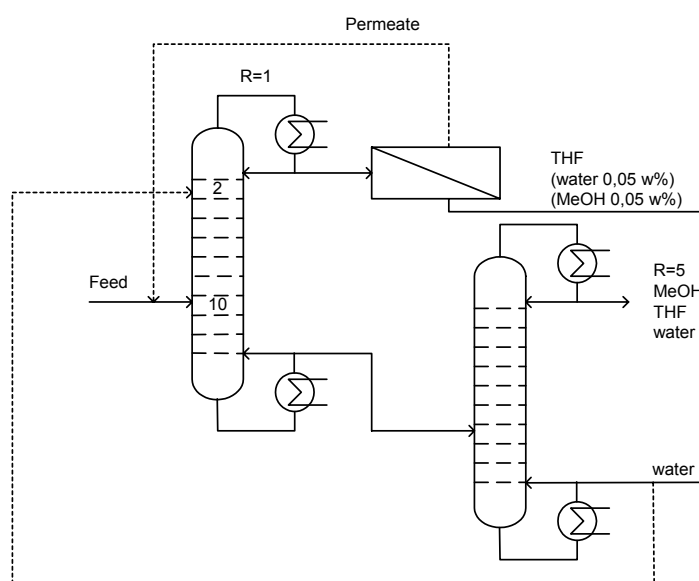


Figure 3.2., Industrial hybrid separation process

The illustrated separation process is based on extractive distillation, pervaporation, and distillation (ED+PV+D). Water addition can change significantly the vapour-liquid equilibrium of the THF-methanol system. The water addition can eliminate the THF-methanol azeotrope and this operation can be realised with extractive distillation applying water as extractive agent (Figure 3.2).

### 3.3 Entrainer-addition distillation methods

#### 3.3.1 Entrainers

A common technique to break the azeotrope *is* the addition of a third component, the entrainer, to the mixture.

One of the most difficult tasks in designing a separation sequence is the proper choice of entrainers which has been extensively discussed in literature (Doherty and Calderola, 1985; Stichlmair et al., 1989; Laroche et al., 1992; Foucher et al., 1991; Westerberg and Wahnschafft, 1993, Wasylkiewicz et al. 2000) and is also subject of chemical engineering textbooks about separation processes (Doherty and Malone, 2001; Stichlmair and Fair, 1998). Ewell et al. (1944), Bossen et al. (1993)) studied the relationship between hydrogen bonding and azeotrope formation and classified entrainers into groups according to their molecular interactions. From this they developed guidelines to identify chemical classes suitable as entrainers for heteroazeotropic and extractive distillation. Berg (1969) developed the classification of organic and inorganic mixtures and used information about the molecular structure to point out promising entrainers for extractive and heteroazeotropic distillation. Berg (1969) states, the successful entrainers for extractive distillation are highly hydrogen-bonded liquids (such as water, amino alcohols, amides, phenols alcohols and organic acids). The effectiveness of the entrainer is based on its ability to modify the relative volatility of the original mixture. Various approaches for this evaluation are given, for example by Van Winkle (1967).

There are four different kinds of entrainers:

- homogeneous entrainers: these change the relative volatility of the two azeotropic components without inducing a liquid immiscibility with either one of the

components. These types of entrainers can be subdivided into three classes for separating a minimum boiling azeotrope depending on the boiling temperature compared to the azeotropic components: light, intermediate and heavy entrainers.

- heterogeneous entrainers: these change the relative volatility of the two azeotropic components and induce a liquid immiscibility with one of the components that is used as an additional separation step.
- reactive entrainers: they react reversibly and preferentially with only one of the azeotropic components changing the components involved in the separation.
- “salting” entrainers: they dissociate ionically in the solution altering the azeotropic composition of the mixture to be separated.

The important task is the reduction of the extractive agent. (Hilal et al. (2001))

Three different conventional entrainer-addition based distillation methods can be distinguished depending on the properties and role of the entrainer:

- homogeneous azeotropic distillation: the entrainer is completely miscible with the components of the original mixture. It may form homoazeotropes with the original mixture components. The distillation is carried out in a conventional single-feed column. This kind of separation was studied in details by Thong et al. (2001a, 2001b, 2001c)
- heteroazeotropic distillation (decanter-distillation hybrids that involve heteroazeotropes): the entrainer forms a heteroazeotrope with at least one of the original mixture components. The distillation is carried out in a combined column and decanter system. Pham et al.(1990a, 1990b, 1990c), Ryan et al. (1989) and Wasylkiewicz et al (2003) studied this method in detail.
- extractive distillation: the entrainer has a boiling-point that is considerably higher than the original mixture components and is selective to one of the components. The distillation is carried out in a two-feed column where the entrainer is introduced above the original mixture feed point. The main part of the entrainer is removed as bottom product. This separation method was investigated in details by Jimenez et al (2001), Ligeró et al. (2003) and Langston et al (2005).

The definition of extractive distillation includes the symmetrical process of separating maximum-boiling azeotropes using a low-boiling entrainer (re-extractive distillation), and

combined heteroazeotropic and extractive distillation schemes (heteroextractive distillation) or extractive heterogeneous azeotropic distillation.

There are other methods that may also be called entrainer-addition distillations, including:

- reactive distillation: the entrainer reacts preferentially and reversibly with one of the original mixture components. The reaction product is distilled out from the non-reacting component and the reaction is reversed to recover the initial component. The distillation and reaction is usually carried out in one column (catalytic distillation). Giessler et al. (2001) studied the systematic structure generation method for the reactive distillation.
- chemical drying (chemical action and distillation): the volatility of one of the original mixture components is reduced by chemical means.
- distillation in the presence of salts: the entrainer (salt) dissociates in the mixture and alters the relative volatilities sufficiently so that the separation becomes possible. A salt added to an azeotropic liquid mixture will reduce the vapour pressure of the component in which it is more soluble.

### **3.3.2 Heteroazeotropic distillation**

Heteroazeotropic distillation involves the formation of a heteroazeotrope (or the use of an existing heteroazeotrope) to effect the desired separation. The important difference compared to homoazeotropic distillation is that a heteroazeotrope can be separated easily by liquid-liquid phase splitting (decantation). The distillation boundary is “crossed” by the decantation of the heteroazeotrope e.g. Doherty (2001), Widagdo and Seider and coworkers (1992; 1996).

The typical example of heteroazeotropic distillation is the dehydration of ethanol using benzene as entrainer that was presented by Young in 1902 (Pratt, 1967). Today, cyclohexane is a more common entrainer for ethanol dehydration by heteroazeotropic distillation.

### 3.3.3 Extractive distillation

Extractive distillation is the oldest known method for separating azeotropic mixtures. The basic principle is that the extractive entrainer interacts differently with the components of the original mixture and thus changes their relative volatility. These interactions occur principally in the liquid phase and the entrainer is introduced above the original mixture feed point to guarantee that the entrainer remains in appreciable concentration in the liquid phase in the column section below. The *extractive distillation*, according to the classical definition, is a method of separating minimum boiling binary azeotropes by use of an entrainer that is the heaviest species in the mixture, does not form any azeotropes with the original components, and is completely miscible with them in all proportions [ Doherty (2001)] . Today, extractive distillation is defined in a wider manner, namely the entrainer can also be the lightest and the middle boiling component as well. If the entrainer is the lightest component, the so called "reverse extractive distillation" is reported by Hunek (1989) that has been already used for successful separation. Extractive distillation of maximal azeotrope with middle boiling entrainer has also already been reported by Lelkes (2002).

A common restriction on the "extractive distillation" is that the entrainer should not introduce new azeotropes in the system, that is, no new distillation boundaries can be formed (Stichlmair *et al.*, 1989; Doherty and Knapp, 1993; Gmehling and Möllmann, 1998).

### 3.3.4 Heteroextractive distillation

A special alternative of the extractive distillation is if the entrainer forms a new heteroazeotrope with one of the components of the mixture. The entrainer may well form new azeotropes and this may even be preferably as in the process of heteroextractive distillation where the entrainer forms a heteroazeotrope with one of the original mixture components and it is miscible and selective to the other. The extractive distillation scheme may operate within one distillation region of the ternary mixture composition space, and still realize a desirable separation.

If a new heteroazeotrope is formed between the extractive entrainer and the component of the original mixture that is to be removed as distillate, then both heteroazeotropic and the extractive distillation can be combined into a single process as illustrated in Figure 3.3. The

heteroazeotrope  $A_2E$  (saddle) is removed overhead and separated by condensation and decantation, while excess of the entrainer is removed in the bottom product together with the one of the original mixture component that it extracts (here: component 1). The extractive process works within one distillation line (residue curve) region of the complex diagram, and the distillation boundaries are crossed by the liquid-liquid phase splitting in the heterogeneous region. This method was first studied by Wijesinghe (1985), and mentioned by Hilmen (2000). This is in fact a very attractive separation method because the entrainer is double-effective.

Example mixtures of the type given in Figure 3.3 are methyl ethyl ketone (2-butanone) - water - cyclohexanone. In the screening for entrainer such candidates are often ruled out, e.g. by the entrainer selection criteria given by Doherty and coworkers (1985; 1993) and Seader and Henley (1998). Thus, many of the entrainer selection criteria are too limiting, and one should not narrow the search for a new separation system by using conditions that apply for “old” processes, but rather see the possibilities and limitations that lie within each system in question.

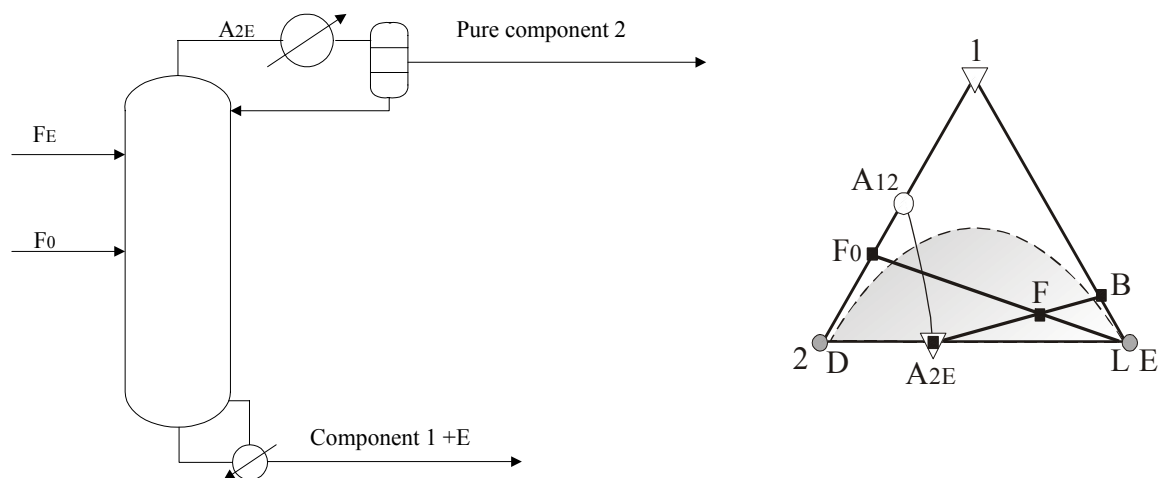


Figure 3.3., Heteroextractive distillation investigated by Wijesinghe (1985)

Another interesting example, given by Petlyuk and Danilov (2000), is the separation of acetone and chloroform, which form a maximum-boiling homoazeotrope by using water as an entrainer. Lelkes et al (2003) and Rodriguez et al. (2003) investigated also the heteroextractive distillation and its feasibility.

### 3.4 Feasibility study

An important part of the design of the different distillation based separation processes is its feasibility study. Skouras (2005) described the feasibility study for the separation of close-boiling and azeotropic binary mixtures by the addition of an entrainer introducing a heterogeneous azeotrope. The basic idea of this study is the calculation of the composition profiles for the rectifying and stripping section of the distillation column on the basis of vapour-liquid equilibrium and material balance (operating line) of each section. The method for binary system is well known, especially for constant molar overflow. For ternary mixtures Doherty (2001) gives an introduction to the application of this method, applying simplifications for the vapour liquid equilibrium and material balance. With the application of this feasibility investigation alternative it is possible to estimate the column behaviour at different operating conditions and to see the differences and internal dependencies of the different column operation policies. . If a column is psychically feasible then the stripping and rectifying profiles must intersect at the feed stage.

The feasibility study for the distillation of non-ideal ternary mixtures can be represented by Fidkowski et al. (2004) and Prokopakis et al. (1983).

For special distillation solutions, e.g. batch distillation, heteroextractive distillation, the feasibility investigations applying simplifying assumptions can be also completed (Lang, et al., 2000; Lelkes et al., 1998a, 1998b, 1998c). Their results obtained by feasibility studies agree well with simulation data obtained with rigorous column simulations.

Thong et al. (2001a, 2001b, 2001c, 2004) published a new approach of the feasibility. This new possibility of study has two stages. The first was the identification of classes of splits. The second stage assesses the feasibility of proposed flowsheets. The column parameters are determined numerically, based on geometric principles. The feasible combination of design parameters can be represented in a feasibility matrix, which can be used to identify advantageous parameters.

## 4. The mixtures selected for investigation

For the investigation of the quaternary mixtures and their separation such mixtures are selected that are arising as waste streams in the different industries. The industrial case studies show that such mixtures usually contain acetone, ethyl acetate (ETAC), ethanol (ETOH), isopropanol (IPOH), methyl-ethyl-ketone (MEK), isopropyl acetate (IPAC), heptane, and water. These components are found in several cases in the waste stream as quaternary mixtures. It is also typical for these waste stream quaternary mixtures that water is always present as one of the four components.

From the waste stream mixtures ten quaternary mixtures are selected on a systematic way for the investigation. The idea of the systematic selection is that the complexity of the mixtures should increase. On the other hand, the quaternary mixtures are so selected that always two should have similar vapour-liquid-liquid equilibrium. With this systematic selection the design alternatives can be tested on different mixtures.

The summarising table (Table 4.1) shows the systematic change in the complexity of the mixtures of the different groups. The number of the azeotropes is increasing. There are such azeotropes that cannot be found in the literature as measured ones; however, the vapour-liquid equilibrium calculations prove that they are existing. Such azeotropes are also listed in the tables but indicated as calculated (calc) ones. Table 4.2 and Table 4.3 show the binary and ternary azeotropes of the ten selected mixtures, respectively.

<i>Groups</i>	<i>1</i>				<i>2</i>		<i>3</i>		<i>4</i>	
<i>Mixtures</i>	1a	1b	2a	2b	3	4	5	6	7	8
	Water (1)	Water (1)	Ethylene Glycol (1)	Ethylene Glycol (1)	Water(1)	Water(1)	Water(1)	Water(1)	Water(1)	Water(1)
	ETOH (2)	ETOH(2)	Water (2)	Water (2)	ETOH(2)	ETOH(2)	ETOH(2)	IPOH(2)	ETOH(2)	ETOH(2)
	MEK (3)	ETAC(3)	ETOH (3)	ETOH(3)	ETAC(3)	MEK(3)	ETAC(3)	ETAC(3)	MEK(3)	ETAC(3)
	Acetone (4)	Acetone (4)	MEK (4)	ETAC(4)	IPAC(4)	IPAC(4)	MEK(4)	MEK(4)	n-Hept(4)	n-Hept(4)
No. and pairing of binary azeot.	3 (1)- (2) (1)- (3) (2)- (3)	3 (1)- (2) (1)- (3) (2)- (3)	3 (2)- (3) (2)- (4) (3)- (4)	3 (2)- (3) (2)- (4) (3)- (4)	5 (1)- (2) (1)- (3) (1)- (4) (2)- (3) (2)- (4)	5 (1)- (2) (1)- (3) (1)- (4) (2)- (3) (2)- (4)	6 (1)- (2) (1)- (3) (1)- (4) (2)- (3) (2)- (4) (3)- (4)	6 (1)- (2) (1)- (3) (1)- (4) (2)- (3) (2)- (4) (3)- (4)	6 (1)- (2) (1)- (3) (1)- (4) (2)- (3) (2)- (4) (3)- (4)	6 (1)- (2) (1)- (3) (1)- (4) (2)- (3) (2)- (4) (3)- (4)
No. and pairing of ternary azeot. liter.	1 (1)- (2)-(3)	1 (1)- (2)-(3)	1 (2)- (3)-(4)	1 (2)- (3)-(4)	2 (1)- (2)-(3) (1)- (2)-(4)	2 (1)- (2)-(3) (1)- (2)-(4)	3 (1)- (2)-(3) (1)- (2)-(4) (1)- (3)-(4)	1 (1)- (3)-(4)	2 (1)- (2)-(4) (1)- (2)-(3)	2 (1)- (2)-(4) (1)- (2)-(3)
calcul.								2 (1)- (2)-(4) (1)- (3)-(4)	2 (1)- (3)-(4) (2)- (3)-(4)	2 (1)- (3)-(4) (2)- (3)-(4)

Table 4.1.,. Four groups of the investigated mixtures

	Boil. T [°C]	Component (1) [wt %]	Component (2) [wt %]
ETAC (1) -n-Heptane (2)	70	83.3	16.7
Water (1)– ETAC(2)	70.4-72.3	7.9-8.6	91.4-92.1
ETOH (1) – n-Heptane(2)	70.9-72	48.3-49	51-51.7
ETOH (1)– ETAC(2)	70.9-72.1	28-31.2	68.8-72
Water (1) – MEK (2)	73.7-73.8	11-12	88-89
ETOH (1) – MEK (2)	74-75	34.3-40.4	59.6-65.7
IPOH (1)– ETAC(2)	74.5-76.11	19.6-26	74-80.4
ETOH (1)– IPAC(2)	76.4-76.7	51.4-53.7	46.3-48.6
ETAC (1)– MEK(2)	76.4-77.1	82-88.2	11.8-18
IPOH (1)-MEK(2)	77.5-77.7	29.6-34.2	65.8-70.4
MEK (1)– n-Heptane(2)	77.6	69	31
Water (1)- ETOH (2)	78-78.3	4-4.6	95.4-96
Water (1)– n-Heptane(2)	79.2	13	87
Water (1)-IPOH(2)	79.7-80.72	11.2-13.1	86.9-88.8
Water (1) – IPAC(2)	81.7-82.8	12.2-16.2	83.8-86.8

Table 4.2., Binary azeotropes of the investigated mixtures

	Boil. T [°C]	Component (1) [wt %]	Component (2) [wt %]	Component (3) [wt %]
Water(1) - ETOH(2) - n-Hept(3)	68	12.1	25.9	62
MEK(1) - n-Hept(2) - Water(3)	69.5	8.4	51	40.6
ETOH(1) - ETAC(2) - n-Hept(3)	70.1	29.5	39.5	31
Water(1) - ETOH(2) - ETAC(3)	70.2-70.4	7.8-8.3	8.4-9	83.2-83.3
Water(1) - ETAC(2) - MEK(3)	71.1	8.7	85	6.3
MEK(1) - n-Hept(2) - ETOH(3)	71.2	36.5	46	17.5
Water(1) - ETOH(2) - MEK(3)	73	10	11	79
Water(1) - IPOH(2) - MEK(3)	73.4	11.7	4	84.3
Water(1) - ETOH (2) - IPAC(3)	74.8	10	18.4	71.6
IPOH(1) - ETAC(2) - MEK(3)	75.4	20.4	68.1	11.5

Table 4.3., Ternary azeotropes of the investigated mixtures

## 4.1 Classification of the quaternary mixtures according to their VLLE

As a first step of designing any separation alternative it is inevitable to investigate the vapour-liquid-liquid equilibrium of the quaternary mixtures. Such investigation has been done by Serafimov (1968a, 1970), but only for ternary mixtures. Serafimov has also classified the ternary mixtures into several groups (see chapter 2.2.2.2).

The preliminary classification shown in Table 4.1 gives a summary of both the literature and the calculated azeotropes. This summary represents the complexity of the systems and indicates also the difficulty of their possible separation. However, for the design of the possible separation schemes, a deeper insight into the vapour-liquid-liquid equilibrium (VLLE) of the systems is also needed.

The study of the VLLE of quaternary mixtures is a bit handicapped by the fact that it needs a presentation in the space in a three dimensional tetrahedral diagram that is in a tetrahedron. This problem can be solved if a quaternary mixture is built up from its ternary sub-mixtures. That would mean that one quaternary mixture consists of four ternary sub-mixtures. Since the ternary mixtures have already been exhaustively investigated and also classified, this way can be followed. In this work, the classification and representation developed by Serafimov (1968a, 1970) is followed and applied for the ternary sub-mixtures.

After determining the four ternary sub-mixtures as a first step, the quaternary mixture is investigated. In the first step the VLLE of the ternary sub-mixtures is described, (i.e. residue curve map, separation boundaries, and the area of limited miscibility. In Serafimov's presentation (Figure 2.3) the pure components are presented in the vertex of the triangle and they are also called nodes. The binary and ternary azeotropes are also indicated as nodes. There are three kinds of nodes: stable, unstable, and saddle. The classical definitions for these nodes are the following:

- the stable node is the component or azeotrope with the highest boiling point in the region. All the residue curves in the region go to this point,
- the unstable node is the component or azeotrope with the lowest boiling point in the region. All the residue curves in the region originate from this point,

- the saddle is if the residue curves move toward and then away from this point. Pure components and azeotropes which have a boiling point between the stable and unstable nodes are saddles.

To classify the ten quaternary mixtures, having minimum boiling both homogeneous and heterogeneous azeotropes, selected for this study, first the VLLE of the ternary sub-mixtures are determined. In the second step, the VLLE of the quaternary mixture is determined considering also the VLLE of the individual ternary sub-mixtures. The result is presented in a three dimensional tetrahedral diagram. It is, however, interesting to find connections to the work of Serafimov who comprehensively classified the ternary mixtures. Therefore, the tetrahedrons are also presented in a so called “open form”. In this open form the triangles representing the ternary sub-mixtures can be identified and it is possible to recognise the connection to the Serafimov’s classification. It is also possible to detect when a node of a ternary sub-mixture changes its character if the fourth component appears that is the system becomes a quaternary one.

#### **4.1.1 Group 1**

The four mixtures studied in this group are listed in Table 4.1.,. The significant characteristic of this group is that there is a ternary sub-mixture (water, ethanol, ethylacetate and water, ethanol, methyl ethyl ketone) forming three binary azeotropes and one ternary azeotrope. The fourth component is either acetone with the minimum boiling point or ethylene glycol with the maximum boiling point forming no azeotropes with any of the other three components. The tetrahedron and the open tetrahedron are shown in Figures 4.1 and 4.2.

It can be seen that in the case of mixtures 1a and 1b the non-azeotropic forming component is the most volatile component of the mixture (acetone), the nodes of the four ternary sub-mixtures keep their character and there is no change in the types of the nodes: the pure components are stable nodes except the most volatile, acetone, which is an unstable node. The binary azeotropes are saddles, the ternary one is unstable.

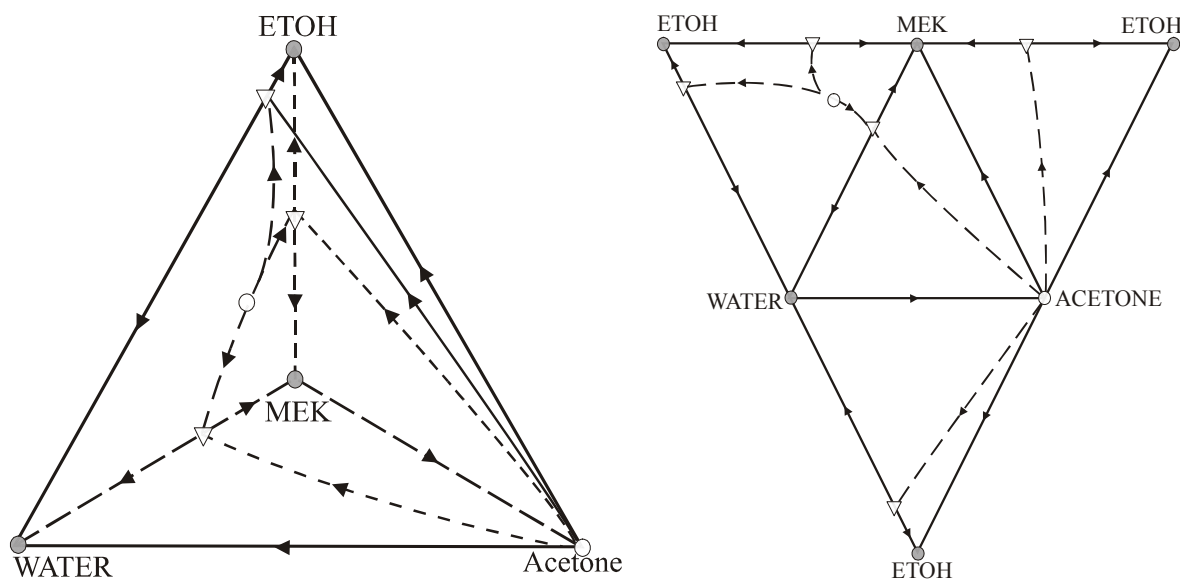


Figure 4.1. Tetrahedron and its “open form” for the mixture 1a

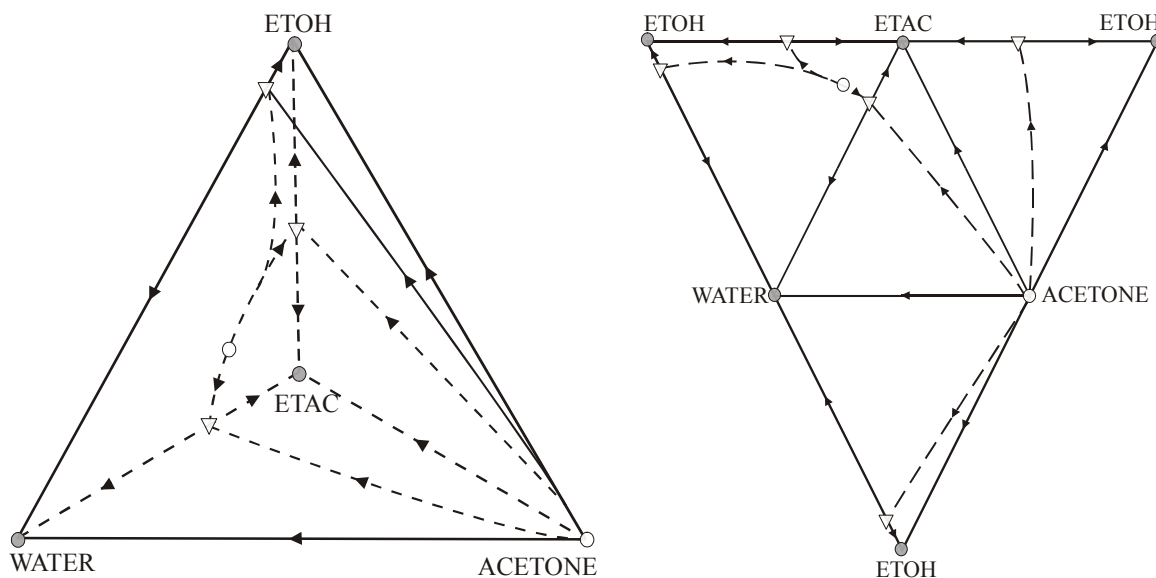


Figure 4.2., Tetrahedron and “open form” for the mixture 1b

If the non-azeotropic forming component has the maximum boiling point (ethylene glycol) it is always a stable node. The character of the other pure components depends on the existence of this component. They will change their character from stable node to saddle if the ethylene glycol is present (Figure 4.3, Figure 4.4). The binary azeotropes will change

their character from saddle to unstable nodes, the ternary one remains; however, an unstable node.

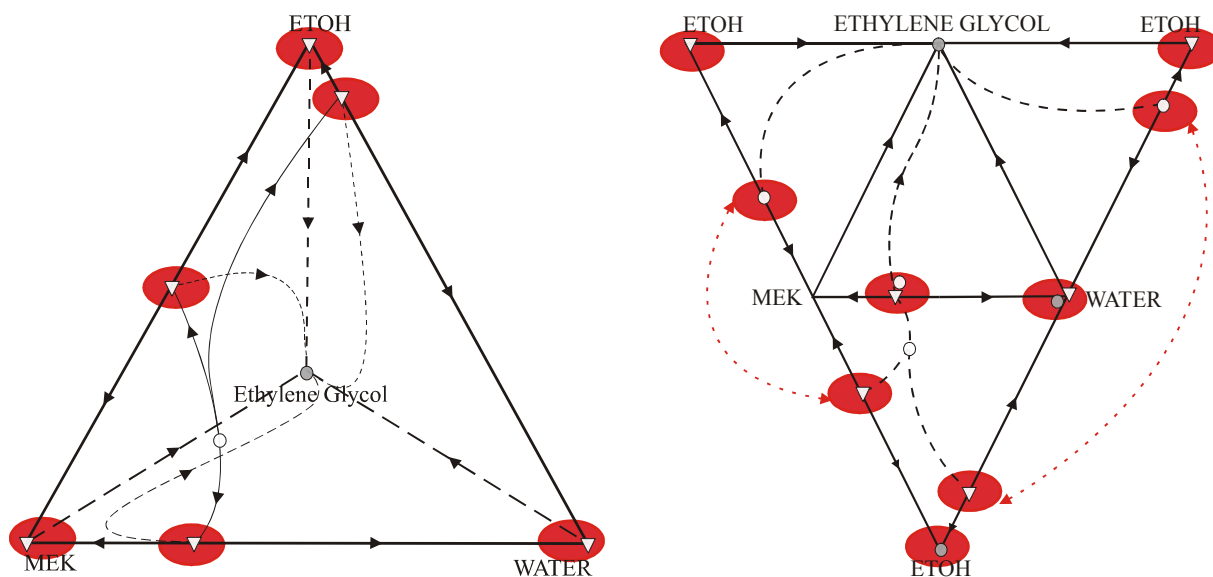


Figure 4.3., Tetrahedron and "open form" for the mixture 2a

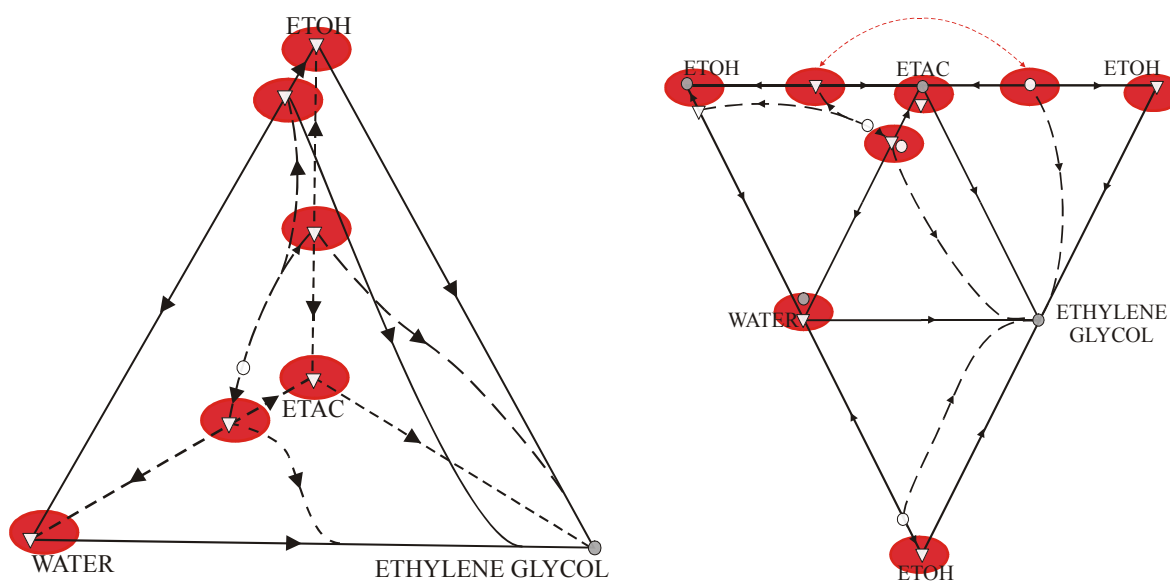


Figure 4.4., Tetrahedron and "open form" for the mixture 2b

The shaded marking shows the change of the types of nodes.

### 4.1.2 Group 2

The two mixtures, mixture 3 and 4 are shown in Table 4.1.

In these mixtures there is one component pair which does not form azeotrope with each other. The other components form minimum boiling azeotropes. If the character of the nodes of the four ternary sub-mixtures are considered it can be determined that there are changes in their character. The reason is that two components, ethyl acetate - isopropyl acetate and the methyl ethyl ketone – isopropyl acetate, do not form azeotropes and if both are present in mixture then the pure component of the lower boiling point will change its character from a stable node into a saddle. This will result in that the binary azeotropes will change between this saddle component and the others from saddle into unstable node.

In both mixtures this will result in three changes of the characters of the nodes of the four ternary sub-mixtures if the quaternary mixture is investigated (Figure 4.5, Figure 4.6).

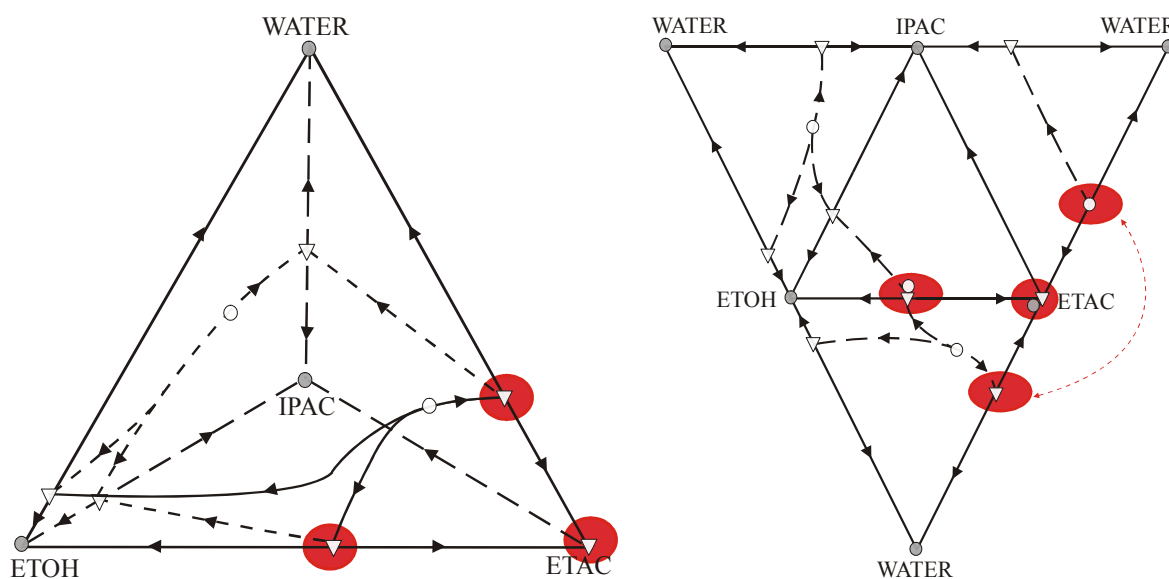


Figure 4.5., Tetrahedron and “open form” for the mixture 3

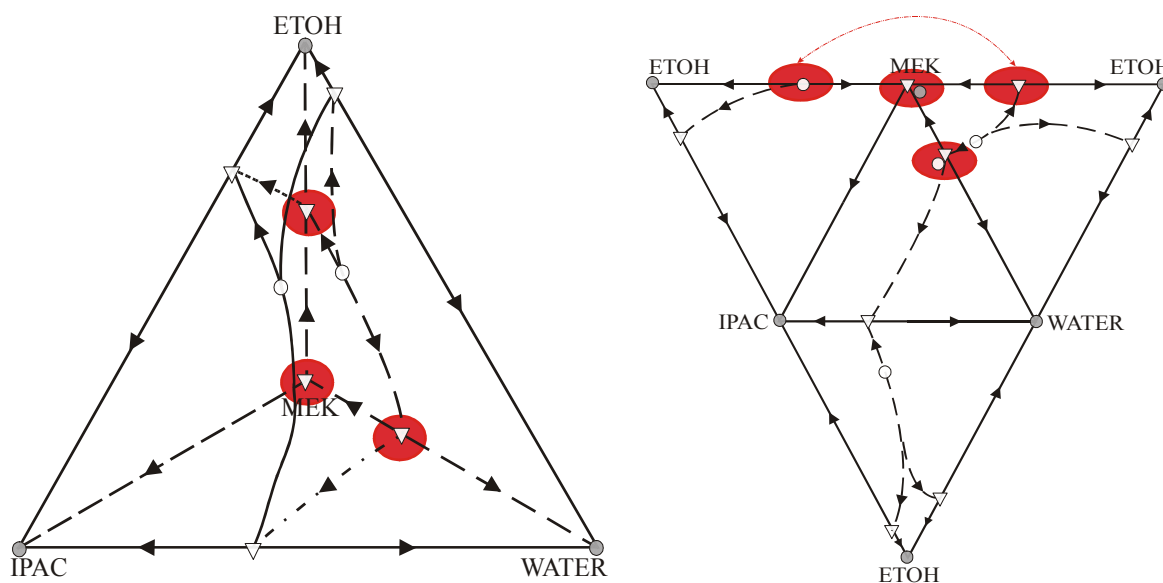


Figure 4.6., Tetrahedron and “open form” for the mixture 4

### 4.1.3 Group 3

The mixtures of this group are mixtures 5 and 6 (Table 4.1).

The four ternary sub-mixtures form in each combination binary azeotropes. However, in one of the ternary sub-mixtures there is no ternary azeotrope. In this ternary sub-mixture there is one binary azeotrope which has the lowest boiling point. Its character is unstable. If, however, this point is investigated in the quaternary system it will turn into a saddle.

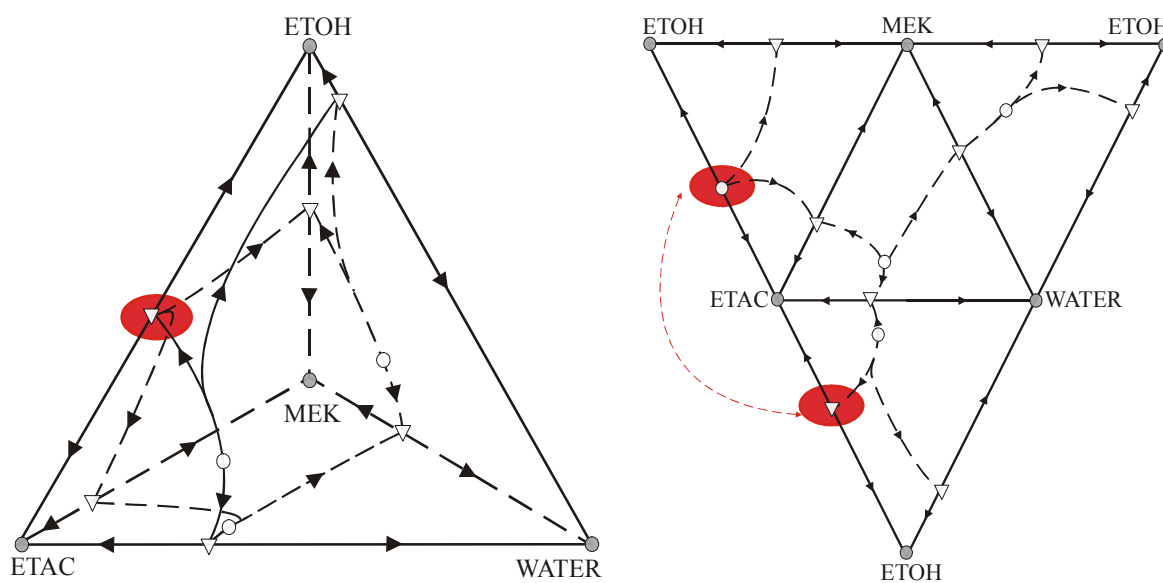


Figure 4.7., Tetrahedron and “open form” for the mixture 5

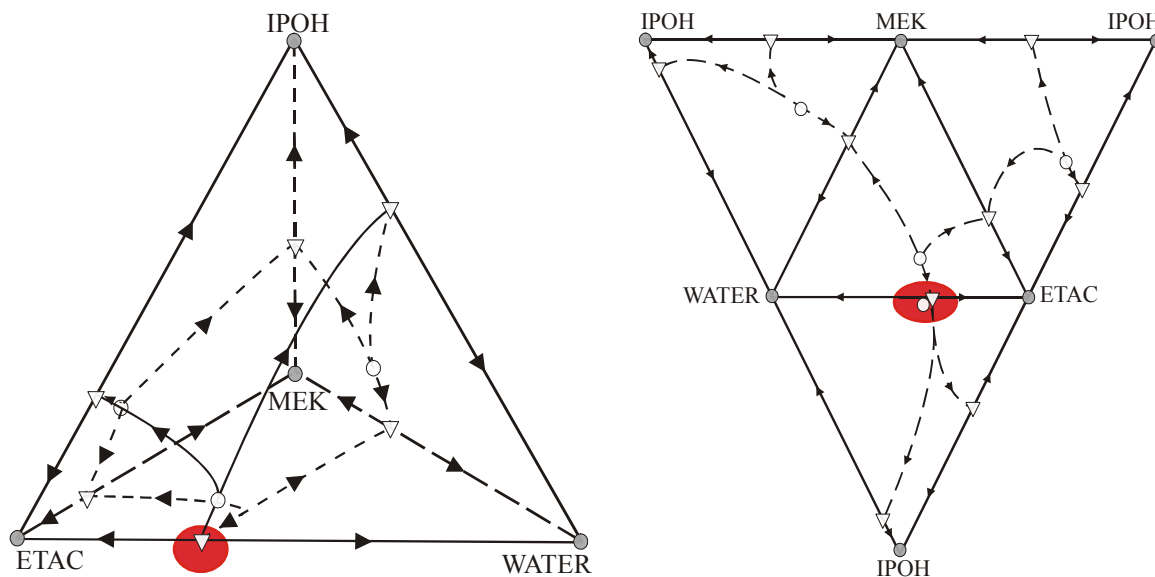


Figure 4.8., Tetrahedron and “open form” for the mixture 6

#### 4.1.4 Group 4

The mixtures of this group are the most complicated ones (mixtures 7 and 8), because in each combination binary azeotropes form, and each ternary sub-mixture also has ternary azeotropes.

The character of the nodes of each ternary sub-mixture keeps its character regardless of whether the mixtures are in the ternary sub-mixture or the quaternary mixture. Thus, there will be no change in the character of the nodes in this group.

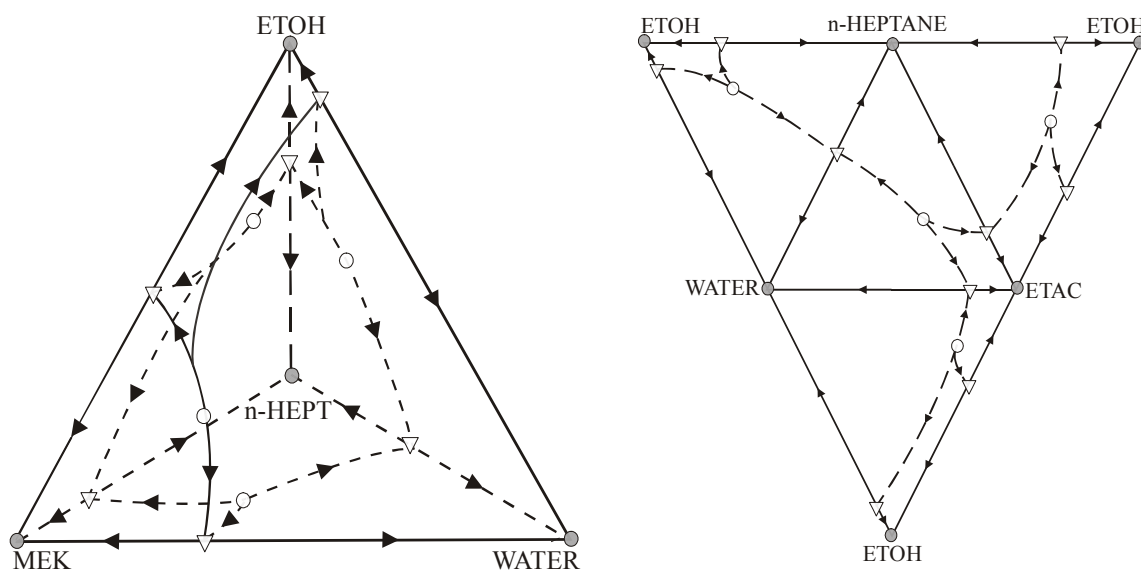


Figure 4.9., Tetrahedron and “open form” for the mixture 7

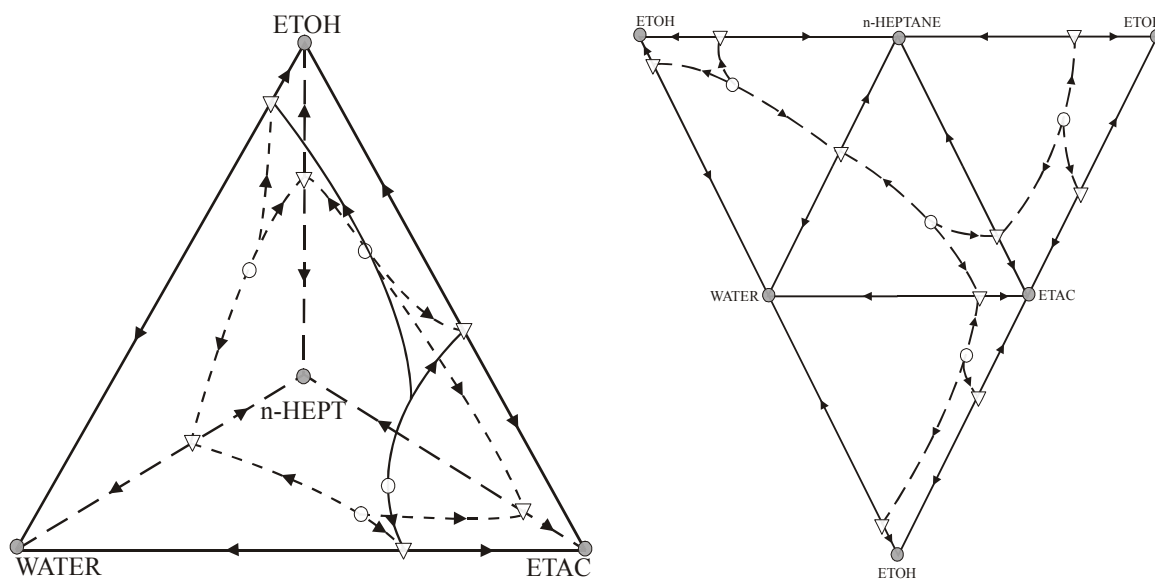


Figure 4.10., Tetrahedron and “open form” for the mixture 8

#### 4.1.5 Conclusions

After studying the ten quaternary mixtures that form minimum boiling both homogeneous and heterogeneous azeotropes, several conclusions can be drawn from the change of the character of the nodes when the components are studied in the ternary sub-mixtures or in the quaternary mixture.

##### *Rule 1*

If a node changes its character, the change is from stable or unstable to saddle. There is no change into stable or unstable node.

##### *Rule 2*

If a ternary azeotrope exists in a ternary sub-mixture, this ternary azeotrope is an unstable node. In this case the binary azeotropes are saddles and the pure components are stable nodes. If, however, no ternary azeotrope exists in the ternary sub-mixture, the binary azeotrope of the lowest boiling point is an unstable node. In this case it will turn into saddle if there is a ternary azeotrope of the lowest boiling point in the quaternary mixture.

*Rule 3*

If there are binary azeotropes in a quaternary mixture, they will be saddle; however, in the ternary sub-mixture they can be also unstable. They are never stable nodes.

*Rule 4*

If one of the four components has the minimum boiling point and this component does not form azeotrope with the others, its presence will not influence the character of the nodes.

*Rule 5*

If the non-azeotropic forming component has the highest boiling point it will cause several changes in the character of the nodes.

*Rule 6*

If in a ternary sub-mixture there is a component pair which forms no binary azeotrope while the others do, then the lower boiling component of this component pair will turn into a saddle from a stable node.

## 5. Extractive heterogeneous-azeotropic distillation

If such non-ideal mixtures are to be separated where both homogeneous and heterogeneous azeotropes are present, a new hybrid tool devoted to the separation of such quaternary mixtures, the extractive heterogeneous-azeotropic distillation (EHAD) can be used. This new hybrid separation tool, first introduced by Szanyi *et al.* (2004a), combines the advantages of the extractive and the heterogeneous azeotropic distillations. Figure 5.1 shows the EHAD. A component that has both entrainer and extractive agent functions is fed to the top of the column. In the mixtures investigated in this work this component is always the water, which is called extra water. In the top of the column a two phase product is always obtained and a phase split decanter is applied. The organic rich phase is the top product and the water rich phase is applied as reflux. The bottom product is a one phase product.

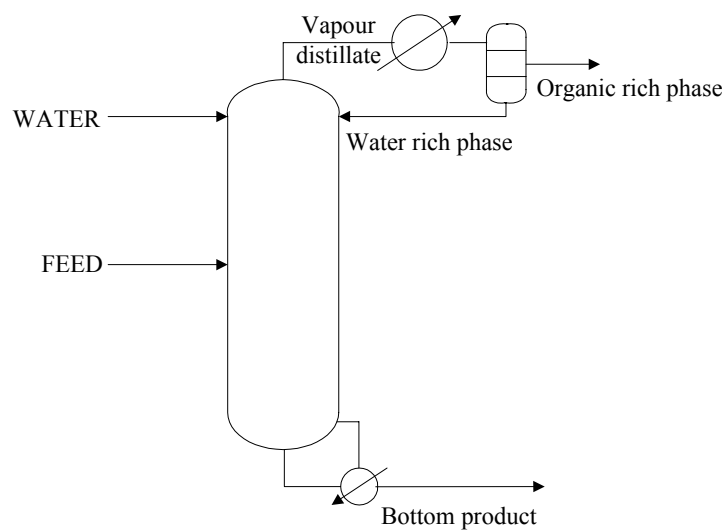


Figure 5.1. The extractive heterogeneous azeotropic distillation

In the case of ternary mixtures (e.g. ethanol, ethyl-acetate, water, Figure 5.2) one of the objectives of the EHAD is to produce a saddle distillate. This separation method is applicable to situations where the distillation region is bound by (generally) four stationary points typically involving a high-boiling pure component node, a low-boiling ternary azeotropic node that is an unstable node, and two binary azeotropic saddles where an objective is to produce one of the binary azeotropic saddles as distillate using the pure

component as an extractive distillation solvent. EHAD can produce one or the other binary azeotrope as distillate using the common pure component depending on the specific shape of the residue curves even though the pure component does not have a particular affinity for either of the other two components (else it would not have formed the binary minimum-boiling azeotropes) and normally would not have been selected as an extractive distillation solvent. The important characteristic of the addition of the extractive agent/entrainer (extra water) is the crossing distillation boundary. The above mentioned characteristic of the extra water offers that the suitable extractive agent is the component with the higher boiling point; however, this conservative option is not always true (see the separation of mixtures 2a, 2b). If the feed composition is in the other distillation region, the crossing is realized.

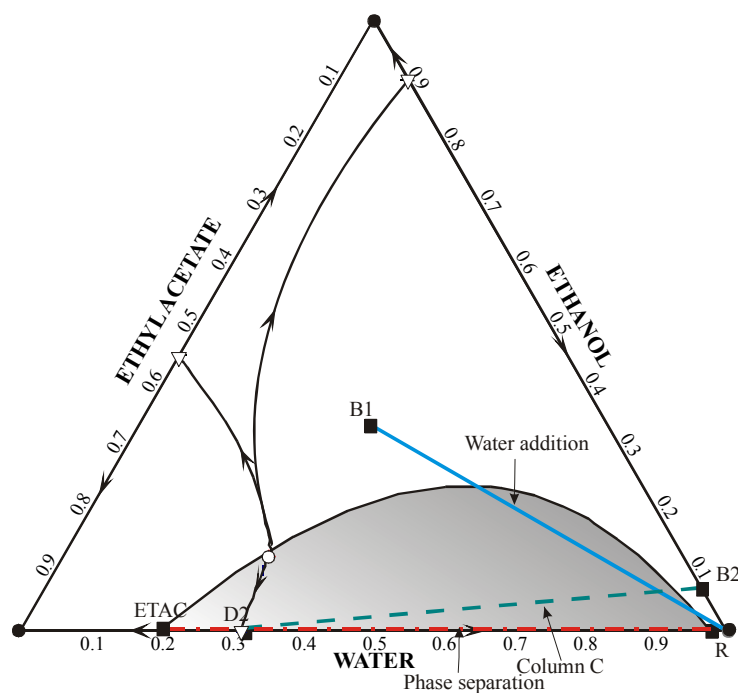


Figure 5.2., Water – Ethyl acetate – ethanol diagram

In the case of quaternary mixtures the above mentioned features can be different however. In some cases the distillate is not a saddle binary azeotrope, but it can be a ternary mixture. It can be interpreted with the presence of distillation boundary surfaces. The extractive agent/entrainer changes the volatility. As a result one of the components goes into the bottom product with the extractive agent, extra water and the water of the feed, and the ternary distillate composition lies on a distillation boundary line of the ternary sub-mixture.

This boundary line is the closest one to the extractive agent, in the cases investigated: water.

The volatility change effect of the water is also shown in Chapter 6.1 for binary component pairs (Figure 6.2, Figure 6.3).

## 5.1 Feasibility study of the EHAD

For the proper design of the EHAD (Figure 5.1) its feasibility should be investigated that is the proper condition of its operation where the desired separation is achieved. It is necessary to determine (i) the number of theoretical plates, (ii) the corresponding extractive agent (water) flow, (iii) the location of the extractive agent, (iv) the location of the feed stream, (v) the heating requirement.

These parameters are investigated with rigorous modelling while the separation requirements are fulfilled. This investigation is presented for the water-ethanol-ethyl acetate ternary sub-mixtures to be separated in the separation train designed for the mixtures of group 1. For the other EHAD the same investigation is carried out.

*a.) Number of theoretical plates, water consumption (extractive agent), and reboiler duty*

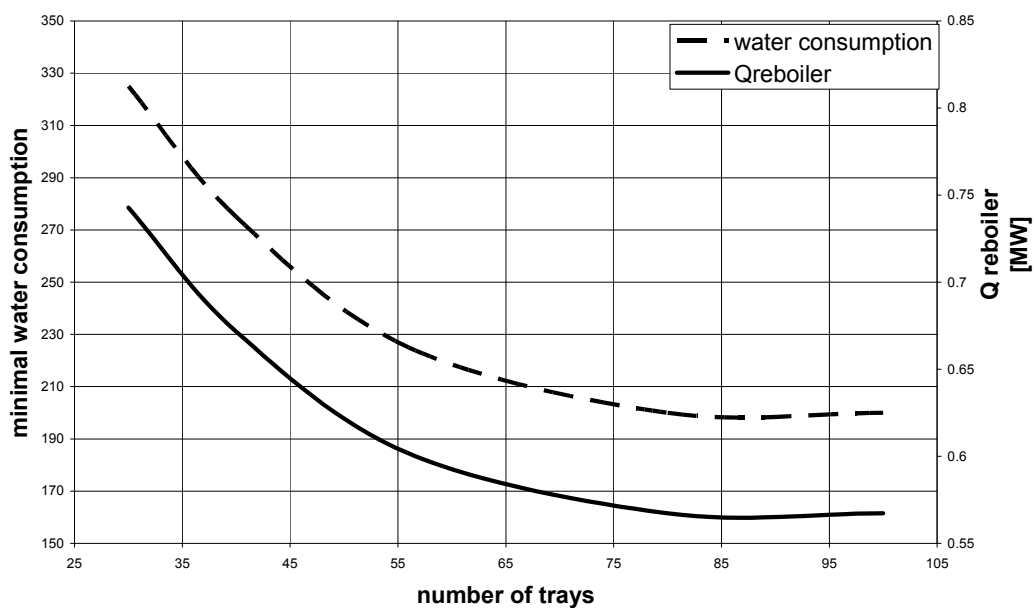


Figure 5.3., Minimal water (extractive agent) consumption and reboiler duty in the function of the number of trays

First the dependencies between the minimal water consumption, which is the extractive agent, the reboiler duty, and the number of theoretical plates is determined (Figure 5.3). As it can be seen the minimal water consumption together with the reboiler duty shows a minimum in the function of the number of theoretical plates. This is around 80 plates. In spite, based on engineering judgment, 50 theoretical plates, around 100 real trays, are selected to avoid unrealistic columns height.

*b.) Feed tray location for the extractive agent*

After determining the number of theoretical plates, the location of the feed tray of the extractive agent (water) is determined. Figure 5.3 shows that if the feed tray location is varied and the other parameters are unchanged the separation of the EHAD gets worse that meaning that the concentration of the ethyl-acetate is increasing in the bottom.

Therefore, the extractive agent is to be fed onto the top tray of the EHAD.

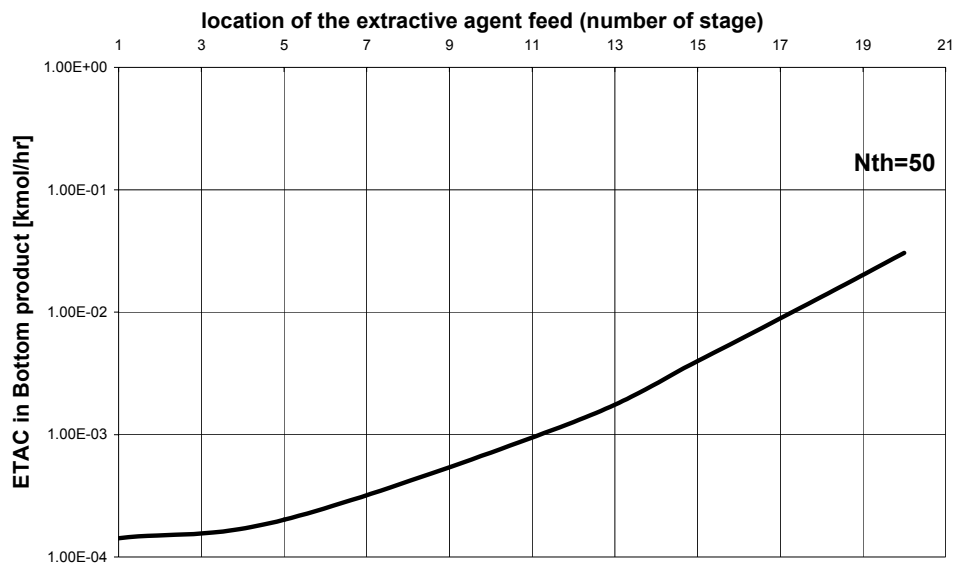


Figure 5.4., Feed tray location of the extractive agent (water)

## c.) Feed tray location

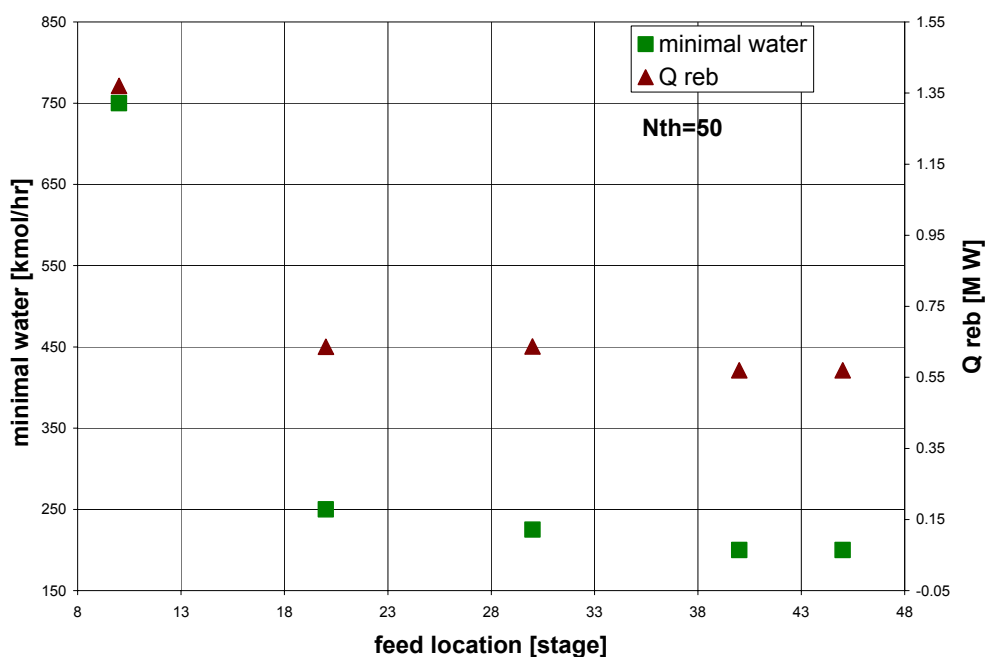


Figure 5.5., Feed tray location of the extractive agent (water)

The feed tray location is determined at constant separation while the extractive agent quantity is varied. As shown in Figure 5.5, the 30th tray should be selected to work at the lowest water quantity and reboiler duty.

## 5.2 Comparison of EHAD and the heteroextractive distillation

Extractive heterogeneous-azeotropic distillation (EHAD) differs from the heteroextractive distillation since no new azeotrope is formed. The extractive agent/entrainer is water and this component is already present in the mixtures studied. On the other hand, the extractive and relative volatility changing effect of the autoentrainer/extractive agent is fully utilised and there is no rectifying section in the column. The extractive process works within one distillation line (residue curve) region of the complex diagram, and the distillation boundaries are crossed by the liquid-liquid phase splitting in the heterogeneous region.

On the other hand, the application of extra water as extractive agent/entrainer corresponds to the basic principle of the “green chemistry” (Anastas (1998)) since no new material is added to the mixture for the sake of proper separation.

## 6. Novel hybrid processes for the separation of the mixtures

### 6.1 Group 1

The mixtures of group 1 are quaternary mixtures where there are azeotropes in only one ternary sub-mixture (Table 6.1, Table 6.2). The fourth component is a non-azeotropic forming component having the lowest or the highest boiling point in the quaternary mixture.

Binary azeotropes				
	Boil. T [°C]	Water [wt %]	ETOH [wt %]	MEK [wt %]
Water – MEK	73.7-73.8	11-12	-	88-89
ETOH – MEK	74-75	-	34.3-40.4	59.6-65.7
Water- ETOH	78-78.3	4-4.6	95.4-96	-
Ternary azeotropes				
Water-ETOH-MEK	73	10	11	79

Table 6.1., Binary and ternary azeotropes for mixture 1

Binary azeotropes				
	Boil. T [°C]	Water [wt %]	ETOH [wt %]	ETAC [wt %]
Water – ETAC	70.4-72.3	7.9-8.6	-	91.4-92.1
ETOH – ETAC	70.9-72.1	-	28-31.2	68.8-72
Water- ETOH	78-78.3	4-4.6	95.4-96	-
Ternary azeotropes				
Water-ETOH-ETAC	70.2-70.4	7.8-8.3	8.4-9	82.7-83.8

Table 6.2., Binary and ternary azeotropes for mixture 1

The topology analysis of the ternary sub-mixture (water, ETOH, MEK/ETAC) shows, that this ternary sub-mixture exhibits two binary homoazeotropes between ethanol-water and MEK/ETAC-ethanol, one binary heteroazeotropes between MEK/ETAC-water, and a

ternary heteroazeotrope. The ternary heteroazeotrope is the only unstable node, the three binary are the saddles, and the three pure component vertexes are stable nodes. Three distillation boundaries exist— these are unstable separatrices (the residue curve separatrix goes from an unstable node to a saddle) - running from the ternary azeotropes to each one of the binary azeotropes. Figure 6.1 shows the VLLE data for the ternary sub-mixture (ethanol, ethyl-acetate, water) of mixture 1.

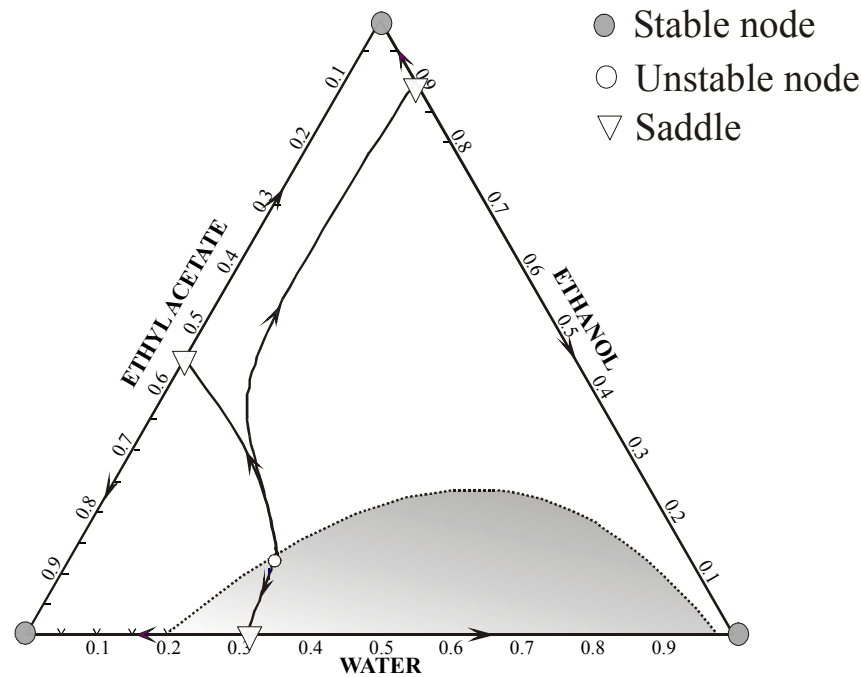


Figure 6.1., Diagram of the ternary the sub-mixture of mixture 1a

It is one of the major aims of this work to design a separation scheme based on the EHAD for these non-ideal mixtures.

In the case of the non-ideal binary systems, it is interesting to see how to water addition changes the VLE and makes the desired separation possible.

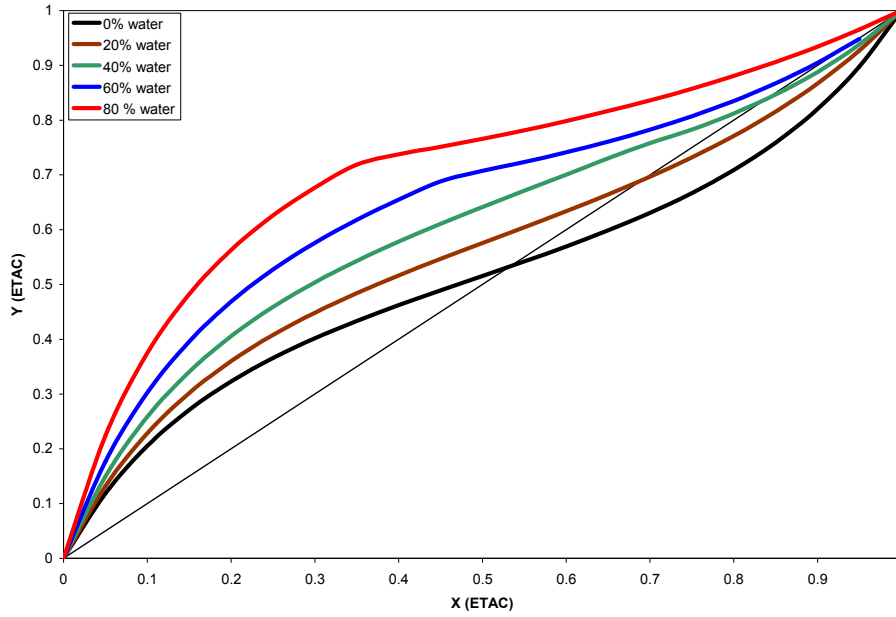


Figure 6.2., Water addition to the ETAC-ETOH binary azeotropes

In the ethyl acetate – ethanol system, the water changes volatility in the order of the value of volatility. It becomes possible with the addition of appropriate water quantities that the azeotrope disappears. In the case of the system MEK – Ethanol the water changes volatility in the opposite order (Figure 6.3).

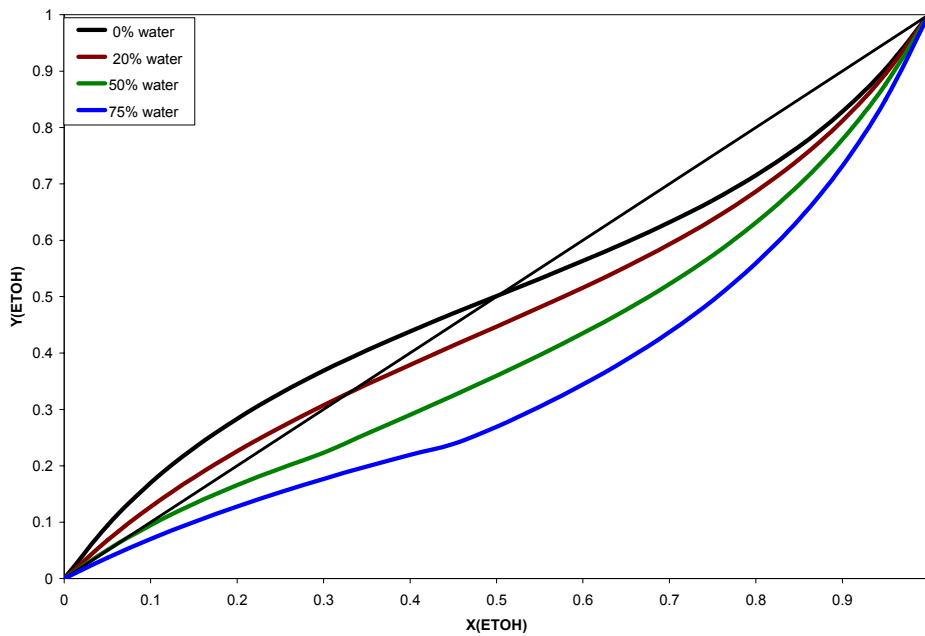


Figure 6.3., Water addition to the MEK-ETOH binary azeotropes

Other components are also tested as possible entrainer and/or extractive agent, but results show that water properly changes the VLLE behaviour of the system. These features of the water addition unify the advantages of the extractive and the heterogeneous azeotropic distillation and are typical features for the EHAD.

Moreover, the four mixtures of group 1 offer also another possibility to investigate different separation policies. These policies come from the separation heuristics determined for ideal mixtures and summarised by e.g. Douglas (1989), Mizsey and Fonyo (1990), and Biegler (1997). These heuristic rules can be used as general guidelines and they have proven to be powerful tools at the synthesis step for the design of separation structures for ideal mixtures.

Because of the complex behaviour of the different non-ideal mixtures, however, the synthesis step of their separation cannot always be generalized and there are practically no general guidelines for the synthesis like in the case of the ideal mixtures.

Among the several heuristic rules, one important rule recommends doing the easy split first and leaving the most difficult one to the end. This rule has not been investigated for non-ideal mixtures, yet. The mixtures of group 1 could, however, be suitable since the separation of the non-azeotropic forming components (acetone or ethylene glycol) can be carried out with common distillation. Therefore, this separation can be considered an “easy split”. So, while synthesizing separation alternatives for the mixtures of group 1, the validity of this heuristic rule can be also tested.

For the synthesis step of the different feasible separation alternatives the procedure recommended by Rev et al. (1994) and Mizsey et al. (1997) is followed. It is, however, always considered that the mixtures are suitable for the right application of the EHAD; thus the synthesis procedure is always directed for its application.

### **6.1.1 Separation schemes for mixtures 1a and 1b**

Separation alternatives Figure 6.4 shows the case when the most volatile non-azeotrope forming component (acetone) is separated first with an ordinary distillation and the more complicated separation that is the separation of the ternary mixture with EHAD is left to the end of the process. This separation (column 2, C2) is already analyzed and explained in Figure 5.2.

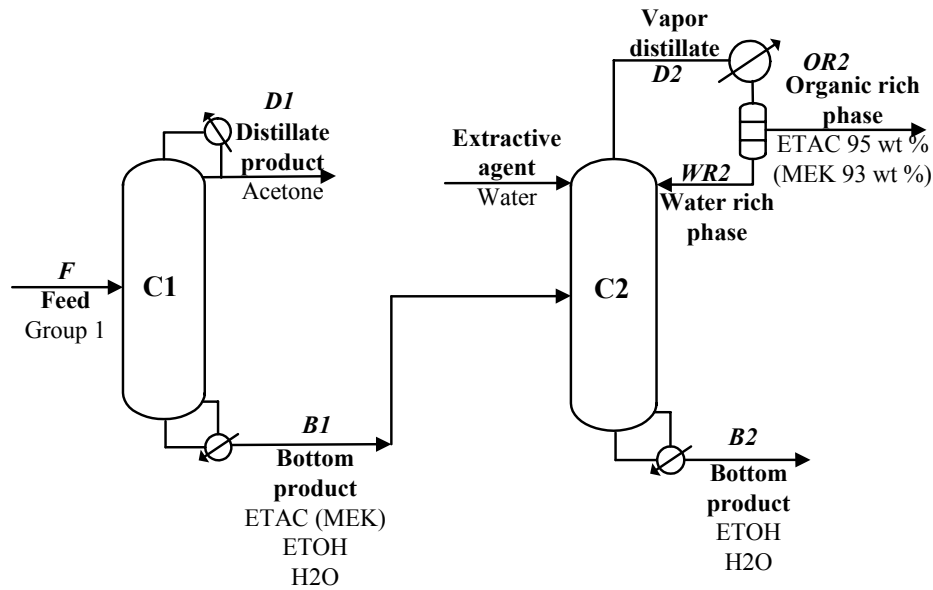


Figure 6.4., Separation scheme starting with “easy split” for mixtures 1a,b

Figure 6.5 shows the opposite alternative where EHAD is applied first to the separation of the quaternary mixture and the easy separation of the acetone is left to the end of the process. The operation of the EHAD for this particular case is discussed in Chapter 5 and shown in Figure 5.1.

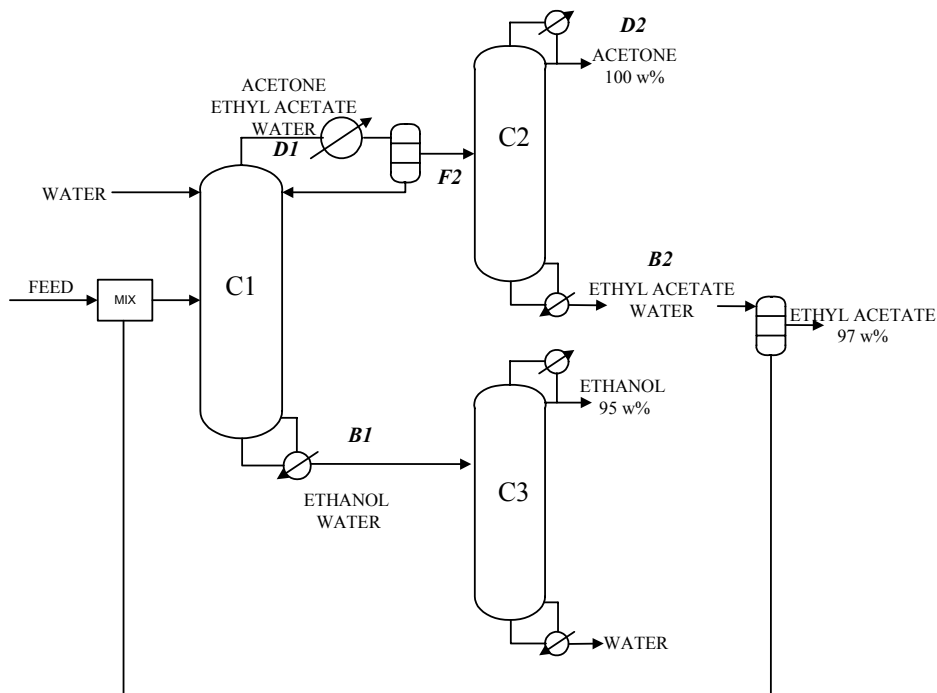


Figure 6.5., Separation scheme starting with the EHAD for mixtures 1a,b

The VLLE equilibrium and the separation of the quaternary mixture 1a in the EHAD of the separation scheme starting with the EHAD are shown in Figure 6.6.

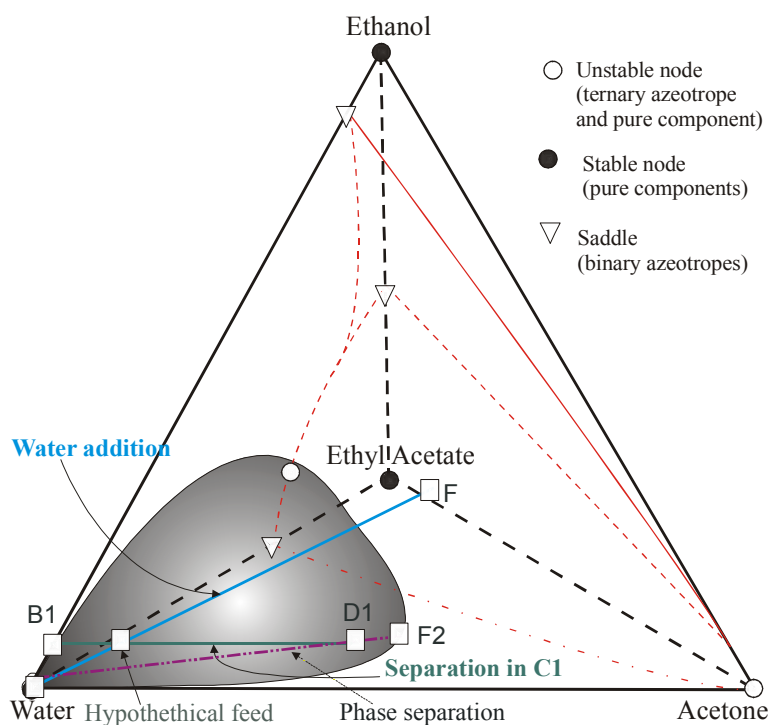


Figure 6.6., 3-dimensional tetrahedral diagram for the presentation of the separation in the EHAD column

The presentation of the quaternary mixture shows in a tetrahedron. In the 3-dimensional system the simple distillation regions are bounded by 2-dimensional surfaces called 2-dimensional separatrixes which are indicated by the 1-dimensional separatrix lines.

In this case the azeotrope points (binaries are indicated with a square, ternary ones are indicated with a triangle) and separation boundaries are indicated. This separation boundary lines form a surface in the space. (The surfaces formed by residue curves are not indicated for the sake of a simpler overview.) In this system the three surfaces are present. All surfaces contain two binary azeotropes and one ternary azeotrope. The two liquid phase area is also shown as a shaded area. The feed composition is shown with the point F. The hypothetical feed is the mix of the real feed and water addition stream. The operating line of the EHAD (column 1, C1) is shown, the top product, being the organic reach phase of the phase separation, is D1 and the bottom product is B1. The top product is processed in column 2. Figure 6.7 shows the VLLE equilibrium and the operating line of this column. The ternary system of MEK/ETAC – acetone – water represents Serafimov's class 1.0.-2.

The MEK/ ethyl acetate form a heterogeneous azeotrope and an immiscibility gap over a limited region of ternary compositions exists. A distillation boundary, running from acetone vertex (this is the unstable node) to the binary heteroazeotrope (this is the saddle) divides the composition space into two regions, thus limiting the feasible products under distillation. In this case, the distillate product is the pure acetone, and the bottom is the mixture of ethyl acetate and water with the composition near to the binary azeotropic composition. The phase separator is also indicated, and ethyl acetate is obtained in 97 w % purity corresponding to the VLLE.

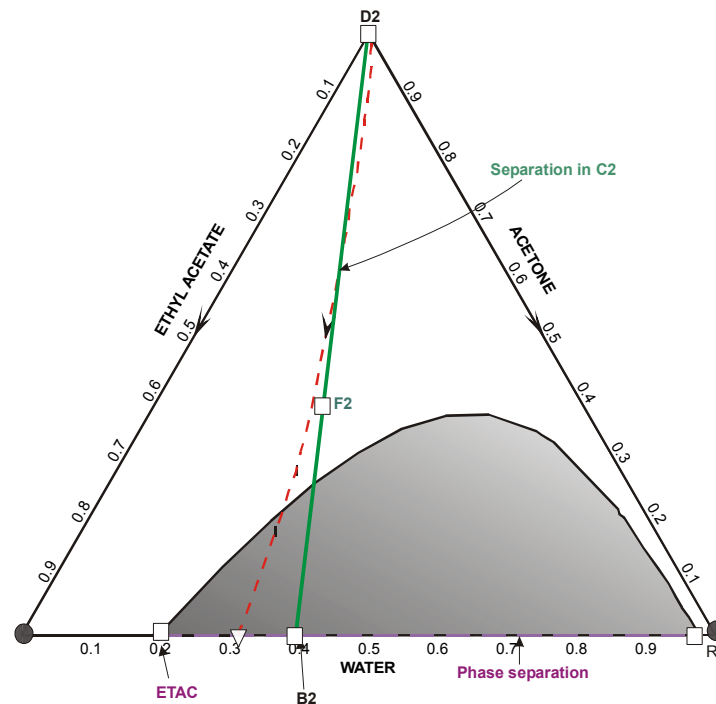


Figure 6.7., Ternary diagram of the mixture

To determine the better separation process of these two alternatives, economic evaluation is carried out investigating the total annual cost (TAC). European utility prices are applied (Table 6.3).

Capital cost	
Marshall & Swift index (1056.8/280) [16]	
Project life 5 years	
Utility	Price
LP-steam	17 euro/ton
Cooling water	0.04 euro/ton
Electricity	41 euro/MWh

Table 6.3., The basic data for the calculation of TAC

The project life is five years. The same tendency is typical for the case if the project life is ten years.

Figure 6.8 shows the calculated total annual cost (TAC) data for both separation process alternatives at different acetone compositions in the feed. According to the TAC calculations it becomes obvious that the structure starting with the ordinary distillation proves to always be the cheaper one. This corresponds to the heuristic rule determined for an ideal system that states the easiest separation should be made first and the most difficult should be left to the end.

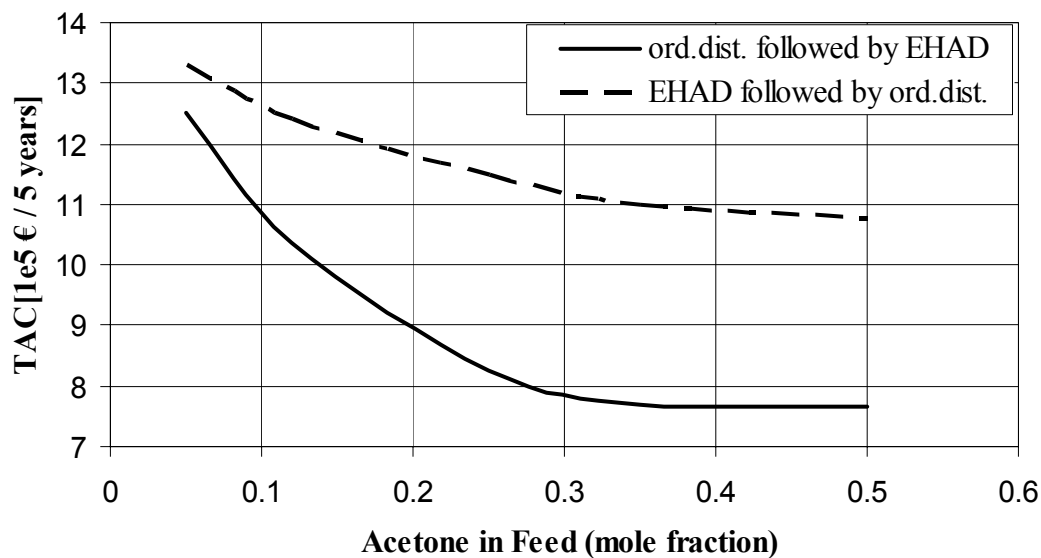


Figure 6.8., Total annual cost of the different separation processes

### 6.1.2 Separation schemes for mixtures 2a and 2b

If the non-azeotrope forming component is the least volatile one (ethylene glycol), the separation of the quaternary mixture can be solved in three ways. Figure 6.9 shows the first possible solution, in which the least volatile non-azeotrope forming component (ethylene glycol) is separated first with an ordinary distillation (“easy split” first) and the more complicated separation, the separation of the ternary mixture with EHAD, is left to the end of the process.

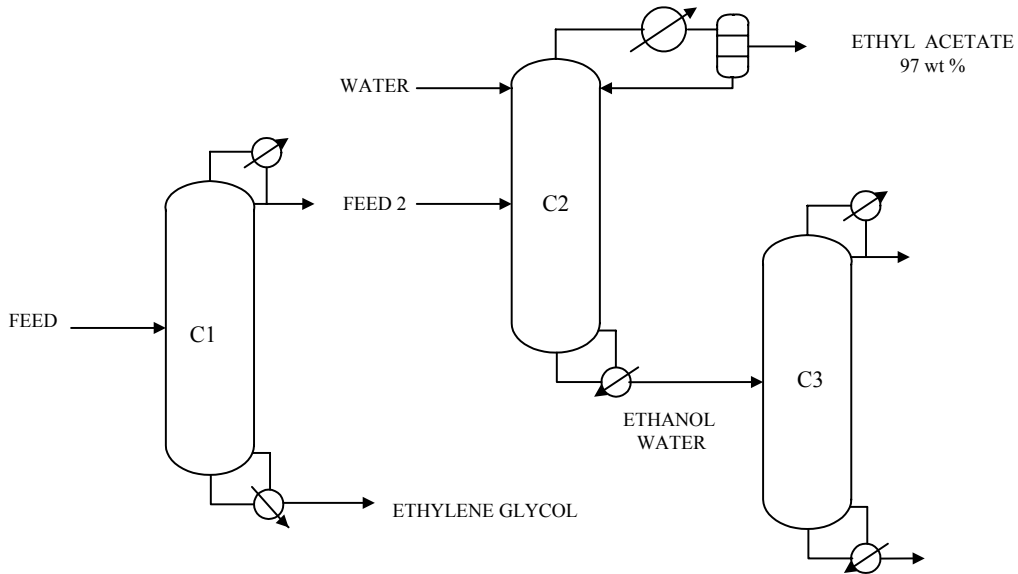


Figure 6.9., Separation structure starting with "easy split"

This difficult separation (column 2, C2) has already been analyzed and explained earlier in Chapter 5. The separation of ethanol (95wt %) and water can be solved with an ordinary distillation (column 3, C3).

Figure 6.10 shows the next alternative in which the EHAD is applied first for the quaternary mixture. Similar to the previous case, the water is selected as extractive agent, which also helps to utilize its ability to facilitate heterogeneous azeotropy helping to cross separation boundary.

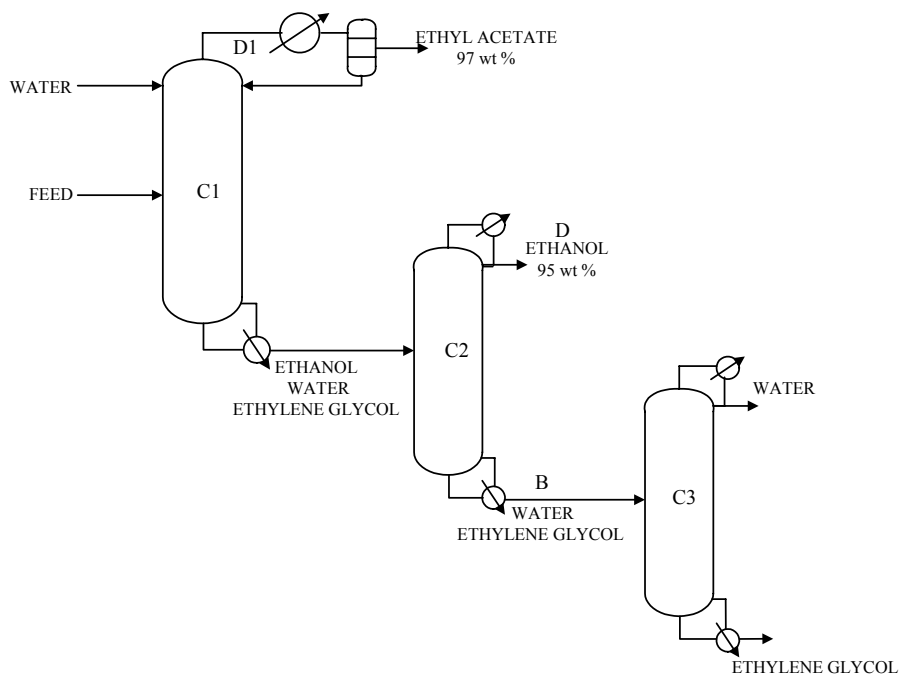


Figure 6.10., Separation structure starting with the EHAD

This separation alternative differs from the previous ones in the sequence. The top product of the EHAD is the ethyl acetate-water binary azeotropic point. This heterogeneous azeotrope in the phase separator splits into ethyl acetate of 97 w % and water rich phase. The water rich phase feeds back to the EHAD. The VLLE and the operating line of the EHAD are described in a tetrahedron in Figure 6.11. In the bottom there are ethanol, water, and ethylene glycol.

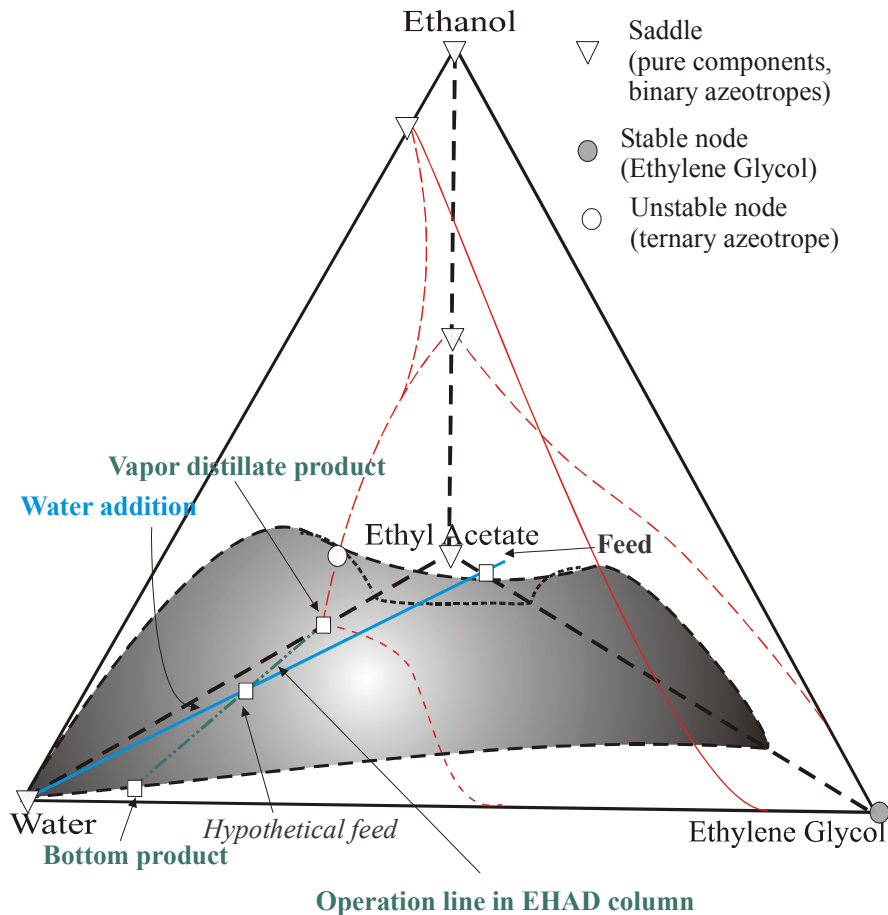


Figure 6.11., Tetrahedral diagram for the separation structure in Figure 6.9

The ternary bottom product of the EHAD is separated in column C2 with an ordinary distillation into ethanol (95 w %) and the mixture of water and ethylene glycol. The operation of this column and the VLE are described in Figure 6.11. In column C3 the water and the least volatile non-azeotropic forming component, ethylene glycol, are separated with an ordinary distillation.

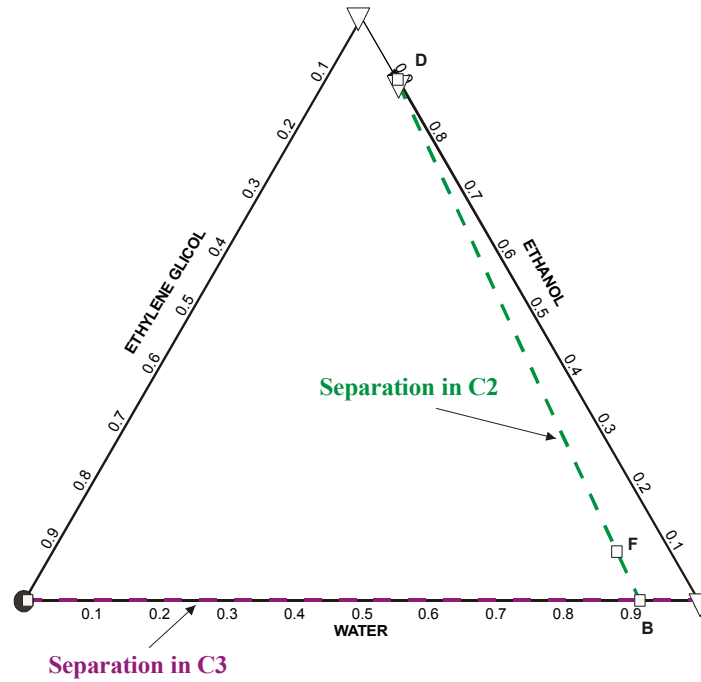


Figure 6.12., Representation of the operation in the C2 and C3

The classical principle of the extractive distillation, where the extractive agent is the least volatile and heaviest component (ethylene glycol) in the mixture is shown in Figure 6.13. This alternative is also investigated. The vapour distillate contains only one phase, meaning that in the first column a classical extractive distillation takes place. Thus, this separation is not an exact example for a separation process based on EHAD because of the one phase distillate.

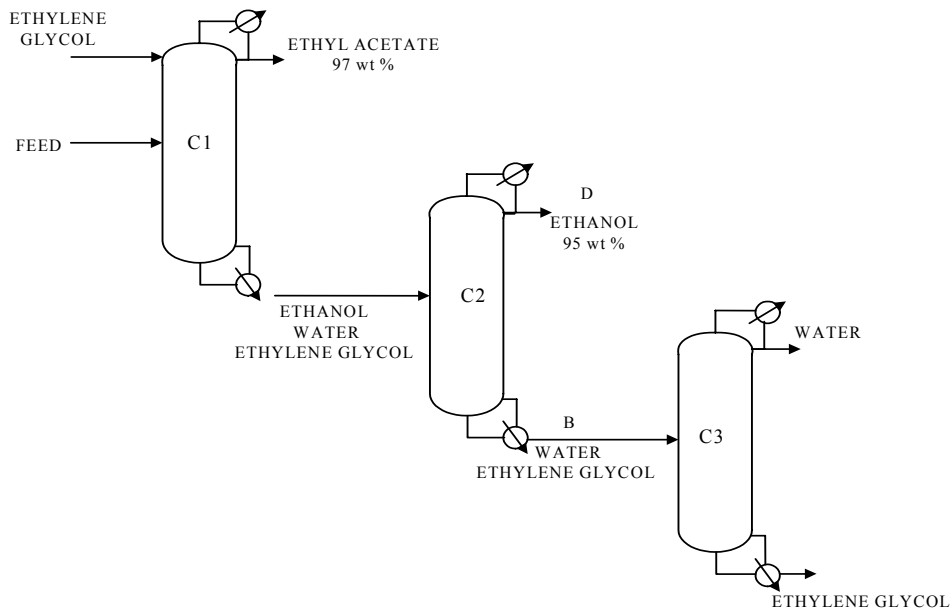


Figure 6.13., Separation scheme started with extractive distillation with ethylene glycol followed by two ordinary distillation

The VLLE and the operating line of column C1 are described in a tetrahedron in Figure 6.14. With the application of the extractive agent the original feed move to the other distillation region. The distillate is located on the distillation boundary surface, and the bottom product contains ethanol, water, and ethylene glycol.

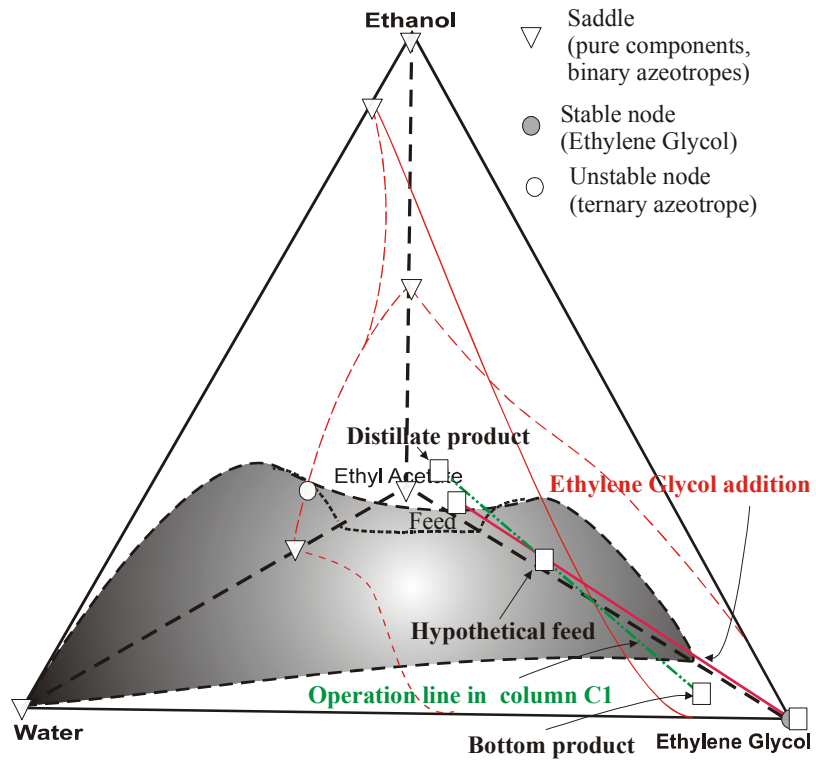


Figure 6.14., VLLE representation and the operation line in the separation structures in Figure 6.12

An economic comparison is made for these three cases at different ethylene glycol compositions in the feed, too (Figure 6.15). The total annual cost data are compared.

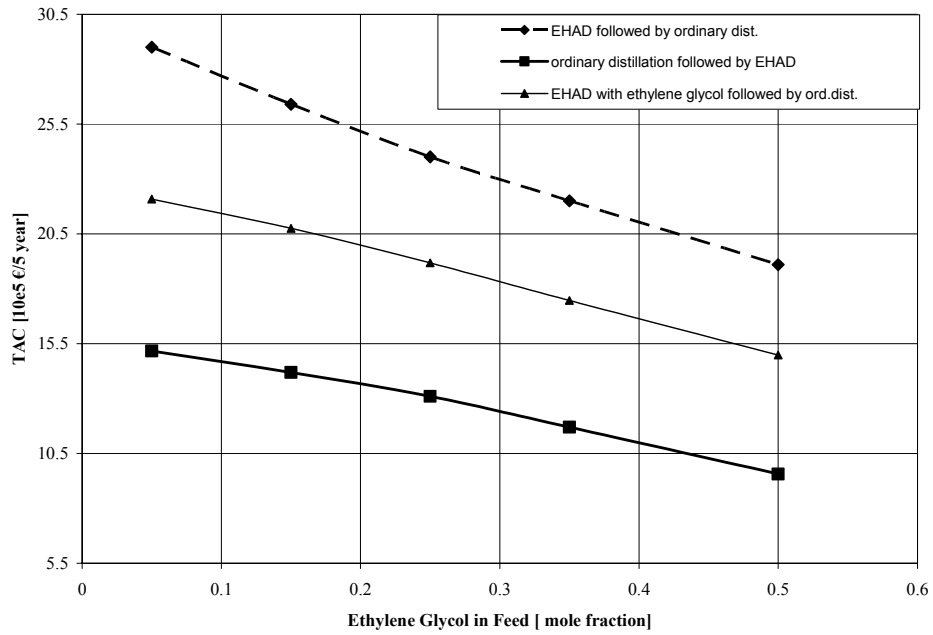


Figure 6.15., The economic comparison of the different separation structures

It is also true that the easiest separation should be completed first in which the ethylene glycol is separated in the first column and the ternary system should be separated last.

## 6.2 Group 2

The quaternary mixtures are classified into group 2 are mixtures 3 and 4 (Table 4.1). They contain ethanol, ethyl acetate, isopropyl acetate, water, and methyl-ethyl-ketone. The four components form six binary and two ternary azeotropes (Table 6.4, Table 6.5); all of them are minimal boiling azeotropes. The interval of the boiling point and the composition can be found in the data books created by Gmehling (1988, 1994) and Horsley (1973).

Binary azeotropes					
	Boil. T [°C]	Water [%]	ETOH [%]	ETAC [%]	IPAC [%]
Water – ETAC	70.4-72.3	7.9-8.6	-	91.4-92.1	-
ETOH – ETAC	70.9-72.1	-	28-31.2	68.8-72	-
ETOH – IPAC	76.4-76.7	-	51.4-53.7	-	46.3-48.6
Water- ETOH	78-78.3	4-4.6	95.4-96	-	-
Water – IPAC	81.7-82.8	12.2-16.2	-	-	83.8-86.8
Ternary azeotropes					
Water-ETOH-ETAC	70.2-70.4	7.8-8.3	8.4-9	82.7-83.8	-
Water–ETOH – IPAC	74.8	10	18.4	-	71.6

Table 6.4., Binary and ternary azeotropes in mixture 3

Binary azeotropes					
	Boil. T [°C]	Water [w %]	ETOH [w %]	MEK [w %]	IPAC [w %]
Water – MEK	73.7-73.8	11-12	-	88-89	-
ETOH – MEK	74-75	-	34.3-40.4	59.6-65.7	-
ETOH – IPAC	76.4-76.7	-	51.4-53.7	-	46.3-48.6
Water- ETOH	78-78.3	4-4.6	95.4-96	-	-
Water – IPAC	81.7-82.8	12.2-16.2	-	-	83.8-87.8
Ternary azeotropes					
Water-ETOH–MEK	73	10	11	79	-
Water–ETOH – IPAC	74.8	10	18.4	-	71.6

Table 6.5., Binary and ternary azeotropes in mixture 4

### 6.2.3 Separation structures

For the separation of the quaternary mixtures of group 2, two separation technologies have been developed and tested in detail by Mizsey (1997) and Raab (2001).

The first separation structure called the ternary-cut-system (Figure 6.16) is designed specifically for the recovery of the solvents of mixture 3 in the frame of an industrial solvent recovery problem. According to the exhaustive study of the VLLE data, it is possible to split the quaternary mixture in one distillation column into two ternary ones. Afterwards, the two ternary mixtures, due to their similar VLLE data, can be separated in two similar ways (ethyl acetate cycle, isopropyl acetate cycle) with the use of extractor and three distillation columns into components of the prescribed purity. Internal recycling is also needed. (Raab, 2001).

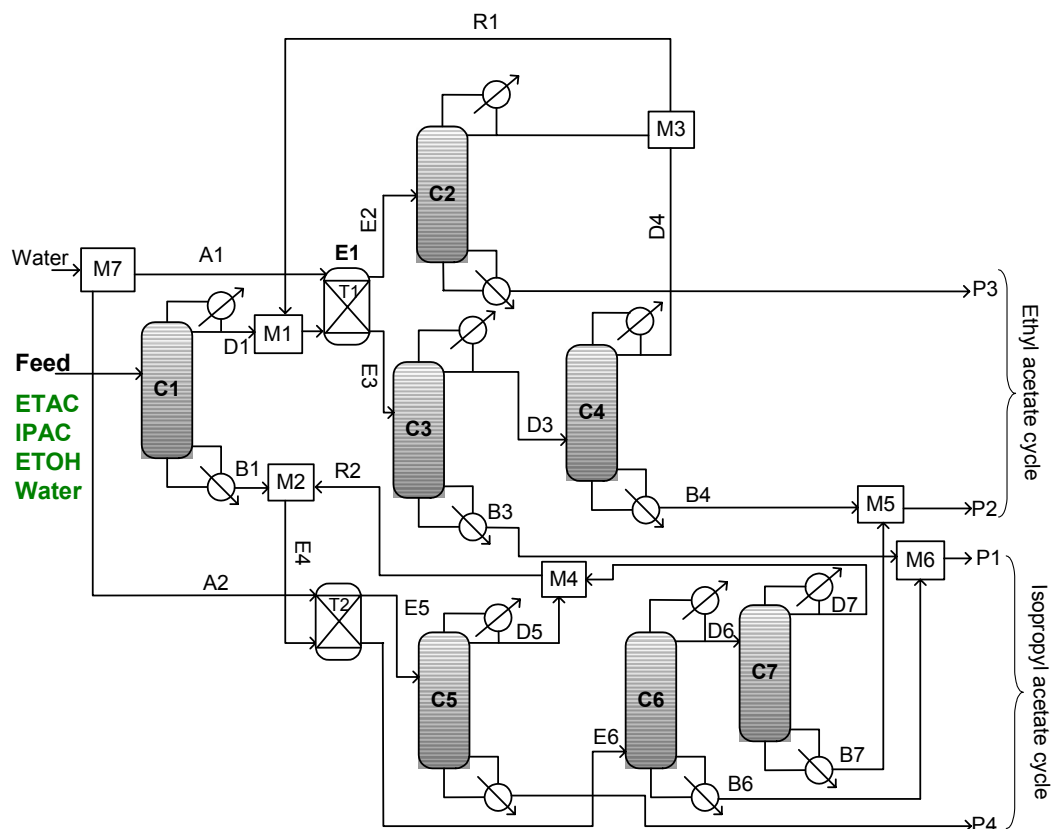


Figure 6.16., The separation scheme of the ternary-cut-system  
(W, P2 = water, F = feed, P1 = ethanol, P3 = ethyl acetate, P4 = isopropyl acetate)

Due to the complexity of the ternary-cut-system, attempts are made to design simpler separation processes. First, an earlier separation scheme, the two-column-system, (Mizsey,

1991, Rev et al., 1994, Mizsey et al., 1997), which has been designed to separate mixture 4 into two binary mixtures is considered and tested also for mixture 3. The system containing two coupled distillation columns and a three phase flash proves to be successful also for mixture 3 and splits this quaternary mixture into two binary ones (ethanol-water, ethyl acetate-isopropyl acetate).

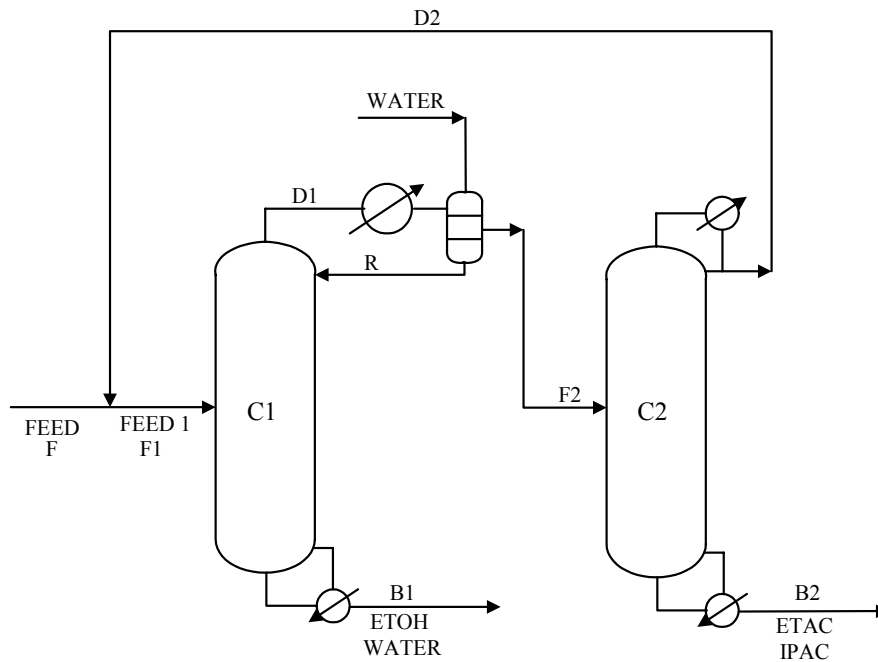


Figure 6.17., Two-column system

Since water is used in the previous separation technologies to exploit the advantage of the immiscibility regions allowing the step over separation boundaries, a generalization of synthesizing hybrid separation technologies for azeotropic mixtures proves to be possible. The application of extractive heterogeneous-azeotropic distillation allows significant simplification of the separation scheme, see Figure 6.18. The VLLE data indicates that with subsequent distillation it is possible to obtain the individual components with the prescribed purity.

An important comment to this structure is the robust of this separation structure. The separation structure is suitable for the separation of the mixtures with composition in the other distillation region.

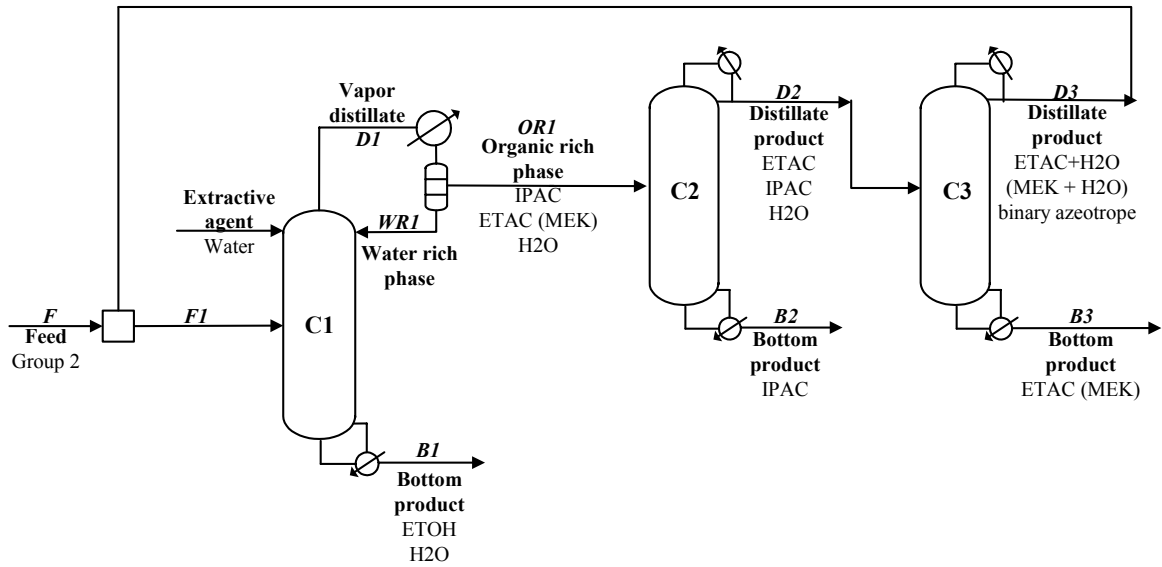


Figure 6.18., Separation structures based on the EHAD

The VLLE data and the operation of the EHAD are shown in the 3-dimensional tetrahedral diagram (Figure 7.2). In this case the separatrices divide the solution space into three distinct distillation regions. The first region is generated by the two heterogeneous binary azeotropes, the second one with the two ethanol acetate binary azeotropes, and the last one with the water ethanol azeotropes. Every region contains two ternary azeotropes. The shaded area marks the immiscibility region. The operating lines of the EHAD, column C1, and the phase separator are described. The water as the autoentrainer helps both to cross the separation boundaries and to change the relative volatilities. This double effect makes the desired separation possible. The recycle stream from the second ordinary distillation column contains the azeotrope of ETAC (or MEK) and water.

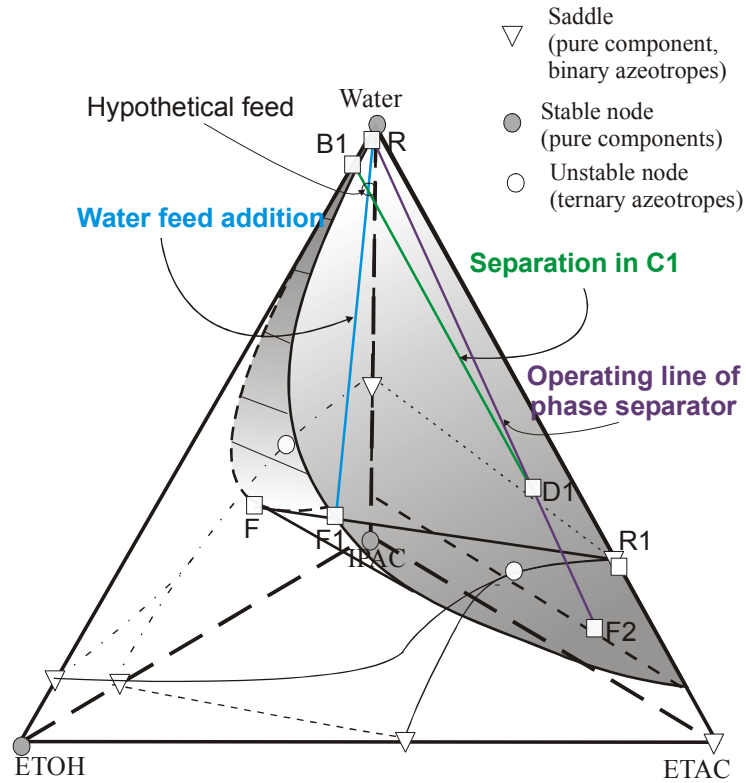


Figure 6.19., Tetrahedral diagram of the mixture 3

The separations in the subsequent distillation columns (C2, C3) are shown the Figure 6.20.

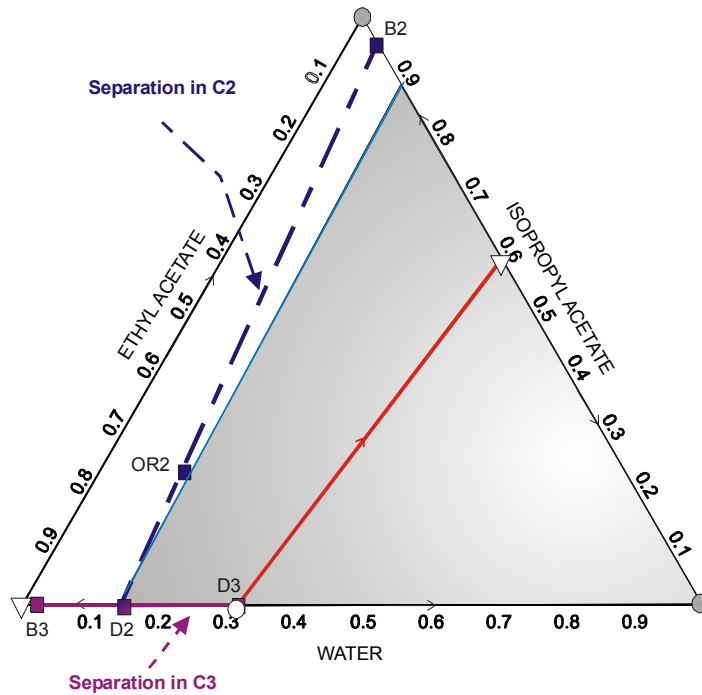


Figure 6.20., Triangular diagram for the representation of the separation lines of columns C2 and C3

#### 6.2.4 Comparison of energy consumption

The three separation technologies are investigated from the points of feasibility and energy consumption. The simplest system is the integrated-system and the total minimal energy consumption (heating and cooling) of the three systems are also determined.

The separation started with the extractive heterogeneous-azeotropic distillation proves to be not only the simplest but also the most attractive for the energy consumption (Table 6.6). According to estimations, the savings of the solvent recovery depends on the actual prices and range between 70-95%.

	Extractive heterogeneous-azeotropic dist. [MW]	Two-column-system [MW]	Ternary-cut-system [MW]
Mixture 3	12.04	57.86	23.26
Mixture 4	14.62	35.44	—

Table 6.6., Comparison of separation technologies

### 6.3 Group 3

The mixtures of the group 3 (mixtures 5 and 6) have more complicated characteristics than the mixtures of previous groups. Table 6.7 and Table 6.8 points to the increasing complexity of these mixtures; that is, the mixtures belonging to this group have six binary and three ternary azeotropes. All azeotropes are minimal boiling azeotropes, heterogeneous or homogeneous ones.

Binary azeotropes					
	Boil. T [°C]	Water [w %]	ETOH [w %]	ETAC [w %]	MEK [w %]
Water – ETAC	70.4-72.3	7.9-8.6	-	91.4-92.1	-
ETOH – ETAC	70.9-72.1	-	28-31.2	68.8-72	-
Water – MEK	73.7-73.8	11-12	-	-	89-88
ETOH – MEK	74-75	-	34.3-40.4	-	59.6-65.7
ETAC – MEK	76.4-77.1	-	-	82-88.2	11.8-18
Water- ETOH	78-78.3	4-4.6	95.4-96	-	-
Ternary azeotropes					
	Boil. T [°C]	Water [w %]	ETOH [w %]	ETAC [w %]	MEK [w %]
Water-ETOH-ETAC	70.2-70.4	7.8-8.3	8.4-9	82.7-83.8	-
Water-ETAC-MEK	71.1	8.7	0	85	6.3
Water-ETOH-MEK	73	10	11	-	79

Table 6.7., Azeotropes of Water-ETOH-ETAC-MEK mixture (mixture 5)

Binary azeotropes					
	Boil. T [°C]	Water [w %]	IPOH [w %]	ETAC [w %]	MEK [w %]
Water-ETAC	70.4-72.3	7.9-8.6	-	91.4-92.1	-
Water-MEK	73.7-73.8	11-12	-	-	88-89
IPOH – ETAC	74.5-76.11	-	19.6-26	74-80.4	-
ETAC – MEK	76.4-77.1	-	-	82-88.2	11.8-18
IPOH-MEK	77.5-77.7	-	29.6-34.2	-	65.8-70.4
IPOH-Water	79.7-80.72	11.2-13.1	86.9-88.8	-	-
Ternary azeotropes					
Water-ETAC-MEK	71.1	8.7	-	85	6.3
Water-IPOH-MEK <sup>calc</sup>	73.4	11.7	4	-	84.3
MEK–IPOH-ETAC <sup>calc</sup>	75.4	-	20.4	68.1	11.5

Table 6.8., Azeotropes of mixture Water-IPOH-ETAC-MEK mixture (mixture 6)

### 6.3.1 Separation method

A novel separation scheme is designed for the quaternary mixtures of group 3. Two EHAD, one heteroazeotropic distillation and one ordinary distillation are applied to complete the separation problem. The proper positioning of the extractive heterogeneous-azeotropic distillations within the separation train is of paramount importance in this separation problem. The VLLE nature of these mixtures requires that the extractive heterogeneous-azeotropic distillation can be applied twice (Figure 6.21).

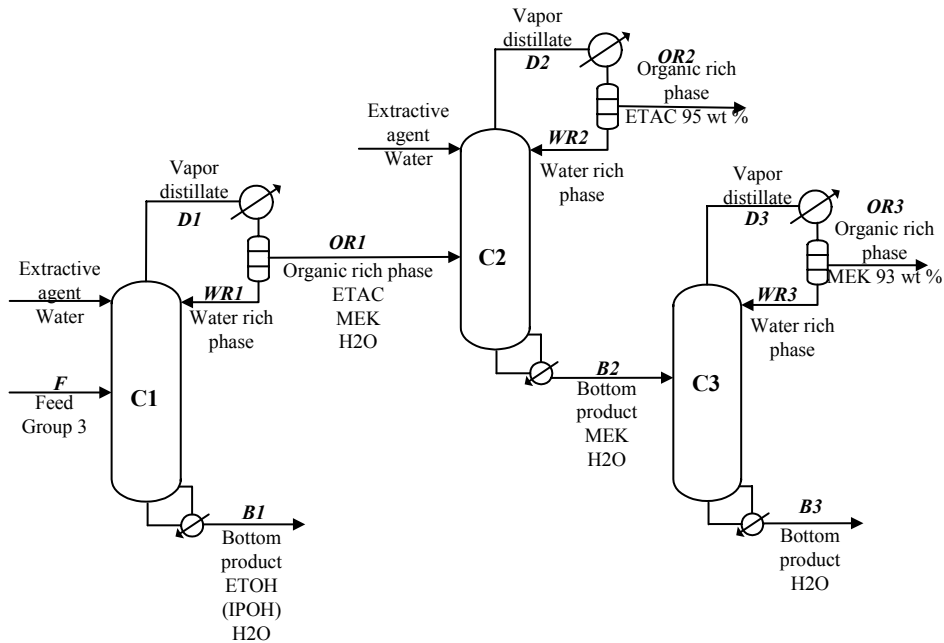


Figure 6.21., Separation scheme for the mixtures of group 3

The first extractive heterogeneous-azeotropic distillation column can be represented in a tetrahedral diagram (Figure 6.22). The water addition allows for the transfer of the feed composition to the other distillation region and for the phase separation to cross the distillation boundary surface.

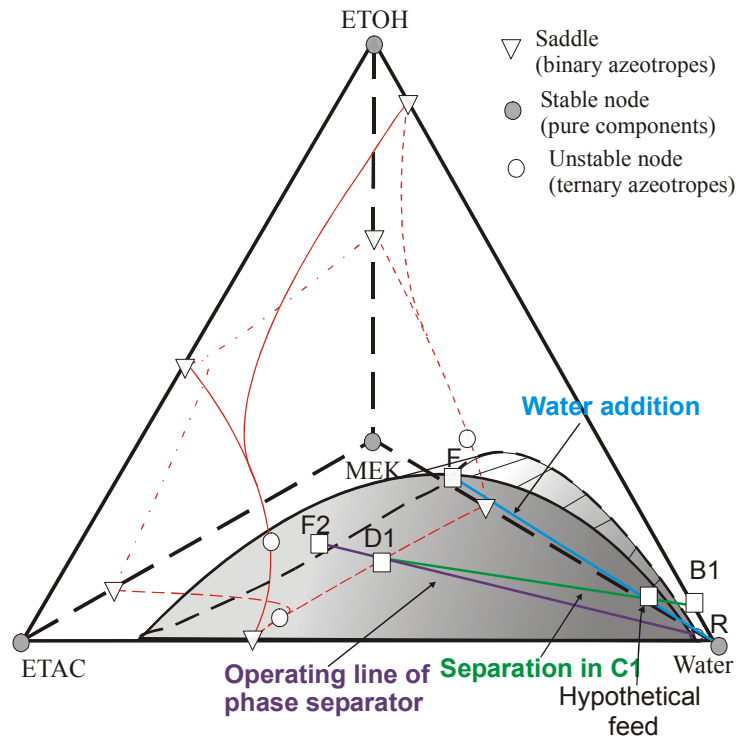


Figure 6.22., Tetrahedral diagram for the representation of the separation in the column C1

The organic rich phase of the condensed vapour top product of the first extractive heterogeneous-azeotropic distillation must be further separated, and a subsequent extractive heterogeneous-azeotropic distillation can resolve the separation (Figure 6.23).

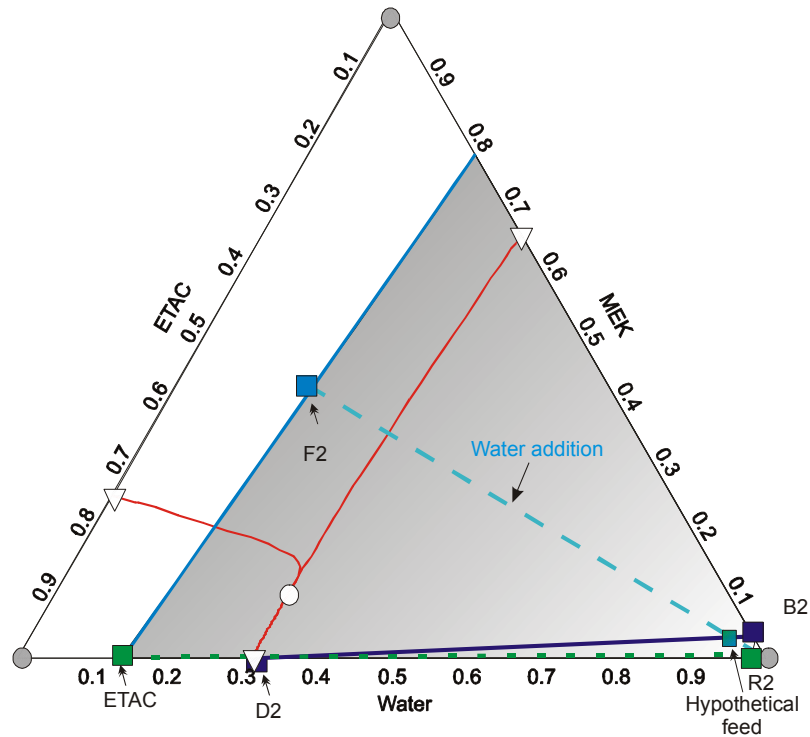


Figure 6.23., VLE data of mixture 5 (group 3) and representation of the EHAD in the column C2

The water addition to the second EHAD (C2) allows for the formation of the new feed composition, for the hypothetical feed, and is followed by the saddle distillation. The phase separation allows for the cross of the separation boundary.

The bottom product of the second extractive heterogeneous-azeotropic distillation is separated with a subsequent heterogeneous-azeotropic distillation column, column C3. The organic rich phase contains MEK in the prescribed purity.

## 6.4 Group 4

The most complicated mixtures (7 and 8) are in group 4. These mixtures contain the azeotropic points in every combination (Table 6.9 and Table 6.10), meaning there are six binary and three ternary azeotropes. The data are collected from the databook created by Gmehling (1994) and Horsley (1973). The missing parameters are calculated by software package ASPENTECH.

Binary azeotropes					
	Boil. T [°C]	Water [w %]	ETOH [w %]	MEK [w %]	Heptane [w %]
ETOH – N-Heptane	70.9-72	-	48.3-49	-	51-51.7
Water – MEK	73.7-73.8	11-12	-	-	88-89
ETOH – MEK	74-75	-	34.3-40.4	59.6-65.7	-
MEK – N-Heptane	77.6	-	-	69	31
Water- ETOH	78-78.3	4-4.6	95.4-96	-	-
Water – N-Heptane	79.2	13	-	-	87
Ternary azeotropes					
	Boil. T [°C]	Water [w %]	ETOH [w %]	MEK [w %]	Heptane [w %]
Water-ETOH-N-Hept	68	12.1	25.9	-	62
MEK-N-Hept-Water <sup>calc</sup>	69.5	8.4	-	51	40.6
MEK-N-Hept-ETOH <sup>calc</sup>	71.2	-	36.5		
Water-ETOH-MEK	73	10	11	-	79

Table 6.9., Azeotropes of mixture Water-ETOH-MEK – N-Heptane (mixture 7)

Binary azeotropes					
	Boil. T [°C]	Water [w %]	ETOH [w %]	ETAC [w %]	Heptane [w %]
ETAC-N-Heptane	70	-	-	83.3	16.7
ETAC-Water	70.4-72.3	7.9-8.6	-	91.4-92.1	-
ETOH – ETAC	70.9-72.1	-	28-31.2	68.8-72	-
ETOH – N-Heptane	70.9-72	-	48.3-49	-	51-51.7
Water- ETOH	78-78.3	4-4.6	95.4-96	-	-
Water – N-Heptane	79.2	13	-	-	87
Ternary azeotropes					
	Boil. T [°C]	Water [w %]	ETOH [w %]	ETAC [w %]	Heptane [w %]
ETOH-N-Hept-Water	68	12.1	25.9	-	62
ETAC-N-Hept-Water <sup>calc</sup>	68.6	7.3	-	65.8	26.9
ETAC-N-Hept-ETOH <sup>calc</sup>	70.1	-	29.5	39.5	31
Water-ETOH-ETAC	70.2-70.4	7.8-8.3	8.4-9	83.2-83.3	-

Table 6.10., Azeotropes of mixture Water-ETOH-ETAC-N-Heptane (mixture 8)

#### 6.4.1 Separation schemes for Group 4

After exhaustive study of the VLLE data, novel separation scheme is designed for the separation based on the proper positioning of the EHAD in the separation train. Similar to the separation of the mixtures of group 3, two EHAD are also needed; however, their positioning is different. Figure 6.24 shows a possible separation structure. Between the two extractive heterogeneous-azeotropic distillations an ordinary distillation is needed and an internal recycle is also applied. The final column is a heterogeneous-azeotropic distillation. The ethanol is recovered in 95 w % purity in an ordinary distillation column.

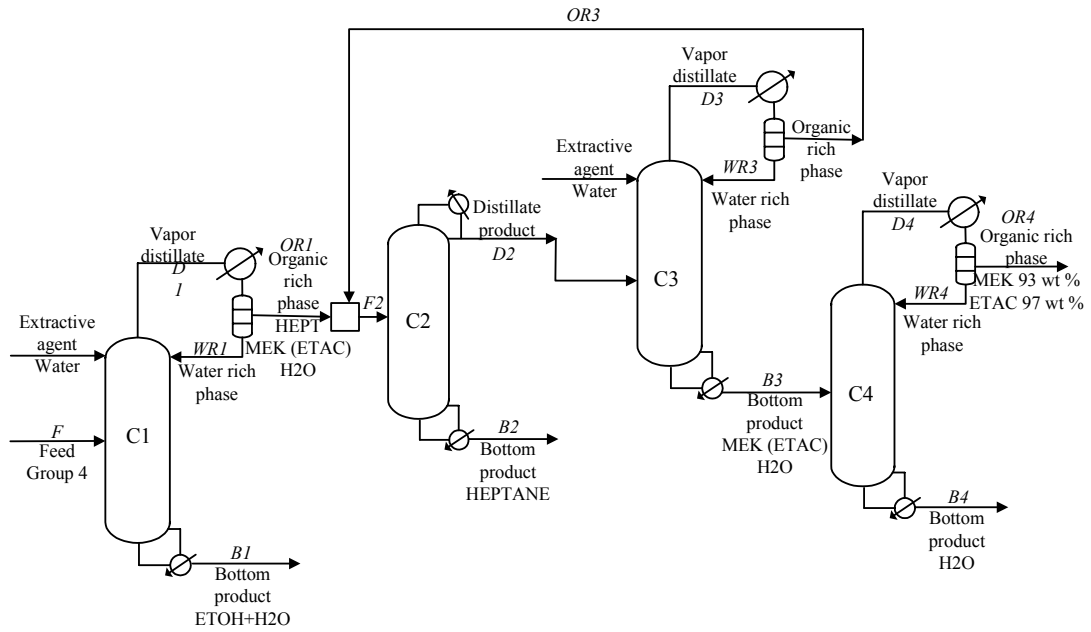


Figure 6.24., Separation scheme for the mixtures of group 4

The visualization of the extractive heterogeneous-azeotropic distillation column in the tetrahedron is very confusing, and this time it is avoided since the composition space is practically the immiscibility region (Figure 6.25).

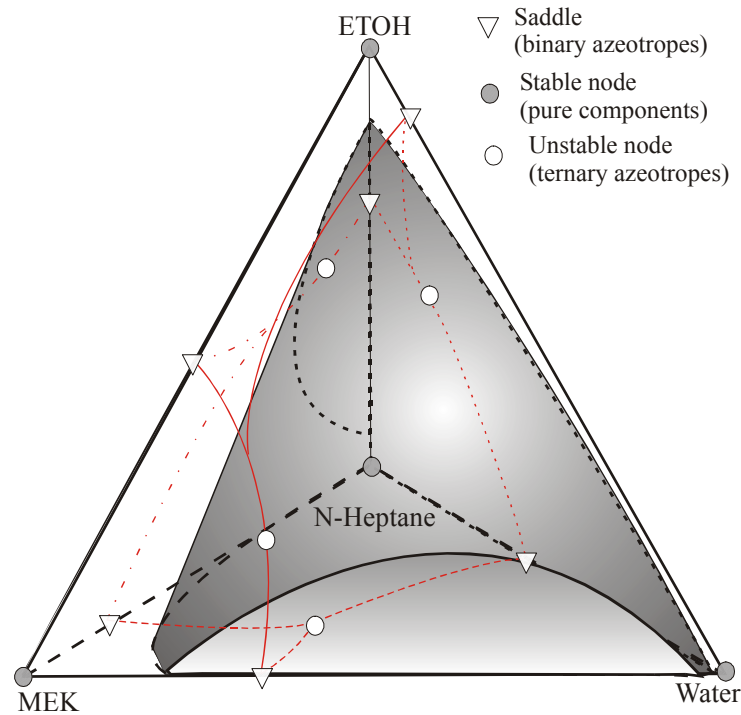


Figure 6.25., VLE data of mixture 7 (group 4)

The first extractive heterogeneous-azeotropic distillation allows the separation of the ethanol in the bottom product. The remaining ternary sub-mixture can be separated with an ordinary distillation. The steps of this separation are described in Figure 6.26. This operation results the heptane recovery from the ternary sub-mixture; however, this recovery is only a partial one and some n-heptane still remains in the distillate. The presence of the n-heptane requires that the EHAD be applied a second time. In this column the addition of water allows for the cross of the distillation boundary, and the separation results in the ternary vapour distillate and the binary mixture of MEK (ETAC) and water in the bottom product. The distillate is heterogeneous, and the organic rich phase can be recycled into the organic rich phase of the first extractive heterogeneous-azeotropic distillation since it does not contain ethanol. The bottom product can be separated with the heterogeneous azeotropic distillation to the organic components with the prescribed purity.

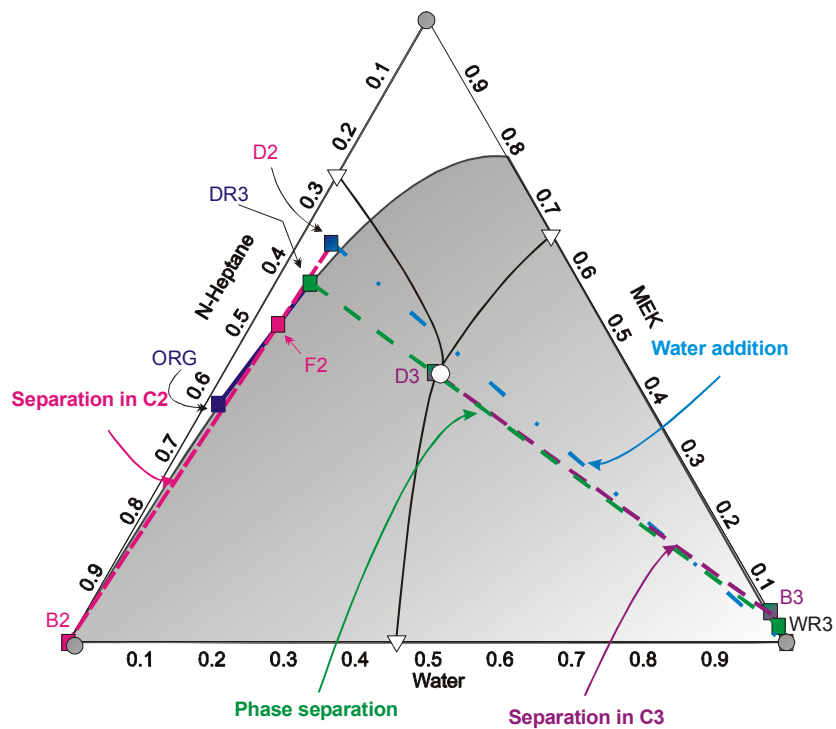


Figure 6.26., VLE data of mixture 7 (group 4) after the separation of ETOH, and representation of the subsequent separation processes

The complexity of this mixtures causes that the feed composition can influence the separation structure and other alternatives can be also applied. If the feed contains only a

little amount of n-heptane another separation scheme can be also applied (Figure 6.27). In this alternative the scheme consists of the same units but their positioning is different.

This shows again that for the separation of highly non-ideal mixtures, due to their VLE complexity, several separation alternatives can be designed and applied. The selection needs nevertheless the right engineering judgment based on proper understanding of the physico-chemical behaviour of the system.

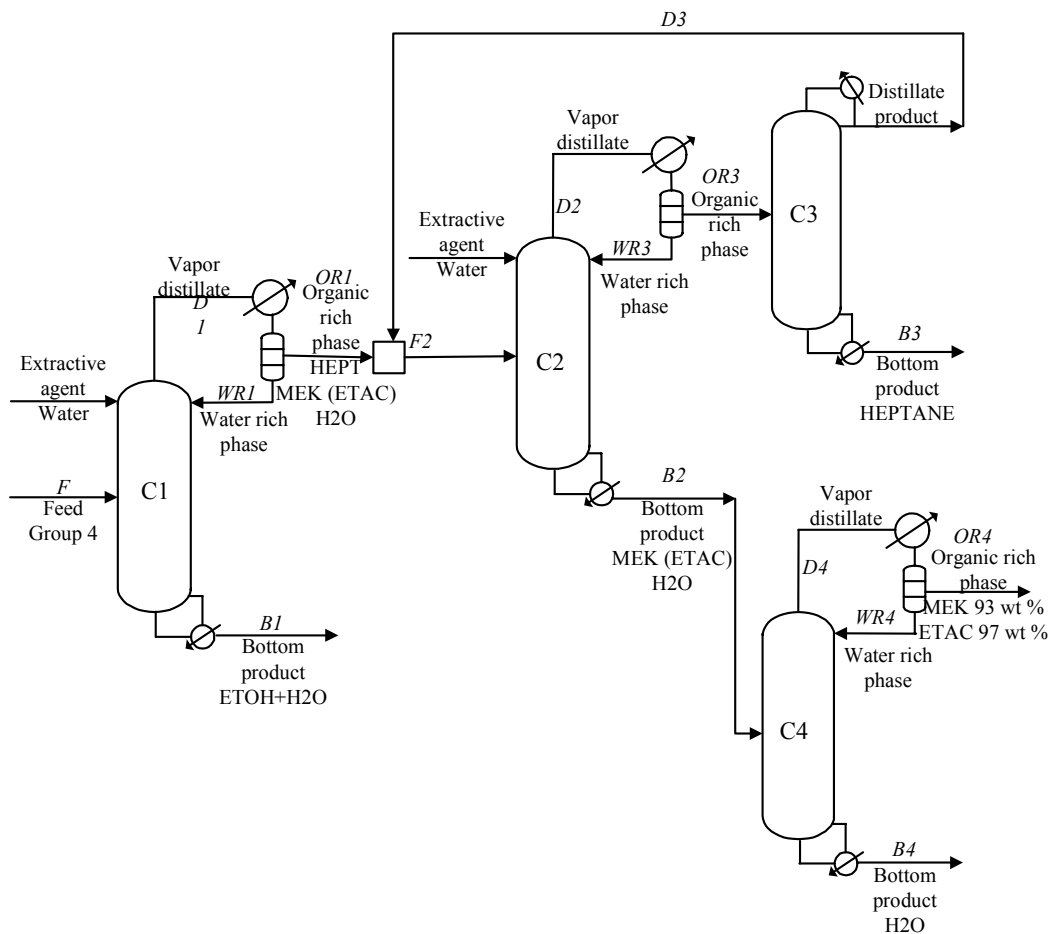


Figure 6.27., Separation scheme alternative for the mixtures of group 4

## 6.5 Experimental verification

In the previous chapters several novel design alternatives are recommended for the separation of the highly non-ideal mixtures. Today's software tools like *HYSYS*, *CHEMCAD* and *ASPEN* supply quite reliable and checked results. With these simulators, we can investigate the behaviour of mixtures and column sequences without expensive tests. On one hand, such process simulators are successful in their ability to predict thermodynamic behaviour of ideal and also highly non-ideal mixtures based on experimental databases. On the other hand, it is still necessary to conduct tests to verify the simulated results because:

- a plant unit does not exist for this separation process,
- when the mixture contains unknown compounds,
- experimental data is not available for the system conditions,
- when a high purity is required.

In order to check the validity, it is necessary to verify the solution predicted by the process simulator with experimental data.

First, test measurements with a suitable test mixture are used to determine the number of theoretical stages in a laboratory column. In case of packing, this number refers to the packing height used in the column. This is followed by a laboratory test with the process mixture. The necessary reflux ratio is determined and if the separation turns out well in general. The laboratory column is modified until it meets the desired optimal separation.

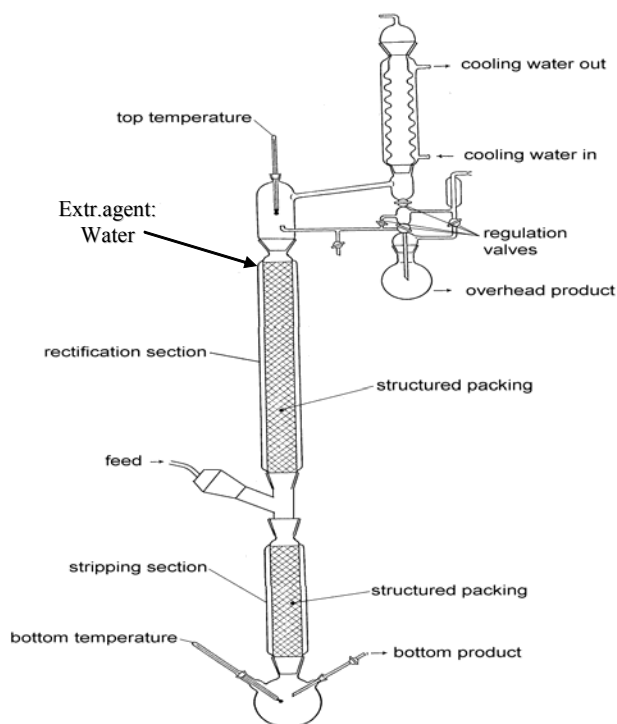


Figure 6.28., Test equipment

Figure 6.28 shows the schematic arrangement of the test equipment. The unit essentially consists of an evaporator, a condenser, a feed-pump, and the column. The test column operates with variable reflux. The temperature in the top and the bottom of the column, the removed amount of liquid flows in order to simulate continuous distillation and the composition of the mixture taken away are measured.

The experiments are carried out as long as reliable steady state data obtained. Every 15 minutes, there were fractions drawn off at the bottom and the top of the column to simulate nearly continuous behaviour. The products are analyzed for the organic compounds with the gas chromatograph and the water content of the sample measured by Karl-Fischer-method.

The results are compared with the data calculated with the software package *ASPEN*. To compare the measurement with the simulation it is necessary to develop a simulation analogous to the measurement. The simulation is made according to the preconditions given by the experiment. The internal diameter of the laboratory distillation column is 3 cm, the column height is about 2 m, and the column internal is structured packing. The height of the packing is varied according to the distillation investigated.

The following mixtures are tested experimentally:

	Feed w %	Simulated data w %		Measured data w %	
		Distillate	Bottom	Distillate	Bottom
Water	21	2.7	96.1	2.8	95.8
ETOH	32	0	3.9	0	4.2
ETAC	26	55	0	53.2	0
IPAC	21	42.3	0	44	0

Table 6.11., Comparison of measurement and simulation results (mixture 3, Group 2)

	Feed w %	Simulated data w %		Measured data w %	
		Distillate	Bottom	Distillate	Bottom
Water	13	9.6	93	7	93.7
ETOH	24	0	7	0	6.3
ETAC	34	49.1	0	50	0
MEK	29	41.3	0	43	0

Table 6.12., Comparison of measurement and simulation results (mixture 5, Group 3)

	Feed w %	Simulated data w %			Measured data w %		
		Distillate		Bottom	Distillate		Bottom
		Organic-rich phase	Water-rich phase		Organic-rich phase	Water-rich phase	
Water	0.9	0.6	91.7	98.8	1.3	89	99
ETOH	10	0.1	0.1	1.2	0.2	1	1
n-Heptane	57.5	65	0	0	63	0	0
MEK	31.6	34.3	7.5	0	37.5	10	0

Table 6.13., Comparison of measured and simulated data of the first EHAD column (mixture 7, Group 4)

The comparison of the measured and calculated results based on UNIQUAC VLLE data shows a good agreement which gives confidence for the accuracy of the simulation made by the software package ASPEN PLUS 12.1 while determining the separation structures designed in this work.

## 6.6 Strategy for the separation of highly non-ideal quaternary mixtures

After designing the novel separation schemes for the mixtures classified into four groups, (Table 4.1.,. ) similarities of the separation schemes are deduced. Thus, a design strategy for quaternary mixtures having both minimum boiling heterogeneous and homogeneous azeotropes can be concluded. For each mixture of the groups the same separation scheme based on the proper application and positioning of extractive heterogeneous-azeotropic distillation within the separation scheme designed and can be recommended. In this strategy the separation of the alcohol-water binary system, the bottom product of an extractive heterogeneous-azeotropic distillation, is not involved and not indicated.

- For mixtures classified into group 1 the first step is the separation of the non-azeotropic forming component with ordinary distillation, product 1 (P1). The second step is the separation of the remaining ternary highly non-ideal system with extractive heterogeneous-azeotropic distillation. The top product is obtained according to the liquid-liquid equilibrium due to the limited immiscibility (P2), and the bottom product is the alcohol-water binary system (P3+Water).
- For mixtures classified into group 2 the first step is the extractive heterogeneous-azeotropic distillation with alcoholic water mixture as bottom product (P1+water), followed by two subsequent ordinary distillations with bottom products of P2 and P3. The recirculation of the distillate of the second ordinary distillation column, a binary azeotrope, is needed.
- For mixtures classified into group 3 the separation scheme starts with two subsequent extractive heterogeneous-azeotropic distillations. In the first extractive heterogeneous-azeotropic distillation the alcohol is separated with water in the bottom product (P1+water). In the second extractive heterogeneous-azeotropic distillation the limited immiscibility is utilised for the recovery of the desired product (P2). The last step of the separation scheme is a heterogeneous-azeotropic distillation where the top product is obtained according to the liquid-liquid equilibrium (P3). The bottom product is water.
- For mixtures classified into group 4 the separation is the most complicated one. In the first extractive heterogeneous-azeotropic distillation the alcohol is separated with water in the bottom product (P1+water). An ordinary distillation follows to

separate the component of highly limited immiscibility (P2). A second extractive heterogeneous-azeotropic distillation follows and its organic rich phase of the top product is recycled. The bottom product is further processed in a subsequent heterogeneous-azeotropic distillation where (P3) is obtained as a top product. Its bottom product is water.

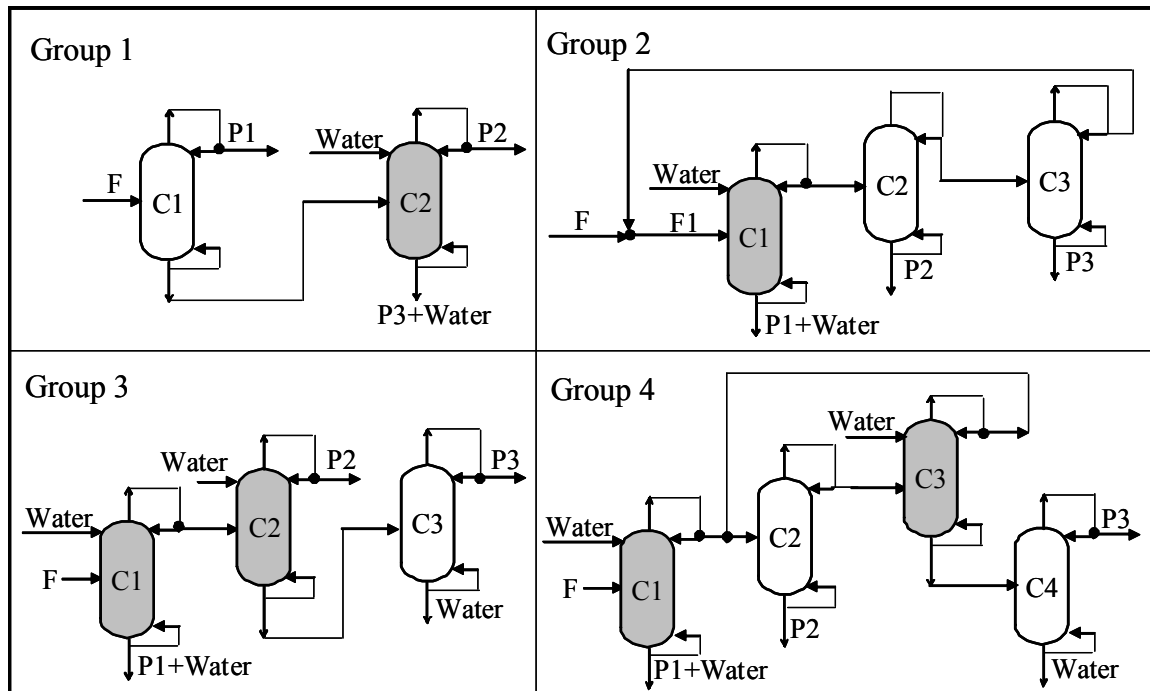


Figure 6.29., Separation alternatives for the different quaternary mixtures classified into four groups

## 7. Major scientific results

Highly non-ideal quaternary mixtures, usually arising as waste streams of process industries, are selected for separation. The mixtures contain minimum boiling both heterogeneous and homogeneous azeotropes. Before designing separation alternatives based on the heterogeneous azeotropic distillation the vapour-liquid-liquid equilibrium (VLLE) of the quaternary mixtures are investigated. For the presentation of the VLLE data a new approach is applied where the data are shown in a two and a three dimensional tetrahedral diagrams. Several specific rules are determined about the dependencies of the different nodes of the tetrahedral diagrams.

### ***Thesis 1:***

*A new approach is elaborated for the classification of highly non-ideal quaternary mixtures containing minimum boiling azeotropes.*

The following rules are determined:

#### *Rule 1*

If a node changes its character, the change is from stable into saddle and from unstable to saddle. There is no change into stable or unstable node.

#### *Rule 2*

If ternary azeotrope exists in a ternary sub-mixture, this ternary azeotrope is an unstable node. In this case the binary azeotropes are saddles and the pure components are stable nodes. If, however, no ternary azeotrope exists in the ternary sub-mixture, the binary azeotrope of the lowest boiling point is an unstable node. In this case it will turn into saddle if in the quaternary mixture there is a ternary azeotrope of the lowest boiling point.

#### *Rule 3*

The binary azeotropes, if existing, are saddle in a quaternary mixture; however, in the ternary sub-mixture they can be also unstable. They are never stable nodes.

*Rule 4*

If one of the four components has the minimum boiling point and this component does not form azeotrope with the others its presence will not influence the character of the nodes.

*Rule 5*

If the non-azeotropic forming component has the highest boiling point it will cause several changes in the character of the nodes.

*Rule 6*

If in a ternary sub-mixture there is a component pair which form no binary azeotrope while the others do, then the lower boiling component of this component pair will turn into a saddle from a stable node if the other component of the pair is present.

According to the deeper insight into the VLLE data of the quaternary mixtures based on the new approach novel hybrid separation schemes are designed. The novel hybrid separation schemes are based on the extractive heterogeneous-azeotropic distillation designed for such mixtures where water is present as one of the four components and applied as autoentrainer/extractive agent.

***Thesis 2:***

*Novel hybrid separation schemes based on the extractive heterogeneous-azeotropic distillation are developed and investigated for the separation of highly non-ideal quaternary mixtures sorted in four groups having similar features of vapour liquid-liquid equilibrium. The separation schemes are based on the proper application and positioning of the extractive heterogeneous-azeotropic distillation.*

1. If such non-ideal mixtures are to be separated where both homogeneous and heterogeneous azeotropes are also presents, a new powerful hybrid tool devoted to the separation of such mixtures, the so-called extractive heterogeneous-azeotropic distillation (EHAD) can be applied. This new hybrid separation tool combines the advantages of the extractive and the heterogeneous azeotropic distillations. Figure 1 shows the EHAD. To the top of the column a component is fed that has both entrainer

and extractive agent functions. In the mixtures investigated in this work this component is always the water, called extra water functioning as autoentrainer/extractive agent. In the top of the column always a two phase product is obtained and a phase split, decanter is applied. The organic rich phase is the top product and the water rich phase is applied as reflux. The bottom product is a one phase product.

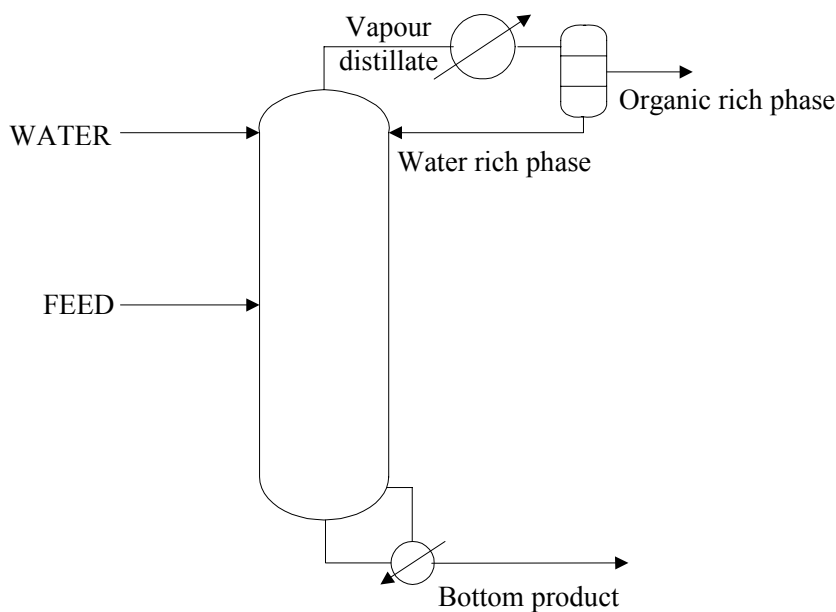


Figure1., The extractive heterogeneous azeotropic distillation

2. The feasibility of the EHAD is studied and it is determined that for the best realisable separation (i) the feed tray of the extractive agent/entrainer is the top tray; (ii) the quantity of the extractive agent and the reboiler heat load are decreasing if the number of theoretical trays is increasing but these have a minimum at the same number of plate; (iii) the feed tray is at the lowest third of the column.
3. The operation of the EHAD can be explained on the example of the separation of a ternary mixture: ethanol, ethyl-acetate, and water (Figure 2). One of the objectives of the EHAD is to produce a saddle distillate. This separation method is applicable to situations where the distillation region is bounded by (generally) four stationary points typically involving a high-boiling pure component node (stable node), a low-boiling ternary azeotropic node that is an unstable node, and two binary azeotropic saddles where an objective is to produce one of the binary azeotropic saddles as distillate using

the pure component as an extractive distillation solvent. EHAD can produce one or the other binary azeotrope as distillate using the common pure component depending on the specific shape of the residue curves even though the pure component does not form new azeotropes since it is already in the mixture. So, as a consequence it is functioning as an auto entrainer/extractive agent. The important characteristic of the addition of the auto entrainer/extractive agent (extra water) is the crossing distillation boundary. The above mentioned characteristic of the extra water offers that the suitable extractive agent is the component with the higher boiling point; however, this conservative option is not always true. If the feed composition is in the other distillation region, the crossing is realized.

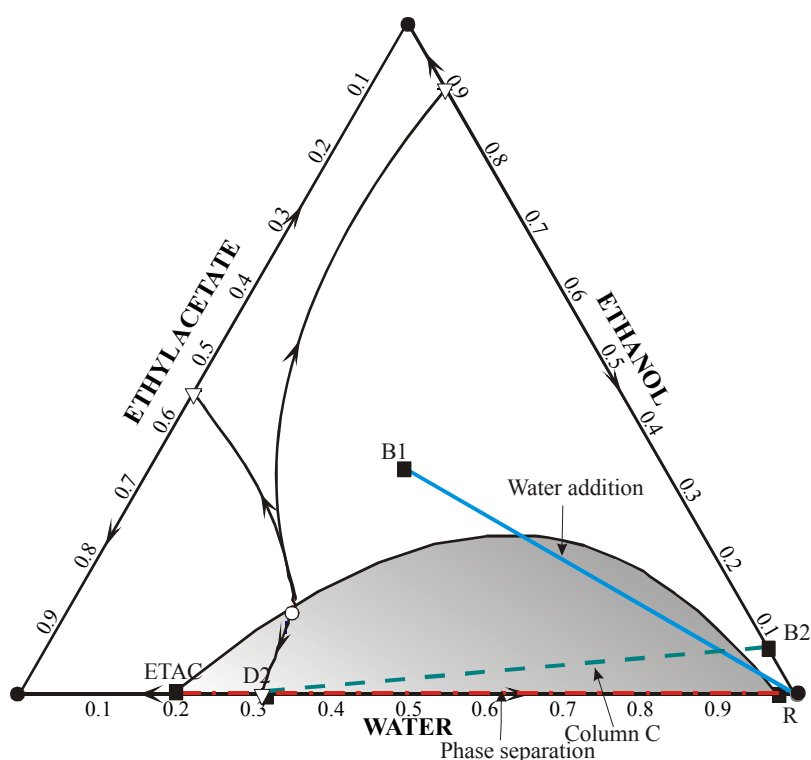


Figure 2, Water – ethyl acetate – ethanol mixture

4. In the case of quaternary mixtures the above mentioned features can be, however, different. In some cases the distillate is not a saddle binary azeotrope but it can be even a ternary mixture. It can be interpreted with the presence of distillation boundary surfaces. The extractive agent/entrainer changes the volatility, and this fact results that one of the components goes into the bottom product with the extractive agent, extra water and the water of the feed, and the ternary distillate composition lies on a distillation boundary line of the ternary sub-mixture. This boundary line is the closest one to the autoentrainer/extractive agent, water.

After designing suitable and uniform hybrid separation processes for the quaternary mixtures of each group, a design strategy is concluded. The strategy is based on the proper application and positioning of the EHAD within the separation processes.

### ***Thesis 3:***

*According to the novel hybrid separation processes developed for the ten mixtures classified into the four groups, a design strategy for quaternary mixtures having both minimum boiling heterogeneous and homogeneous azeotropes is concluded.*

For each mixture of the groups the same separation process based on the proper application and positioning of the extractive heterogeneous-azeotropic distillation within the separation train is designed and recommended (Figure 3). The description of the design strategy does not involve the separation of the alcohol-water mixture.

- For mixtures classified into group 1 (3 binary azeotropes and one ternary azeotrope) the first step is the separation of the non-azeotropic forming component with ordinary distillation, product 1 (P1). The second step is the separation of the remaining ternary highly non-ideal system with extractive heterogeneous-azeotropic distillation. The top product is obtained according to the liquid-liquid equilibrium due to the limited immiscibility (P2) and the bottom product is the alcohol-water binary system (P3+Water).
- For mixtures classified into group 2 (mixtures with 5 binary and 2 ternary azeotropes) the first step is the extractive heterogeneous-azeotropic distillation with alcoholic water mixture as bottom product (P1+water), followed by two subsequent ordinary distillations with bottom products of P2 and P3. The recirculation of the distillate of the second ordinary distillation column, a binary azeotrope, is needed.
- For mixtures classified into group 3 (mixtures containing 6 binary azeotropes and 3 ternary azeotropes) the separation scheme starts with two subsequent extractive heterogeneous-azeotropic distillations. In the first extractive heterogeneous-azeotropic

distillation the alcohol is separated with water in the bottom product (P1+water). In the second extractive heterogeneous-azeotropic distillation the limited immiscibility is utilised for the recovery of the desired product (P2). The last step of the separation scheme is a heterogeneous-azeotropic distillation where the top product is obtained according to the liquid-liquid equilibrium (P3). The bottom product is water.

- For mixtures classified into group 4 (mixtures with 6 binary and 4 ternary azeotropes) the separation is the most complicated one. In the first extractive heterogeneous-azeotropic distillation the alcohol is separated with water in the bottom product (P1+water). An ordinary distillation follows to separate the component of highly limited immiscibility (P2). A second extractive heterogeneous-azeotropic distillation follows and its organic rich phase of the top product is recycled. The bottom product is further processed in a subsequent heterogeneous-azeotropic distillation where (P3) is obtained as a top product. Its bottom product is water.

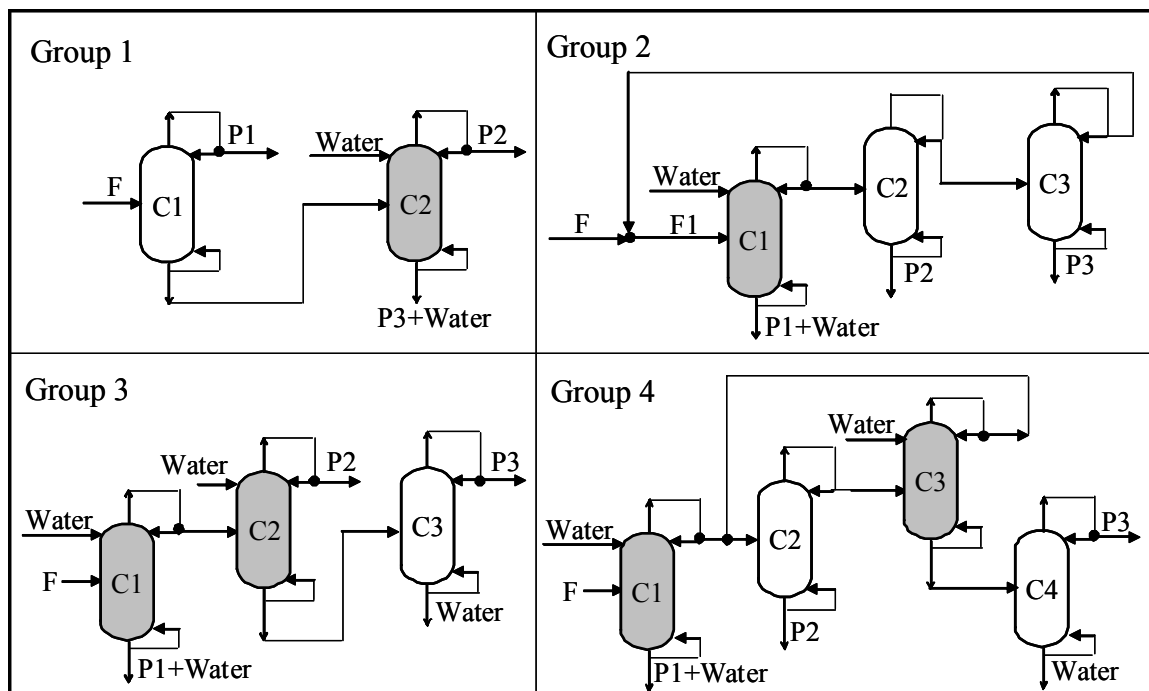


Figure 3., Separation alternatives for the different quaternary mixtures classified into four groups

## 8. List of major publications

### Papers published in scientific journals

1. Agnes Szanyi, Peter Mizsey, and Zsolt Fonyo, Novel Hybrid Separation Processes for Solvent Recovery Based on Positioning the Extractive Heterogeneous-Azeotropic Distillation, *Chem. Eng. Proc.* 43 (2004) 237-338
2. Agnes Szanyi, Peter Mizsey and Zsolt Fonyo, Optimization of Nonideal Separation Structures Based on Extractive Heterogeneous Azeotropic Distillation, *Ind. Eng. Chem. Res.*, 43 (2004), 8269-8274
3. Agnes Szanyi, Peter Mizsey and Zsolt Fonyo: Separation of highly non-ideal mixtures with extractive heterogeneous-azeotropic distillation, *Chemical and Biochemical Engineering Quarterly*, accepted for publication, (June, 2005)
4. Benko, T., A. Szanyi, P. Mizsey, Z. Fonyo: Environmental and Economic Comparison of Waste Solvent Treatment Options, *Central European Journal of Chemistry*, submitted for publication, (2005)

### Conference papers

1. Agnes Szanyi, Tamas Benko, Peter Mizsey, Zsolt Fonyo, Optimisation of separation of non-ideal mixtures, *31th International Conference of SSCHE Tatranské Matliare*, Slovakia Po-We-5, 117p. (2004)
2. Tamas Benko, Agnes Szanyi, Katalin Koczka, Peter Mizsey, Zsolt Fonyo, Environmental and Economical Evaluation and Comparison of Non-ideal Waste Solvent Treatment Options, *31th International Conference of SSCHE Tatranské Matliare*, Slovakia Le-We-2, 114p. (2004)
3. Agnes Szanyi, Peter Mizsey, Zsolt Fonyo: Solvent Recovery from Non-Ideal Quaternary Mixtures with Extractive Heterogeneous - Azeotropic Distillation, *4th European Congress of Chemical Engineering, Topics 10, Book 6, Granada*, (2003)
4. Mizsey, P., A. Szanyi, J. Manczinger, Z. Fonyo, Novel hybrid processes for solvent recovery, 4-9, *VDI Distillation & Absorption 2002*, Germany (2002)
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- Mizsey, P., A. Szanyi, J. Manczinger, Z. Fonyo, Solvent recovery by hybrid separation tools, *1<sup>st</sup> International Symposium on Tools of Sustainability*, EFCE, WPEP, HCS, AEE, EMS organisation, Budapest, October (2001).
  - Szanyi Ágnes, Benkő Tamás, Koczka Katalin, Mizsey Péter, Mészáros Alajos, Borus Andor, Fonyó Zsolt: Négykomponensű nemideális elegyek elválasztása extraktív heteroazeotróp rektifikálással, *Műszaki Kémiai Napok '04*, 2004. április 20-22, Veszprém, 246-247
  - Horváth Marcell, Mészáros Alajos, Szanyi Ágnes, Mizsey Péter: Recirkulációt tartalmazó rendszerek szabályozhatóságának vizsgálata, *Műszaki Kémiai Napok '04*, 2004. április 20-22, Veszprém, 253-257
  - Benkő Tamás, Koczka Katalin, Szanyi Ágnes, Rezessy Gábor, Mizsey Péter, Fonyó Zsolt: Nemideális Oldószer elegyek Hulladékkezelési lehetőségeinek környezetvédelmi és gazdaságossági elemzése, *Műszaki Kémiai Napok '04*, 2004. április 20-22, 250-252

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- Tamas Benko, Agnes Szanyi, Katalin Koczka, Peter Mizsey, Zsolt Fonyo: Environmental and Economical Evaluation and Comparison of Non-ideal Waste Solvent Treatment Options, Full text of the lecture, *31<sup>st</sup> International Conference of Slovak Society of Chemical Engineering* (2004)
- Szanyi, A., P. Mizsey, Z. Fonyo, Solvent Recovery from Non-ideal Quaternary Mixtures with Hybrid Processes Based on Extractive Distillation, *ECCE-4*, Granada (2003)
- Mizsey, P., A. Szanyi, J. Manczinger, Z. Fonyo, Novel hybrid processes for solvent recovery, Oral lecture on *VDI Distillation & Absorption 2002*, Germany (2002)
- Szanyi, A., P. Mizsey, Z. Fonyo, Design and Development of Solvent Recovery Technologies by Hybrid Separation Tools, Lecture on *Chisa-2002*, Praha (2002)
- Szanyi Ágnes, Benkő Tamás, Koczka Katalin, Mizsey Péter, Mészáros Alajos, Borus Andor, Fonyó Zsolt: Négykomponensű nemideális elegyek elválasztása extraktív heteroazeotróp rektifikálással, *Műszaki Kémiai Napok '04*, 2004. április 20-22, Veszprém
- Horváth Marcell, Mészáros Alajos, Szanyi Ágnes, Mizsey Péter: Recirkulációt tartalmazó rendszerek szabályozhatóságának vizsgálata, *Műszaki Kémiai Napok '04*, 2004. április 20-22, Veszprém

7. Benkő Tamás, Koczka Katalin, Szanyi Ágnes, Rezessy Gábor, Mizsey Péter, Fonyó Zsolt: Nemideális Oldószerkelegyek Hulladékkezelési lehetőségeinek környezetvédelmi és gazdaságossági elemzése, *Műszaki Kémiai Napok '04*, Veszprém (2004)
8. Szanyi Ágnes: Solvent Recovery from Non-Ideal Quaternary Mixtures with Extractive Heterogeneous-Azeotropic Distillation, *Richter Gedeon Centenáriumi Alapítvány* ülése, 2004. február 16.
9. Szanyi Ágnes, Mizsey Péter, Fonyó Zsolt : Négykomponensű nemideális elegyek elválasztása extraktív heteroazeotróp rektifikálással, Magyar Tudományos Akadémia, Vegyipari Műveleti Munkabizottság, 2003.11.6
10. Mizsey, P., A. Szanyi, J. Manczinger, Z. Fonyó, Solvent recovery by hybrid separation tools, *1<sup>st</sup> International Symposium on Tools of Sustainability*, EFCE, WPEP, HCS, AEE, EMS organisation, Budapest, October (2001).
11. Fonyó Zsolt, Mizsey Péter, Rév Endre, Szitkai Zsolt, Mansour Emtir, Szanyi Ágnes: Környezetbarát vegyipari folyamatok tervezése, *Ipari Nyílt Napok a Műegyetemen*, 2001. február

## Posters

1. A.Szanyi, P.Mizsey, Zs.Fonyó: Classification and separation of highly non-ideal quaternary mixtures containing minimum boiling azeotropes, CAPE Forum 2005 - ROMANIA, February 25-26, Cluj-Napoca, (2005)
2. T.Benko, A.Szanyi, K.Koczka, P.Mizsey: Comparison of Flue Gas Desulphurization Processes Based on Life Cycle Assessment, CAPE Forum 2005 - ROMANIA, February 25-26, Cluj-Napoca, (2005)
3. Agnes Szanyi, Peter Mizsey, Jozsef Manczinger, Andor Borus, Zsolt Fonyo : Novel hybrid separation processes based on extractive heterogeneous-azeotropic distillation, *CAPE FORUM 2004*, Veszprém, 2004
4. T. Benko, K. Koczka, A. Szanyi, G. Rezessy, P. Mizsey, Zs. Fonyó, Ecological evaluation of comparison of treatment options of non-ideal solvent mixtures, *CAPE Forum 2004*, Veszprém
5. Agnes Szanyi, Peter Mizsey, Jozsef Manzinger, Andor Borus, Zsolt Fonyo : Optimisation of separation of non-ideal mixtures, SSCHI, *31st International Conference of SSCHE*, Slovak Society of Chemical Engineering, Tatranské Matliare, May 24 - 28, 2004
6. T. Benko, A. Szanyi, P. Mizsey, Zs. Fonyó Oldószerkezelési eljárások környezetvédelmi és gazdaságossági elemzése, *BME-Ipari Nyílt Napok* 2004. március

7. T. Benko, K. Koczka, A. Szanyi, G. Rezessy, P. Mizsey, Zs. Fonyó, Ecological evaluation of comparison of treatment options of non-ideal solvent mixtures, Műegyetemi Napok (2004. február)
8. Szanyi Ágnes, Benkő Tamás, Koczka Katalin, Mizsey Péter, Mészáros Alajos, Borus Andor, Fonyó Zsolt : Oldószer-regenerálás Extraktív Heterogén –Azeotróp Desztillációval, Szimpózium az agrár- és élelmiszeripari hulladékok csökkentésének lehetőségeiről, *Symposium on Agroo-Food Wastes Reduction*, Budapest, 2003. október 29. (47-50)
9. Koczka Katalin, Deák András, Szanyi Ágnes, Manczinger József, Rezessy Gábor, Mizsey Péter, Fonyó Zsolt: Pervaporáció vizsgálata alkohol – víz elegyek elválasztásánál, Szimpózium az agrár- és élelmiszeripari hulladékok csökkentésének lehetőségeiről, *Symposium on Agroo-Food Wastes Reduction*, Budapest, 2003. október 29. (40-43)

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## Abbreviations

ETAC	Ethyl Acetate	
MEK	Methyl Ethyl Ketone	
ETOH	Ethanol	
IPOH	Isopropanol	
IPAC	Isopropyl Acetate	
C1, C2	Distillation columns 1, 2	
Boil. T.	Boiling point	[°C]
VLE	Vapor - Liquid equilibrium	
VLLE	Vapour - Liquid - Liquid equilibrium	
wt%	weight fraction	
FH	Hypothetical feed	