

## Separation of Highly Non-Ideal Quaternary Mixtures with Extractive Heterogeneous-Azeotropic Distillation

A. Szanyi\*, P. Mizsey, and Z. Fonyó

Department of Chemical Engineering, Budapest University of Technology and Economics, Research Group of Technical Chemistry of Hungarian Academy of Sciences, 1521 Budapest, Muegyetem rkp. 3, Hungary

Original scientific paper  
Received: February 9, 2005  
Accepted: April 1, 2005

To design suitable, generally applicable separation schemes and to conclude a design strategy, the separation of highly non-ideal quaternary mixtures, containing both heterogeneous and homogeneous minimum boiling azeotropes, is studied. The separation schemes are based on our novel distillation technique, the extractive heterogeneous-azeotropic distillation (EHAD) that simplifies the separation schemes significantly. To determine generally applicable separation schemes based on the EHAD, the separation of eight quaternary mixtures, usually waste streams of different industries, classified into four groups is studied. Since water is always present in the mixtures investigated, it is used in each separation alternatives as auto separating agent and/or entrainer. The visualization of the vapour-liquid-liquid equilibrium and the separation of the quaternary mixtures are also solved. The core of the different novel separation schemes designed is the EHAD and it is always verified experimentally in a laboratory size column. The recommended strategy for the separation of different quaternary mixtures, containing both homogeneous and heterogeneous azeotropes, proves to be successful.

### Keywords:

Extractive heterogeneous-azeotropic distillation, highly non-ideal mixture, waste mixtures, minimum boiling azeotrope

## Introduction

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

The separation of the non-ideal mixtures is a newer area of the engineering sciences and there are several significant contributions; different experimental and theoretical investigations have been done in industries and academia to separate non-ideal mixtures.<sup>1–5</sup> In spite of the several hundreds of publications and books about the separation of the non-ideal mixtures, the topic is still not exhausted and new problems and areas are arising day by day. There are several incentives of these authors and many others to determine any synthesis/design strategy for the separation of the non-ideal mixtures forming azeotropes. It is a difficult task since the vapour-liquid-liquid equilibrium of the non-ideal mixtures is usually quite complex

and unique and, on the other hand, 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 toward 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, too. Because of this problem, basically only the separation of ternary mixtures has been studied so far, where the separation can be represented easily in a triangle. For the sake of simplicity, the investigation of the separation of such non-ideal ternary mixtures is favoured where only homogeneous azeotropes are formed. *Kiva et al.*<sup>6</sup> have made a statistics about the ternary mixtures. They have studied 1609 ternary mixtures published over the period between 1965 and 1988, among them 1365 azeotropic ones.<sup>7</sup> They have classified the ternary azeotropic mixtures according to a Serafimov classification.<sup>8</sup> This classification includes 26 classes of feasible topological structures of VLE diagrams for ternary mixtures. Experimental VLE data indicate the natural occurrence of ternary mixtures for at least 16 of Serafimov's 26 topological classes, and 28 of the 49 antipodal types given by *Zharov* and *Serafimov*.<sup>9</sup>

\*Corresponding author: AgnesSzanyi@mail.bme.hu  
Tel.: +361 463 2202, Fax: +361 463 3197

### Separation solutions for non-ideal mixtures

The separation of highly non-ideal mixtures can be usually not solved with common distillation. Special combinations of different separation alternatives are always needed and they form the so-called hybrid separation techniques. The hybrid separation technique combines the advantages of the different separation alternatives and proves to be more effective than the series of homogeneous units.

Several authors<sup>3,10</sup> give guidelines for the selection and design of separation alternatives for non-ideal mixtures. Due to the complexity of such synthesis problem, however, no general strategy can be recommended. The problems are usually system-specific and the complex VLE behaviours demand newer and newer designs.

Nowadays, membrane separation technologies are getting more and more applied in hybrid separation technologies where they are combined with special distillation alternatives.<sup>11,12</sup> However, the membrane technologies have also their limitations: if high purities are needed the recycle flow becomes significant. If there are impurities in the mixture to be separated special, durable, and not too sensitive membranes are needed for the different separations. Therefore, the design and development of new membranes for new separation purposes poses a significant task for the membrane industry.

A relatively new distillation technique is the so-called *heteroextractive distillation*, first introduced by *Wijesinghe*<sup>13</sup> for ternary mixtures. In the case of heteroextractive distillation the entrainer forms a new heteroazeotrope with one of the original mixture components and it is miscible with the other.

The separation of more than three components of a non-ideal mixture is a less studied area, compared to those of the binary and ternary ones. *Mizsey*<sup>14</sup> has recommended such a novel hybrid separation technique where two coupled distillation columns with phase separation and extra water addition are applied for the separation of a quaternary mixture coming as a waste stream from a printing company. This so-called two-column system can cope with the general problem of splitting quaternary mixtures into two binary ones if immiscibility region exists helping to step over separation boundaries.

Azeotropic distillation can be also successfully used for the separation of special quaternary mixtures;<sup>15</sup> the case studies also show the complexity of the design of the separation schemes for highly non-ideal quaternary mixtures. However, a comprehensive study, classification, and separation structure design for such mixtures, are still under development and research.

### The extractive heterogeneous-azeotropic distillation (EHAD)

If such non-ideal mixtures are to be separated where both homogeneous and heterogeneous azeotropes are also present, a new hybrid tool devoted to the separation of such quaternary mixtures, the so-called extractive heterogeneous-azeotropic distillation, can be applied. This new hybrid separation tool, first introduced by *Szanyi et al.*,<sup>16</sup> combines the advantages of the extractive and the heterogeneous azeotropic distillations.

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.<sup>3,17,18,19</sup> A common restriction on the “extractive distillation” is that the entrainer should not introduce new azeotropes in the system.<sup>5,20,21</sup>

Nowadays, we define extractive distillation 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, we speak about the so-called “reverse extractive distillation”<sup>22</sup> that have been already used for successful separation. The extractive distillation of a maximum boiling azeotrope with a middle boiling entrainer has been already reported, too.<sup>23</sup> This all indicates that in the area of the separation of the non-ideal mixtures we should not strictly insist on the classical definitions, since due to the complex nature of these kinds of separation problems, always newer solutions are required.

The *heterogeneous azeotropic distillation* is defined as a technique that uses minimum-boiling azeotropes and liquid-liquid immiscibilities in combination, in order, to defeat the presence of other azeotropes or tangent pinches in the mixture that would otherwise prevent the desired separation.<sup>4</sup> The azeotropes and heterogeneous liquid phase that are used to make the desired separation feasible may either be induced by the addition of a separating agent, usually called entrainer, or they may already be present, in which case the mixture is called as self-entrained. If heterogeneous azeotropic distillation is applied, it consists of usually two columns in connection with a decanter to separate the organic-rich and water-rich phases.

If the *extractive heterogeneous-azeotropic distillation* is applied for the separation of non-ideal mixtures the minimum-boiling heteroazeotrope is removed overhead and separated by condensation and decantation, while excess of the entrainer is removed in the bottom product together with one of

components of the original mixture that it extracts. Extractive heterogeneous-azeotropic distillation differs from the heteroextractive distillation since no new azeotrope is formed and the extractive and relative volatility changing effect of the autoentrainer is fully utilised. On the other hand, rectification is also taking place while extractive heterogeneous-azeotropic distillation is applied. 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.

In the screening for entrainer, candidates are often ruled out, e.g. by the entrainer selection criteria given by *Doherty* and co-workers.<sup>20,24,25</sup> However, if possible, the basic principle of the green chemistry should be followed that no new material should be added to the systems.

## Discussion and methods

The separation of the highly non-ideal quaternary mixtures is a new research area of the separation technology. In this research work

– the separation of such quaternary mixtures is studied where the separation can be solved with

– the proper application of the extractive heterogeneous-azeotropic distillation.

To complete these research aims, several highly non-ideal quaternary mixtures are selected from industrial case studies. To fully utilise the advantages of the extractive heterogeneous-azeotropic distillation, the mixtures to be separated should contain components which form both the homogeneous and heterogeneous azeotropes; that is, one of the four components is water.

As motivating case studies, the industrial examples are selected from printing and medicine factories. In these industrial examples waste streams, which contain different solvents forming non-ideal mixtures, are quite often obtained. 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 a quaternary mixture. Eight quaternary mixtures are selected for the investigation. Table 1 shows the four components of the investigated mixtures, including the number of existing binary and ternary azeotropes (homogeneous vs. heterogeneous) for each particular mixture. Table 2 shows the boiling point of the individual components forming the quaternary mixtures. Tables 3 and 4

Table 1 – *The investigated mixtures and their azeotropes*

Groups	1		2		3		4	
Mixtures	1	2	3	4	5	6	7	8
	Water (1)	Water (1)	Water(1)	Water(1)	Water(1)	Water(1)	Water(1)	Water(1)
	ETOH (2)	ETOH(2)	ETOH(2)	ETOH(2)	ETOH(2)	IPOH(2)	ETOH(2)	ETOH(2)
	MEK (3)	ETAC(3)	ETAC(3)	MEK(3)	ETAC(3)	ETAC(3)	MEK(3)	ETAC(3)
	Acetone (4)	Acetone (4)	IPAC(4)	IPAC(4)	MEK(4)	MEK(4)	<i>n</i> -Heptane (4)	<i>n</i> -Heptane (4)
No. and pairing of binary azeot.	3 (1)- (2) (1)- (3) (2)- (3)	3 (1)- (2) (1)- (3) (2)- (3)	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 azeotr. Literature <sup>27,28,29</sup>	1 (1)- (2)-(3)	1 (1)- (2)-(3)	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)
Calculated						2 (1)- (2)-(4) (1)- (3)-(4)	2 (1)- (3)-(4) (2)- (3)-(4)	2 (1)- (3)-(4) (2)- (3)-(4)

Table 2 – The boiling points of the individual components

Components	$T_{BP} / ^\circ\text{C}$
Acetone	59.3
ETAC	77.1
ETOH	78.3
MEK	79.6
IPAC	88.5
IPOH	82.3
<i>n</i> -Heptane	98.4
Water	100

Table 3 – Binary azeotropes of the investigated mixtures

Components (1 – 2)	$T_{BP} / ^\circ\text{C}$	Component (1) $w / \%$	Component (2) $w / \%$
ETAC – <i>n</i> -Heptane	70	83.3	16.7
Water – ETAC	70.4-72.3	7.9-8.6	91.4-92.1
ETOH – <i>n</i> -Heptane	70.9-72	48.3-49	51-51.7
ETOH – ETAC	70.9-72.1	28-31.2	68.8-72
Water – MEK	73.7-73.8	11-12	88-89
ETOH – MEK	74-75	34.3-40.4	59.6-65.7
IPOH – ETAC	74.5-76.11	19.6-26	74-80.4
ETOH – IPAC	76.4-76.7	51.4-53.7	46.3-48.6
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
MEK – <i>n</i> -Heptane	77.6	69	31
Water – ETOH	78-78.3	4-4.6	95.4-96
Water – <i>n</i> -Heptane	79.2	13	87
Water – IPOH	79.7-80.72	11.2-13.1	86.9-88.8
Water – IPAC	81.7-82.8	12.2-16.2	83.8-86.8

give information about the binary and ternary azeotropes found in the investigated quaternary mixtures, respectively. The presentation of the VLLE data is made in mole fractions; however, since the product purity descriptions are given in mass fractions it is always indicated if mass fractions are used instead of mole fractions.

Table 4 – Ternary azeotropes of the investigated mixtures

Components (1 – 2 – 3)	$T_{BP} / ^\circ\text{C}$	Component (1) $w / \%$	Component (2) $w / \%$	Component (3) $w / \%$
Water – ETOH- <i>n</i> -Heptane	68	12.1	25.9	62
MEK – <i>n</i> -Heptane – Water(3)	69.5	8.4	51	40.6
ETOH – ETAC – <i>n</i> -Heptane	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
Water – ETAC – MEK	71.1	8.7	85	6.3
MEK – <i>n</i> -Heptane – ETOH	71.2	36.5	46	17.5
Water – ETOH – MEK	73	10	11	79
Water – IPOH – MEK	73.4	11.7	4	84.3
Water – ETOH – IPAC	74.8	10	18.4	71.6
IPOH – ETAC – MEK	75.4	20.4	68.1	11.5

Some of the mixtures have been already studied,<sup>16</sup> but in this research work the investigation is extended for every combination of quaternary mixtures. It can be seen that in this extended investigation the mixtures become increasingly complicated due to the complex immiscibility regions, and the increasing number of both homogeneous and heterogeneous azeotropes. In spite of the complexity of the mixtures, they have some common features:

- water is always present in the mixtures,
- the components form only minimum boiling azeotropes, and
- in every mixture both the homogeneous and heterogeneous azeotropes are found.

The eight mixtures can be classified into four groups according to the number of their azeotropes (Table 1).

The VLLE data are collected from *Gmehling*.<sup>26</sup> If measured data exist, the measured intervals are given. The missing data are calculated by ASPEN PLUS Version 12.1 that is also used for the simulation of the different separation scheme alternatives. During the design work atmospheric pressure in

each column is applied. Since there are both homogeneous and heterogeneous azeotropes in every mixture studied, these cases are typical for such separation schemes where the separation train can be based on the extractive heterogeneous-azeotropic distillation.

Following the principles given by Mizsey *et al.*,<sup>29</sup> after the exhaustive study of the VLE behaviour of the different mixtures it is possible to design uniform separation schemes for the different groups. The application of possible membrane separations is neglected at the point of this research study and the designed separation alternatives are based on the proper positioning of the extractive heterogeneous-azeotropic distillation within the separation scheme combined with phase separation, heterogeneous-azeotropic, and ordinary distillation. The presence of water in every mixture can be utilized, because the extractive heterogeneous-azeotropic distillation may always be solved by using water both as auto extractive agent and separating entrainer added at the right location into the column. This fulfils one of the basic requirements of the green chemistry that is no new material should be added to the systems.<sup>30</sup>

## Results

According to the methodology discussed, separation schemes can be recommended for the mixtures classified into four groups (Table 1).

### Separation scheme for group 1

Figure 1 shows the recommended scheme which is obtained by considering the possible design alternatives after extensive investigation and economic optimization.<sup>31</sup> First, the non-azeotropic forming component, i.e. acetone is separated by distillation. Then, with the use of the extractive het-

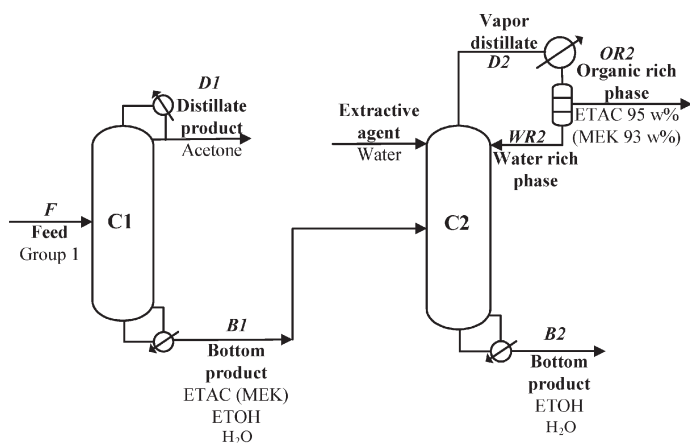


Fig. 1 – Separation scheme for the separation of mixtures of group 1

erogeneous-azeotropic distillation, it is possible to separate the ternary mixture remained. The visualisation of the extractive heterogeneous-azeotropic distillation column is now possible in a triangular diagram (Figure 2). The different streams are indicated in both figures with the same symbols (Figure 1 and 2).

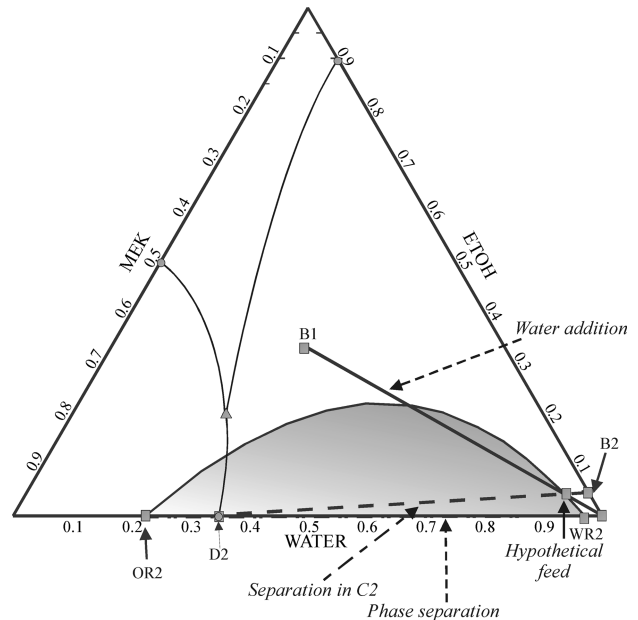


Fig. 2 – Representation of VLE data and the EHAD for mixture 1 in group 1

### Separation scheme for group 2

Several alternatives have been elaborated for the separation of the mixtures of group 2.<sup>32,33</sup> Such design alternatives might contain as many as nine different units, like extractors, distillation columns, and phase separators. The application of extractive heterogeneous-azeotropic distillation, however, allows significant simplification of the separation scheme, Figure 3. On the other hand, according to our previous economic investigation the separation based on the extractive heterogeneous-azeotropic distillation proves to consume the least energy, as well.<sup>32</sup>

The visualisation of such an extractive heterogeneous-azeotropic distillation can be done only in the three-dimensional, tetrahedral diagram (Figure 4). The streams of the separation scheme (Figure 3) are commonly indicated.

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 separatrixes divide the solution space into three distinct distillation regions. The first region is

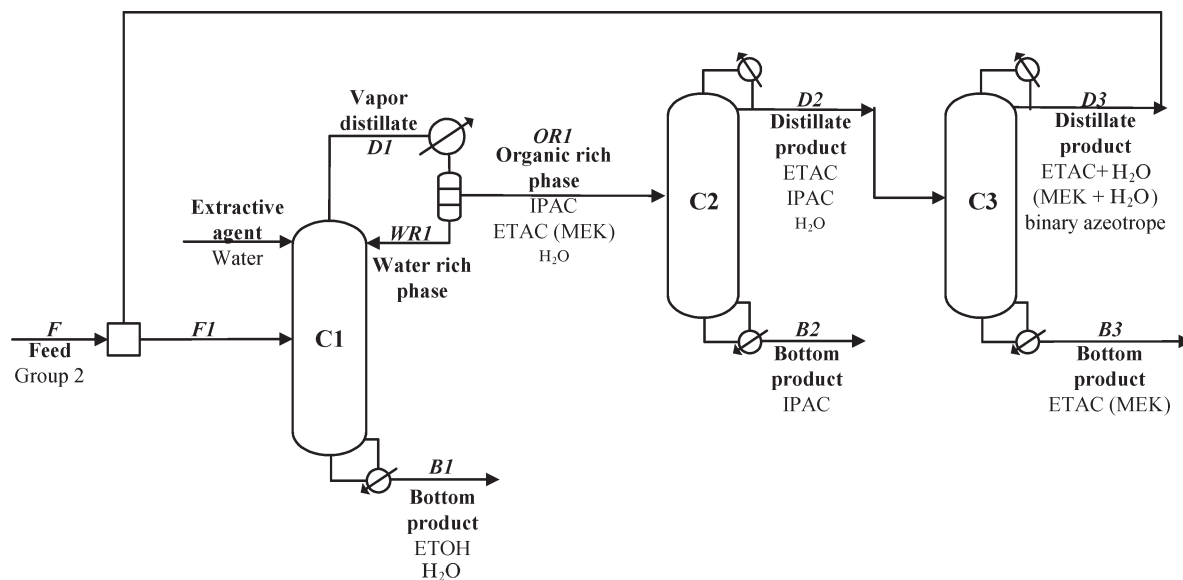


Fig. 3 – Separation scheme for the separation of mixtures of group 2

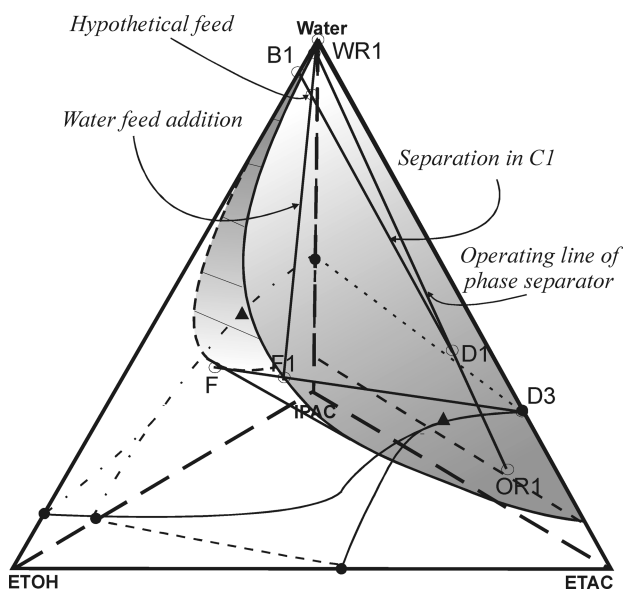


Fig. 4 – VLE data of mixture 4 (group 2) and representation of the EHAD in the column C1

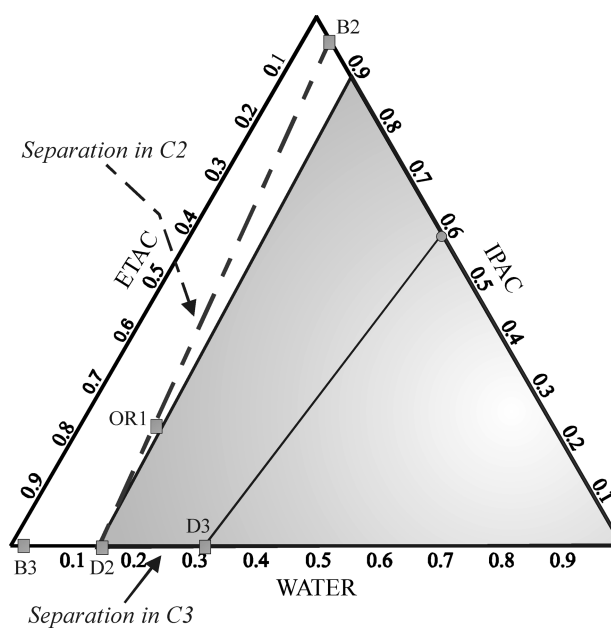


Fig. 5 – VLE data of mixture 3 (group 2) and representation of the separations in the columns C2 and C3

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 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 separations in columns C2 and C3 are represented in a triangular diagram (Figure 5). The recycle stream from the second ordinary distillation column contains the azeotrope of ETAC (or MEK) and water.

### Separation scheme for group 3

The separation of the mixtures of group 3 can also be resolved if the separation is based on the extractive heterogeneous-azeotropic distillation. Table 1, points to the increasing complexity of these mixtures; that is, the mixtures belonging to this group have six binary and two ternary azeotropes. In this case the separation can also be solved by the appropriate positioning of the extractive heterogeneous-azeotropic distillation within the separation train. The extractive heterogeneous-azeotropic distillation should be applied, however, twice due to

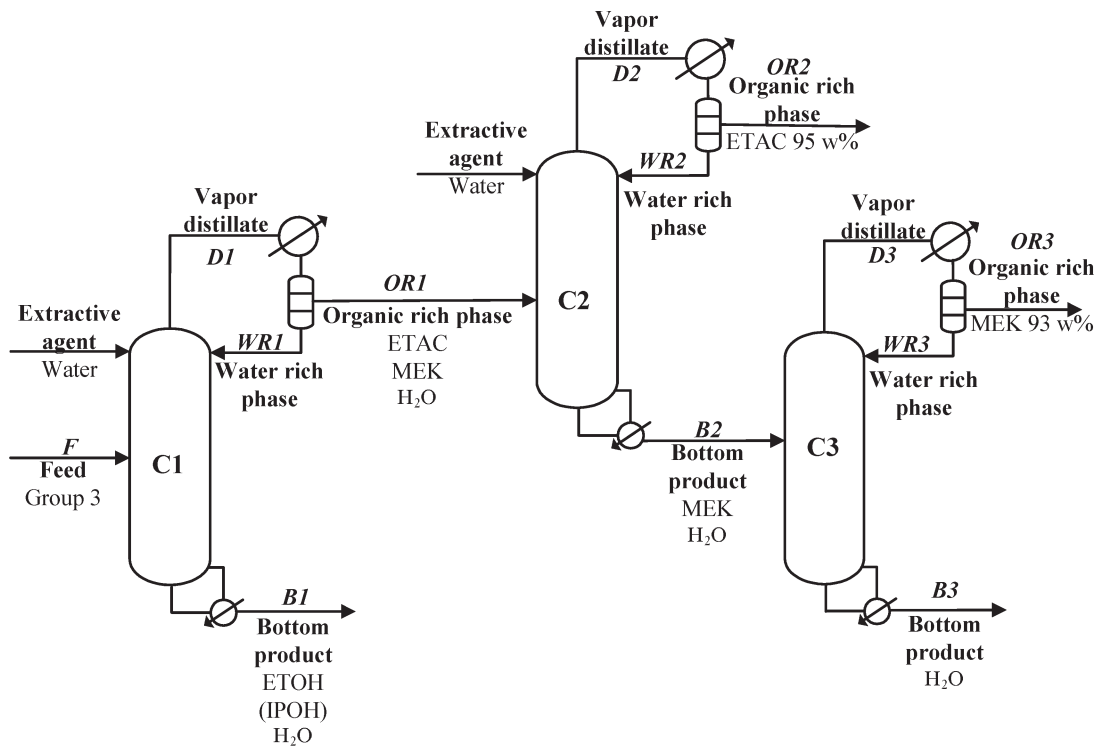


Fig. 6 – Separation scheme for the mixtures of group 3

the complexity of the VLLE nature of these mixtures (Figure 6). The first extractive heterogeneous-azeotropic distillation column can be represented in a tetrahedral diagram again (Figure 7). The streams of this column are indicated in both figures with the same symbols (Figure 6, 7). The top product of the first extractive heterogeneous-azeotropic distillation must be further separated and a subsequent extractive heteroge-

neous-azeotropic distillation can resolve this problem (Figure 8). The proper positioning of the extractive heterogeneous-azeotropic distillations within the separation train plays a paramount importance in this separation problem. The bottom product of the second extractive heterogeneous-azeotropic distillation is separated with a subsequent heterogeneous-azeotropic distillation column, column C3.

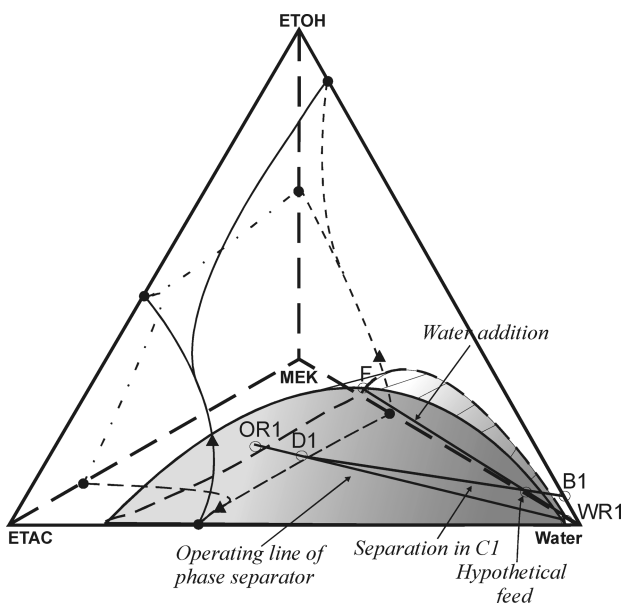


Fig. 7 – VLLE data of mixture 5 (group 3) and representation of the EHAD in the column C1

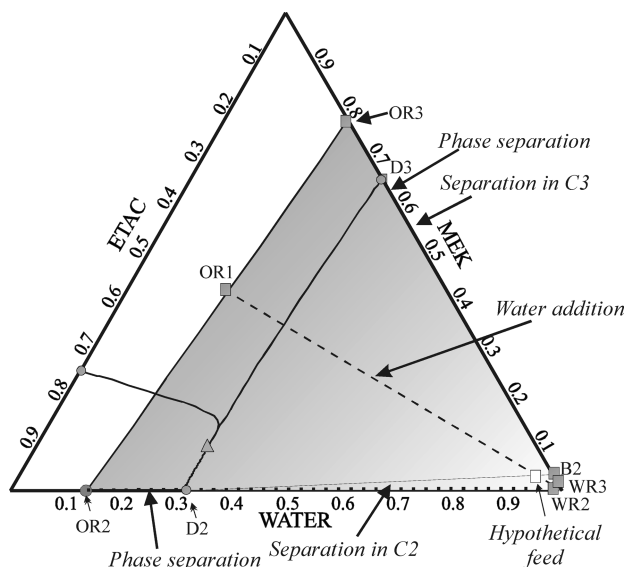


Fig. 8 – VLLE data of mixture 5 (group 3) and representation of the EHAD in the column C2

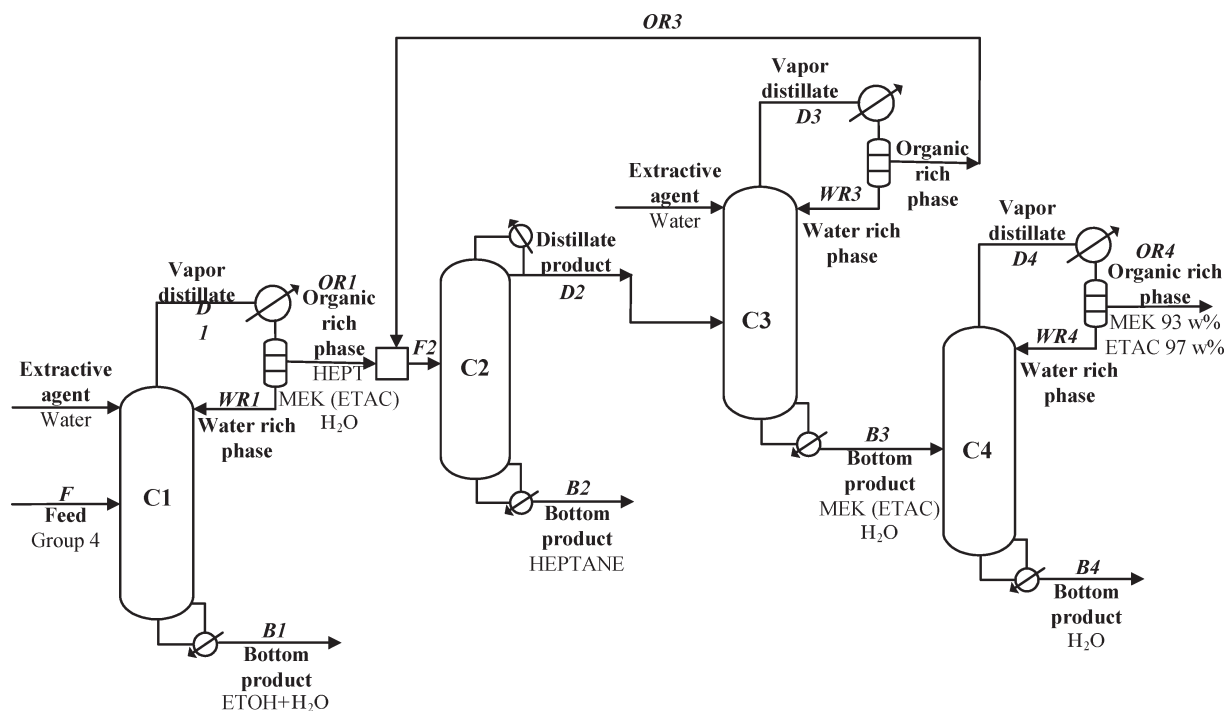


Fig. 9 – Separation scheme for the mixtures of group 4

**Separation scheme for group 4**

The mixtures of the group 4 contain the azeotropes in every possible combination (Table 1); that is, there are six binary and three ternary azeotropes. Figure 9 shows the possible separation structure. Two extractive heterogeneous-azeotropic distillations are needed again, but their positioning in the separation scheme is different to that of the scheme applied for the separation of the mixtures of group 3. An ordinary distillation should be applied between the two extractive heterogeneous-azeotropic distillations. Recycle of the organic rich phase of the top

product (OR3) of the second extractive heterogeneous-azeotropic distillation (C3) is necessary and a heterogeneous-azeotropic distillation (C4) is applied as the last separation unit in this scheme. The visualization of the extractive heterogeneous-azeotropic distillation column in the tetrahedral diagram is very confusing and this time it is avoided, since the composition space is practically the immiscibility region (Figure 10). The VLLE data and the separation steps after the removal of ethanol are visualised in a triangular diagram (Figure 11) since at this point there are only three components in the mixture to be separated. For a better overview, the same symbols of the streams are applied in Figures 9 and 11.

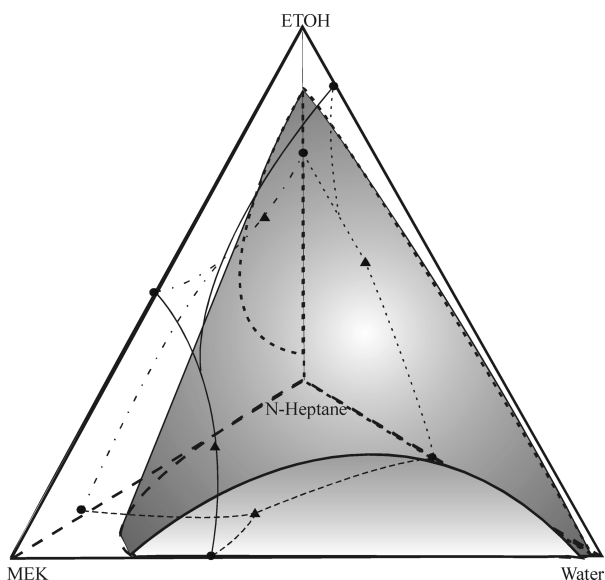


Fig. 10 – VLLE data of mixture 7 (group 4)

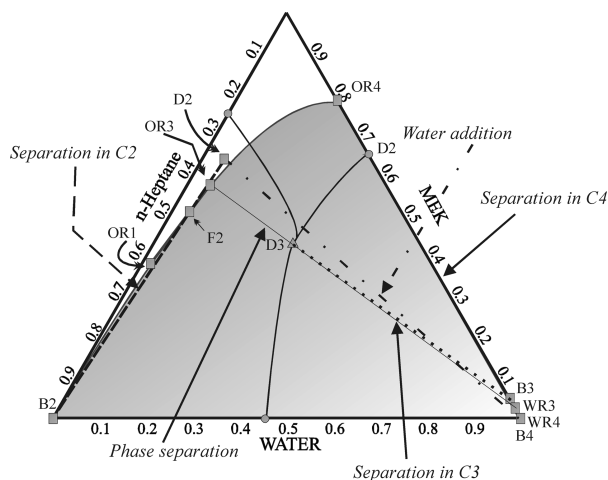


Fig. 11 – VLLE data of mixture 7 (group 4) after the separation of ETOH, and representation of the subsequent separation processes



## Experiments

The results of the simulations are verified experimentally. The most complicated separations are completed in the extractive heterogeneous-azeotropic distillation columns and these ones are tested in a laboratory size column. 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. Tables 5-7 show the comparison of the calculated and measured data for the extractive heterogeneous-azeotropic distillation of mixtures 3, 5, and 7, respectively.

Table 5 – Comparison of measured and simulated data of the EHAD column (mixture 3)

	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 – Comparison of measured and simulated data of the first EHAD column (mixture 5)

	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 7 – Comparison of measured and simulated data of the first EHAD column (mixture 7)

	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
<i>n</i> -Heptane	57.5	65	0	0	63	0	0
MEK	31.6	34.3	7.5	0	37.5	10	0

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

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

After designing the novel separation schemes for the mixtures classified into four groups (Table 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, can be recommended (Figure 12) 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.

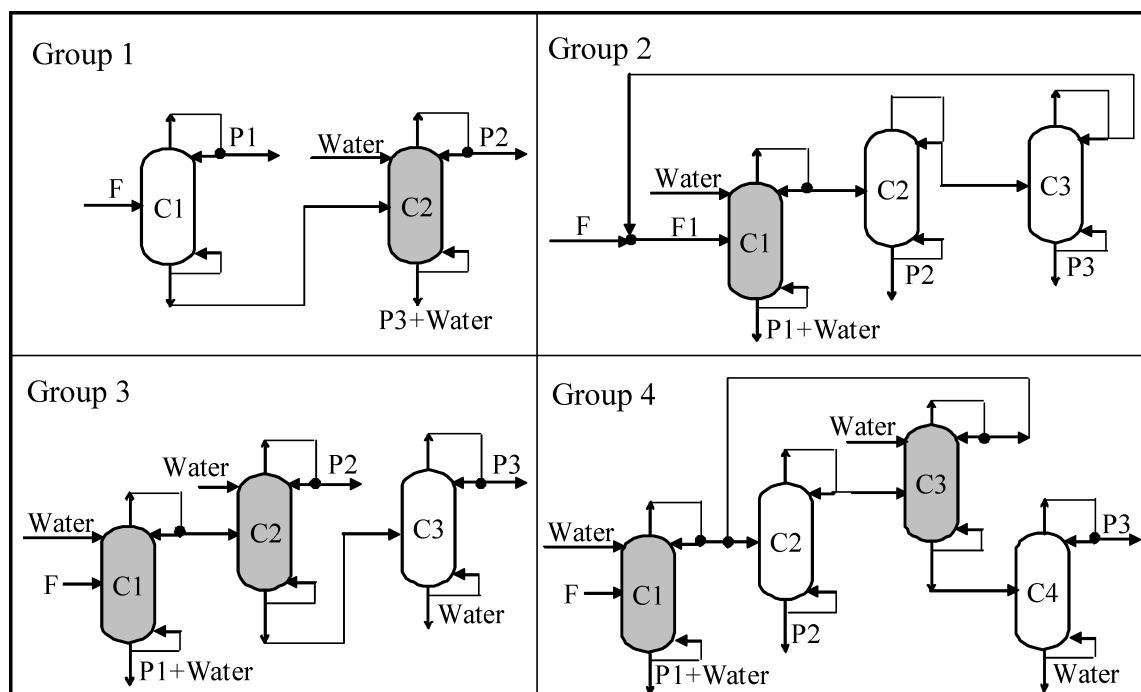


Fig. 12 – Separation alternatives for the different quaternary mixtures classified into four groups

– 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.

## Conclusions

The separation of highly non-ideal quaternary mixtures forming both homogeneous and heterogeneous minimum boiling azeotropes can be efficiently solved if the new separation technique – the extractive heterogeneous-azeotropic distillation is

applied. After studying eight mixtures classified into four groups according to their vapour-liquid-liquid equilibrium properties, generally applicable separation schemes and a strategy are suggested for their separation. The strategy is based on the proper application and positioning of the extractive heterogeneous-azeotropic distillation in the separation scheme, with water as autoentrainer being present in each mixture studied. The proper combination and matching of the extractive heterogeneous-azeotropic distillation with other unit operations form novel hybrid separation schemes. The recommended strategy for the separation of quaternary mixtures is a topic of great practical and industrial interest, since it can realise significant saving and reduction of the burden upon the environment.

## Notation

- EHAD – extractive heterogeneous azeotropic distillation
- ETAC – ethyl acetate
- ETOH – ethanol
- IPAC – isopropyl acetate
- IPOH – isopropanol
- MEK – methyl – ethyl – ketone
- P1 – product 1
- P2 – product 2
- P3 – product 3
- VLE – vapour liquid equilibrium data
- VLLE – vapour liquid liquid equilibrium data
- w – mass fraction, %

## References

1. Biegler, L. T., Grossmann, I. E., Westerberg, A. W., Systematic Methods of Chemical Process Design, Prentice-Hall, Englewood Cliffs, NJ, 1997.
2. Blass, E., Entwicklung verfahrenstechnischer Prozesse, Springer Verlag, 1997
3. Doherty, M. F., Malone, M. F., Conceptual Design of Distillation Systems, McGraw-Hill Book Company, New York, 2001.
4. Schembecker, G. K., Simmrock, H., *Comput. Chem. Eng.* **19** (1995) S253.
5. Stichlmair, J. G., Fair, J. R., Distillation, principles and practices, Wiley-VCH, USA, 1998.
6. Kiva, V. N., Hilmen, E. K., Skogestad, S., *Chem. Eng. Sci.* **58** (2003) 1903.
7. Hilmen, E. K., Kiva, V. N., Skogestad, S., *AIChE Journal* **48**(4) (2004) 752.
8. Serafimov, L. A., *Russ. J. Phys. Chem.* **44**(4) (1970) 567.
9. Zharov, V. T., Serafimov, L. A., Physicochemical Foundations of Simple Distillation and Rectification (in Russian), Chemistry Publishing Co., Leningrad, 1975.
10. Lipski, C., Coté, P., *Environ. Prog.* **9** (1990), 254.
11. Eliceche, A. M., Daviou, M. C., Hoch, P. M., Uribe, I. O., *Comput. Chem. Engn.* **26** (2002) 563.
12. Wilson, I., Encyclopedia of separation science, Academic Press, New York, 2000.
13. Wijesinghe, A. M. J. C., Development of Industrial Complexes of Special Rectification Techniques for Solvent Recovery, PhD thesis. M.V. Lomonosov Institute of Fine Chemical Engineering, Moscow, 1985.
14. Mizsey P., A Global Approach to the Synthesis of Entire Chemical Processes, PhD. Thesis No. 9563, Swiss Federal Institute of Technology, ETH Zurich, 1991.
15. Diamond, D., Hahn, T., Becker, H., Patterson, G., *Chem. Eng. Proc.* **43** (2004) 483.
16. Szanyi, A., Mizsey, P., Fonyo, Z., *Chem. Eng. Proc.* **43** (2004) 327.
17. Hoffman, E. J., Azeotropic and Extractive Distillation, Vol. IV. Intersci. Lib. Chem. Engng. and Processing, John Wiley & Sons, Inc., New York, 1964.
18. Perry, R. H., Perry's Chemical Engineers' Handbook, Chem. Eng. Series. 7th ed. Green, D.W. and Maloney, J.O. (Eds.), McGraw Hill, Inc., New York, 1997.
19. Van Winkle, M., Distillation, Chem. Eng. Series, McGraw Hill, Inc., 1967.
20. Doherty, M. F., Knapp, J. F., Distillation, Azeotropic and Extractive, in Kirk-Othmer Encyclopedia of Chemical Technology, 4<sup>th</sup> ed., Volume 8, John Wiley, New York, 1993.
21. Gmehling, J., Möllmann, C., *Ind. Eng. Chem. Res.* **37**(8) (1998) 3112.
22. Hunek, L., Gal, S., Posel, R., Glavic, P., *AIChE J* **35**(7) (1989) 1207.
23. Lelkes, Z., Rév, E., Stéger, Cs., Fonyó, Z., *AIChE J.* **48**(11) (2002) 2524.
24. Doherty, M. F., Caldarola, G.A., *Ind. Eng. Chem. Fundam.* **24**(4) (1985) 474.
25. Seader, J. D., Henley, E. J., Separation Process Principles. John Wiley & Sons, Inc., New York, 1998.
26. Gmehling, J., Menke, J., Fischer, K., Krafczyk, J., Azeotropic data, VCH, Part I-II., Weinheim, Germany, 1994.
27. Gmehling, J., Onken, U., Arlt, W., Vapour-Liquid Equilibrium Data Collection, Aqueous-Organic Systems, Chemistry Data Series Vol 1, Part 1b, D. Bierens and R. Eckerman, eds., Frankfurt/Main: Dechema, 1988.
28. Horsley, H. L., Azeotropic data, American Chemical Society, Washington D.C., 1973.
29. Mizsey, P., Rev, E., Fonyo, Z., Systematic Separation System Synthesis of a Highly Nonideal Quaternary Mixture, AIChE Spring National Mtg., Chicago, Paper 19f, 1997.
30. Anastas, P. T., Warner, J. C., Green Chemistry, Theory and Praxis, Oxford University Press, Oxford, 1998.
31. Szanyi, A., Mizsey, P., Fonyo, Z., *Ind. Eng. Chem. Res.* **43** (2004) 8269.
32. Mizsey, P., Szanyi, A., Raab, A., Manczinger, J., Fonyo, Z., Intensification of a Solvent Recovery Network Through the Use of Hybrid Equipment, ESCAPE-12, The Haag (2002), pp. 121-126.
33. Raab, A., Separation of Highly Non-Ideal Mixture for Solvent Recovery, Diploma work at Budapest Univ. of Technology and Economics, 2001.