

THESES OF Ph.D. DISSERTATION

Agnes Szanyi

**Separation of non-ideal quaternary mixtures with novel
hybrid processes based on
extractive heterogeneous-azeotropic distillation**

Supervisor:

Dr. Peter Mizsey
Full professor



BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS
DEPARTMENT OF CHEMICAL ENGINEERING

RESEARCH GROUP OF TECHNICAL CHEMISTRY OF
HUNGARIAN ACADEMY OF SCIENCES

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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/synthesis strategies have been recommended in the last decades by several authors.

The separation of the non-ideal mixtures is a newer area of the 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 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 the researchers to determine any synthesis/design strategy for the separation of the non-ideal mixtures forming 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 up till now basically 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. The major works in the

literature deal with the classification and investigation of the ternary, usually homogeneous, mixtures only.

There are just a few attempts to investigate and classify the quaternary non-ideal mixtures and their separation, especially if heterogeneous azeotropes are also present but a comprehensive investigation is still missing.

Therefore, in this work the investigation of the vapour-liquid-liquid equilibrium of quaternary mixtures is carried out and on the behalf of this investigation the mixtures are classified and such separation solutions are developed that 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 be also 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 around several (ten) thousand tones per year, continuous recovery methods are considered. The proper solution of the solvent recovery problems is, on the other hand, a contribution to the 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.

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 studied are classified into four groups according to their vapour-liquid-liquid equilibrium. In this work the following steps are realised:

- detailed study of the highly non-ideal quaternary mixtures according to their VLLE data;
- classification of the quaternary mixtures based on the 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 that is the number of binary and ternary azeotropes;
- design of uniform novel continuous separation schemes 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.

Applied tools

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

Major scientific results

Highly non-ideal quaternary mixtures, usually arising as waster 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.

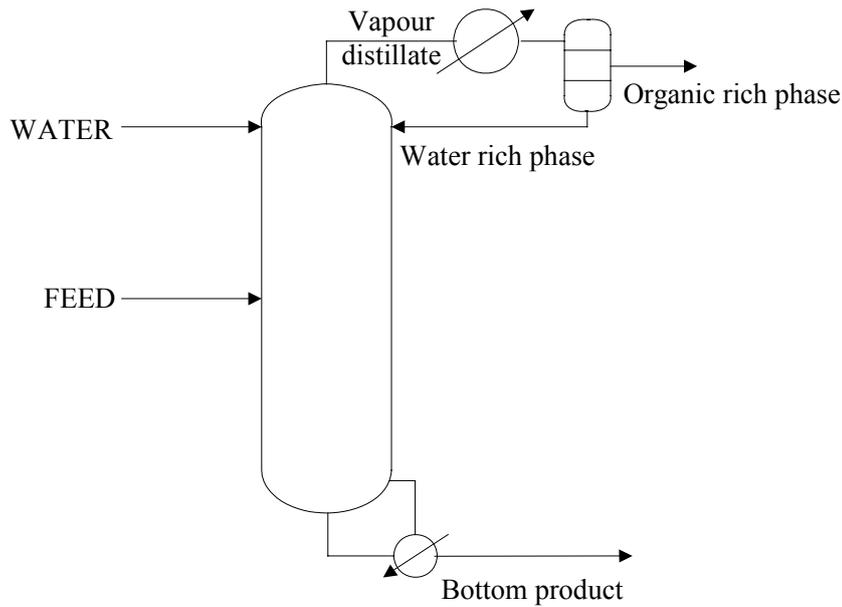


Figure 1. The extractive heterogeneous azeotropic distillation

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.

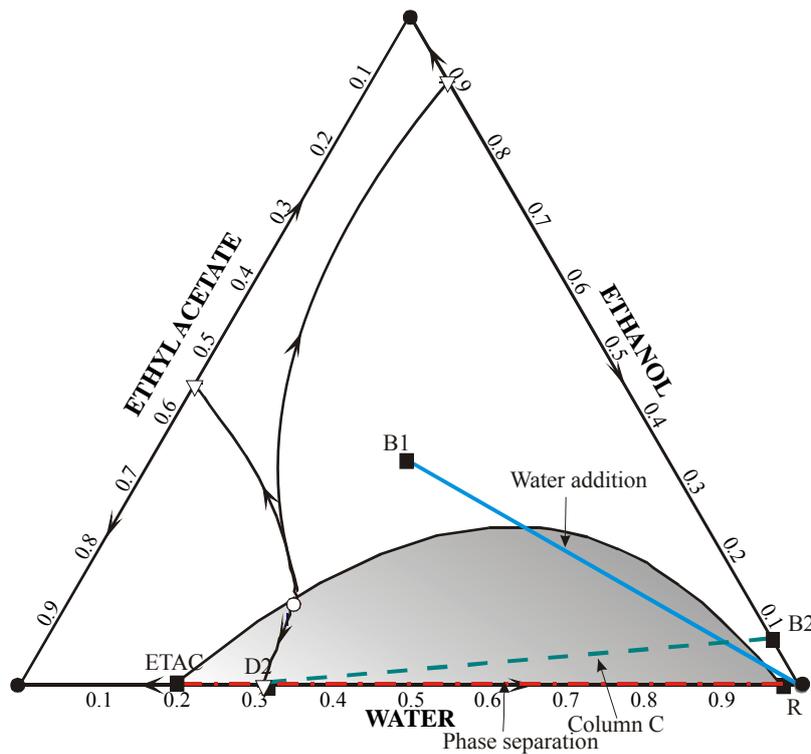


Figure 2, Water – ethyl acetate – ethanol mixture

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.

Applications

The new approach for the classification of the highly non-ideal quaternary mixtures containing minimum boiling azeotropes helps to deeply understand the behavior of such mixtures and to detect dependencies in their vapour-liquid equilibrium.

The design strategy based on the proper application and positioning of the extractive heterogeneous-azeotropic distillation in the separation scheme gives guideline to the designer to select suitable and economic hybrid processes for the separation of quaternary mixtures.

The recommended design strategy for the separation of quaternary mixtures is a topic of great practical and industrial interest, since significant saving and reduction of the burden upon the environment can be realized with its application.

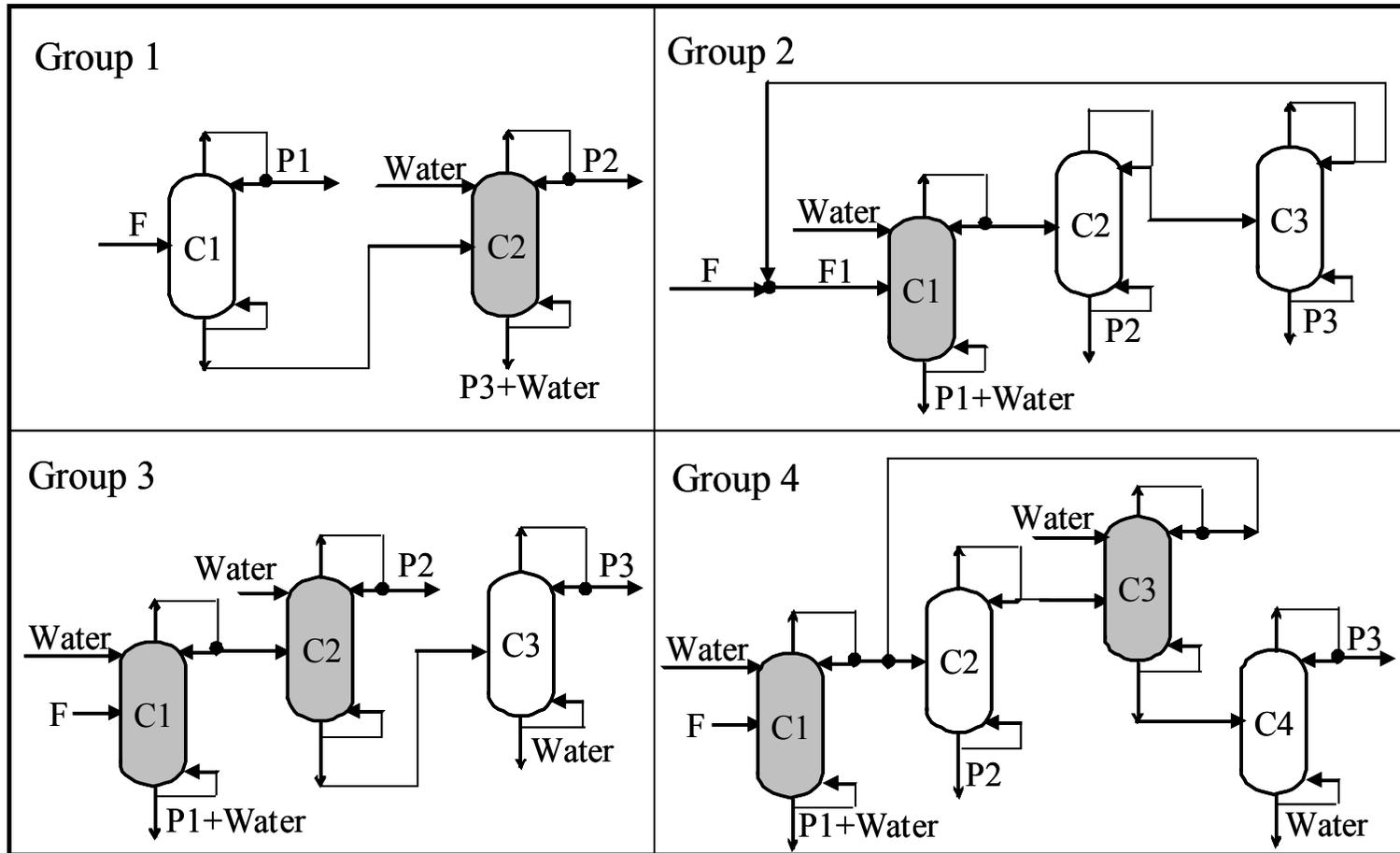


Figure 3, Separation alternatives for the different quaternary mixtures classified into four groups

List of major publications

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