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New double-column systems for batch heteroazeotropic distillation
(Nouveaux systèmes de double colonne pour distillation heteroazéotropique
discontinue)

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NEW DOUBLE-COLUMN SYSTEMS FOR BATCH

HETEROAZEOTROPIC DISTILLATION

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I would like to say many thanks to my parents and my brother who helped me in difficult periods, and who always supported me.

Content

Notation

Latin letters

A	component of the charge (organic)
A	activity coefficient parameter of the UNIQUAC model, cal/mol
A	Antoine constant,
AQ	AQueous phase
AZ	azeotrope
B	component of the charge (water)
B	activity coefficient parameter of the NRTL model, K^{-1}
B	Antoine constant, K
BAZ	Binary AZeotrope
BED	Batch Extractive Distillation
BHD	Batch Heteroazeotropic Distillation
BR	Batch Rectifier
C	Antoine constant, K
CHX	cyclohexane
CMB	Component Material Balance
D	distillate molar flow rate, kmol/s
D	internal diameter of a column, mm
d_p	external diameter and height of a packing particle, mm
DCS	Double-Column System
E	entrainer
F	feed molar flow rate, kmol/s
f	feed tray location
f	fugacity, Pa
GDCS	Generalised Double-Column System
H	height of the packing, m

HETP	height equivalent to a theoretical plate, m
h	dimensionless time
i	component
IPA	isopropanol
j	component
K	vapour-liquid distribution ratio
L	liquid molar flow rate, kmol/s
LAH	low level alarm
LAL	high level alarm
l	length of a tie line, mol%
$\overline{m}$	average slope of the VLE curve weighted by the theoretical plates
N	number of trays
n	molar quantity, kmol
NC	number of components
n_D	refractive index
NHX	n-hexane
ORG	ORGanic phase
P	performance, kW
P	pressure, bar
p	electric heat performance, %
prodA	Product *A*
prodB	Product *B*
PSD	Pressure Swing Distillation
Q	heat duty, kW
q	ratio of division of the total heat duty, kW/kW
R	reflux ratio
RCM	residue curve map
SD	amount of distillate, kmol

SI	selectivity index
T	temperature, °C
TAZ	Ternary AZeotrope
t	time, h or min
TMB	Total Material Balance
U	molar liquid holdup, kmol
u	ratio of division of the charge, kmol/kmol
V	vapour molar flow rate, kmol/h
V	volume, dm^3
v	ratio of division of the total vapour flow rate, mol/mol
W	bottom product molar flow rate, kmol/s
x	liquid mole fraction, mol/mol
$\vec{x}$	composition of the liquid in mole fraction, mol/mol
y	vapour mole fraction, mol/mol
y*	equilibrium vapour mole fraction, mol/mol

Greek letters

α	relative volatility
α	*A*-producing column of the DCS and GDCS
β	*B*-producing column of the DCS and GDCS
γ	activity coefficient
ρ	density. kg/m^3
τ	duration of the step, h
φ	fugacity coefficient

Subscripts

1,2,3,4	column sections of the BR
A	component of the charge (organic)
A1, A2, A3, A4	sections of Column α
AOE	heating oil entering Heater α
AOL	heating oil leaving Heater α
app	applied
Areb	Reboiler α
AQ	AQueous phase
Atop	top of Column α
av	average
AWE	cooling water entering Condenser α
AWL	cooling water leaving Condenser α
AZ	azeotrope
B	component of the charge (water)
b	beginning of the step
B1, B2, B3, B4	sections of Column β
BAZ	Binary AZeotrope
BOE	heating oil entering Heater β
BOL	heating oil leaving Heater β
Breb	Reboiler β
byprod	byproduct
Btop	top of Column β
BWE	cooling water entering Condenser β
BWL	cooling water leaving Condenser β
ch	charge
D	distillate
DEC	decanter
E	entrainer
e	end of the step
HU	HoldUp

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i, j   components

max   maximal

oil   heating oil

ov   overall

ORG ORGanic phase

res   residue at the end of the cycle

spec   specified value

TAZ   ternary azeotrope

w   cooling water

Superscripts

0   preconcentrator column

0   reference state

1   first step of the operation

2   second step of the operation

Ar A-rich phase

BP   Boiling Point

Br B-rich phase

dec   decanter

Er E-rich phase

I, II   liquid phases

ir   i-rich phase

jr   j-rich phase

L   liquid phase

SD   amount of distillate in the product tank

V   vapour phase

α column index (in Chapter 1)

α A-producing column of the DCS and GDCS

β column index (in Chapter 1)

β B-producing column of the DCS and GDCS

General Introduction

Distillation is the method the most frequently applied for the separation of liquid mixtures, e.g. for the recovery of the components of the waste solvent mixtures. It is based on the difference of the volatility of the components. The concentrations of the more volatile components in the vapour phase contacting intensively with the liquid phase are higher than in the liquid. Because of the high energy demand of these processes the optimal design and operation of the distillation equipments are important from economic and also environmental points of view.

By using ordinary distillation the mixtures forming azeotrope cannot be separated. The mixtures whose components have close boiling points can be separated by ordinary distillation only if the number of trays and the reflux ratio are very high but it could not be economic. In these cases special distillation methods must be applied, like heteroazeotropic distillation where the components form a heteroazeotrope or by the addition of an entrainer a heteroazeotrope can be formed. Therefore it is possible to get through the azeotropic composition by decantation.

In the pharmaceutical and fine chemical industries the quantity of the products is often low and they are changed frequently, therefore batch processes are widely applied. It means that the quantities of the mixtures to be separated are often low, their compositions and the products desired vary frequently. Therefore it is worth to apply the batch rectification instead of the continuous distillation. Drawbacks of the batch distillation are that the volume of the reboiler must be larger and the control of the process is more difficult because of the parameters changing continuously.

The Batch Heteroazeotropic Distillation (BHD) is an old method, widespread in the industry. Although several column configurations were developed for the BHD but to our best knowledge, it has been performed in the industry only in (one-column) batch rectifiers equipped with a decanter (in open operation mode, with continuous distillate withdrawal).

I work together with my Hungarian supervisor Prof. Péter Láng since 2005, from 2007 on the topic of the BHD. We developed and studied a double-column system for BHD in cooperation with Prof. Xavier Joulia who is my other supervisor since 2010 when I started my studies in Toulouse in the frame of PhD course under common supervision.

The aim of this work is

- to study the feasibility of a new double-column system for batch heteroazeotropic distillation and to compare it with the traditional batch rectifier,

- to study the above configurations by rigorous simulation,

- to do laboratory experiments for both configuration in order to prove their feasibility and validate them, respectively,

- to extend the double-column system to a generalised configuration and to study it by the above methods.

In Chapter 1 (Theoretical summary) the knowledge necessary for the understanding of this work are presented: first the principles of phase equilibria, then the different distillation methods, highlighted the processing of azeotropic mixtures.

In Chapter 2 (Theoretical study of the new configurations) a new Double-Column System for batch heteroazeotropic distillation then its generalised version are studied. For each configuration first its feasibility is investigated then its operation is modelled by rigorous simulation. On the basis of the results of both methods the configurations are compared with each other and with the Batch Rectifier equipped with a decanter.

In Chapter 3 (Experimental study of the new configurations) the experimental validation of the DCS and that of the GDCS is presented. First laboratory experiments were done for the separation of a binary heteroazeotropic mixture in a simple small size equipment operated as BR and DCS. Then a pilot plant was used for the same separation as DCS. After this experiment the separation of a binary homoazeotropic mixture by using an entrainer was studied in the equipment operated as BR and GDCS.

CHAPTER 1

THEORETICAL LITERATURE SUMMARY

1. Theoretical literature summary

In this chapter the knowledge necessary for the understanding of this work are presented: first the principles of phase equilibria, then the different distillation methods, highlighted the processing of azeotropic mixtures.

1.1. Principles of phase equilibria

First the calculation of phase equilibria is presented. Then the phenomena occurring in the case of the strongly non-ideal behaviour of a mixture (azeotropy and limited miscibility) are described for binary and ternary systems.

1.1.1. Description of phase equilibria

If two phases (I and II) of a mixture contact intensively with each other for a long time then equilibrium comes to be between them. For a system of NC different components being in equilibrium the following equations are fulfilled:

- Thermal equilibrium: $\qquad\qquad\qquad T^I = T^{II}$ $\qquad\qquad\qquad$ (1.1)

- Mechanical equilibrium: $\qquad\qquad\quad P^I = P^{II}$ $\qquad\qquad\qquad$ (1.2)

- Thermodynamic equilibrium: $\qquad\qquad f_i^I = f_i^{II}$ $\qquad i = 1...NC$ $\qquad$ (1.3)

where T, P, f_i denote temperature, total pressure, and fugacity of component i, respectively. In the case of a liquid (L) and a vapour (V) phase the condition of the thermodynamic equilibrium:

$$f_i^L(T,P,\vec{x}) = f_i^V(T,P,\vec{x}) \qquad\qquad i = 1...NC \qquad\qquad (1.4)$$

In both phases the fugacity depends on T, P and the composition $\vec{x}$ (in mole fraction).

1.1.1.1. Description of the vapour-liquid equilibrium (VLE):

The following methods can be used:

- the same model for both phases: $\phi - \phi$,

- different models for the two phases: $\phi - \gamma$ (for vapour phase, γ for liquid phase), where ϕ and γ denote fugacity coefficient and activity coefficient, respectively.

For our calculations $\phi - \gamma$ method is used, by which the calculation of the fugacities for the vapour and liquid phase is performed by a different way:

$$f_i^V(T,P,\vec{x}) = \phi_i \cdot y_i \cdot P \tag{1.5}$$

$$f_i^L(T,P,\vec{x}) = \gamma_i \cdot x_i \cdot f_i^{0L} \tag{1.6}$$

where y and x denote molar fraction of component i in the vapour and liquid phases, and f_i^{0L} is the fugacity of i in the reference state, respectively. In the conditions studied (atmospheric pressure, no molecular association in the vapour phase) the vapour phase can be considered as ideal. On the basis of the definition of the fugacity coefficient

$$\phi \equiv \frac{f}{p} \tag{1.7}$$

partial pressure (p_i) can be used instead of vapour fugacity (f_i^V) and vapour pressure (p_i^0) instead of f_i^{0L} :

$$f_i^V = p_i = y_i \cdot P \tag{1.8}$$

$$f_i^L(T,\vec{x}) = \gamma_i(T,\vec{x}) \cdot x_i \cdot p_i^0(T) \tag{1.9}$$

Eqs. 1.8 is called Dalton's law. Eq. 1.9 is the extension of Raoult's law for non-ideal mixtures, where p_i^0 denotes vapour pressure of i. Its exponential dependence on the temperature can be described e.g. by the Antoine equation:

$$lg\, p_i^0 = A_i - \frac{B_i}{C_i + T} \tag{1.10}$$

where A_i, B_i, and C_i are the Antoine constants of component i.

Since in equilibrium the partial pressures of the phases are equal, the relationship between the mole fractions of a given component in the two phases is the following:

$$y_i \cdot P = \gamma_i \cdot x_i \cdot p_i^0 \qquad (1.11)$$

If the other method is used where for both phases the same equation of state ($\phi - \phi$) is applied then the equilibrium relationship is:

$$\phi_i^L(P,T,\vec{x}) \cdot x_i = \phi_i^V(P,T,\vec{y}) \cdot y_i \qquad (1.12)$$

1.1.1.2. Description of the liquid-liquid equilibrium (LLE):

Two methods can be used:
- $\phi - \phi$ method,
- $\gamma - \gamma$ method.

The $\phi - \phi$ method can be applied as in Subsection 1.1.1.1:

$$\phi_i^I \cdot x_i^I = \phi_i^{II} \cdot x_i^{II} \qquad (1.13)$$

In this work the more common $\gamma - \gamma$ method is used for the calculation of LLE. The partial pressures for the two liquid phases (*I* and *II*) are calculated by the same way:

$$f_i^I = \gamma_i^I \cdot x_i^I \cdot p_i^0 \qquad (1.14)$$

$$f_i^{II} = \gamma_i^{II} \cdot x_i^{II} \cdot p_i^0 \qquad (1.15)$$

After the unification of Eqs. 1.12 and 1.13 the vapour pressures can be eliminated:

$$\gamma_i^I \cdot x_i^I = \gamma_i^{II} \cdot x_i^{II} \qquad (1.16)$$

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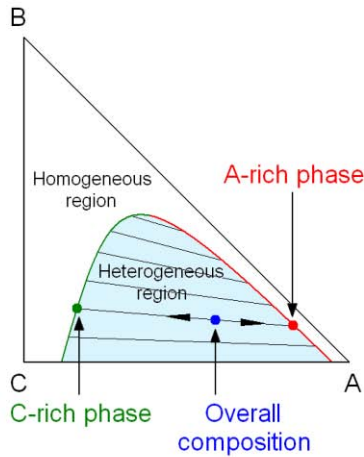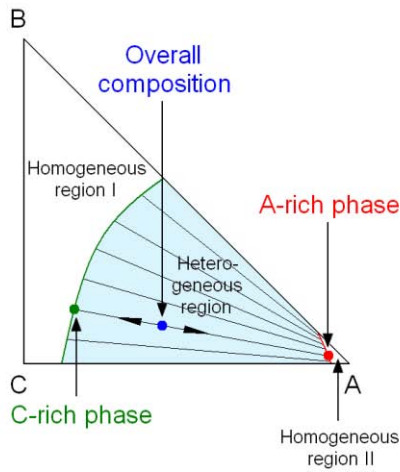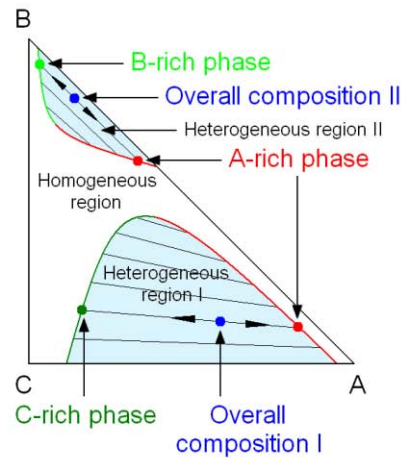
Fig. 1.1. The most common binodal plot types

a. Type 1: one partially miscible pair of components

b. Type 2: two partially miscible pairs of components resulting in one heterogeneous region

c. Type 2a: two partially miscible pairs of components resulting in two separate heterogeneous regions

If a ternary system contains components which are partially miscible then the compositions of the equilibrium phases at a given temperature can be presented in a ternary diagram (*Fig. 1.1,* Sorensen et al. (1979-1987)). It is divided into homogeneous and heterogeneous regions by the isothermal solubility curves. If the overall composition is in the heterogeneous region then the liquid splits into two liquid phases. Their compositions are denoted by the points which are the intersections of the solubility curve(s) and the tie line passing through the overall composition. Types 1 and 2 are far the most common heterogeneous ternary mixture types.

By the variation of the temperature the topology of the ternary diagram can vary. E.g. the system aniline (*A*) – methylcyclopentane (*B*) – n-hexane (*C*) is of Type 2 at 25 °C but if the temperature is increased to 45 °C then it becomes a system of Type 1 (Seader and Henley, 1998).

Examples: - Type 1: water (*A*) – ethanol (*B*) – cyclohexane (*C*)

- Type 2: water (*A*) – chlorobenzene (*B*) – butanone(*C*)

- Type 2a: nitrobenzene (*A*) – methanol (*B*) – isooctane(*C*)

1.1.1.3. Relative volatility

The difficulty of the separation of two components (*i*, *j*) by distillation is expressed by the relative volatility ($\alpha_{i,j}$), which is the ratio of their vapour-liquid equilibrium constants (*K*):

$$\alpha_{i,j} = \frac{y_i / x_i}{y_j / x_j} = \frac{K_i}{K_j} \tag{1.17}$$

The greater the deviation of the value of $\alpha_{i,j}$ from 1.0, the easier the separation of components *i* and *j*. If $\alpha_{i,j} = 1$ the separation by ordinary distillation is not feasible.

1.1.1.4. Deviation from the ideal behaviour

This phenomenon is more frequent in the liquid phase than in the vapour phase. Since the distance of the molecules is shorter, the interaction (attraction or repulsion) between them is stronger.

If the different molecules repel each other in a binary mixture then they enhance mutually their volatility, and the partial pressure of each component increases compared to the ideal case. In this case the activity coefficient is higher than 1.0 for both components ($\gamma_i > 1, \gamma_j > 1$). Thus the mixture has positive deviation compared to Raoult's law. If the repulsion is strong the mixture of positive deviation can form minimum boiling point azeotrope. In extreme case the repulsion between different molecules can be so strong that the components are partially miscible or immiscible.

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If the different molecules attract each other in a binary mixture then they diminish mutually their volatility, and the partial pressure of each component decreases compared to the ideal case. In this case the activity coefficient is lower than 1.0 for both components ($\gamma_i < 1$, $\gamma_j < 1$). Thus the mixture has negative deviation compared to Raoult's law. If the attraction is significant the mixture of negative deviation can form maximum boiling point azeotrope.

1.1.1.5. Activity coefficient models

The activity coefficient of a component depends on the temperature and the composition of the given liquid phase. For the description of function $\gamma_i = f(\vec{x}, T)$ several models are developed. Amongst them NRTL and UNIQUAC models are used in this work. These models are suitable not only for the description of VLE but also that of the liquid-liquid equilibrium (LLE). The description of these models can be found among others in the book of Kemeny et al. (1991). Stichlmair and Fair (1998) also describe the equations of these models in their book.

These activity coefficient models are suitable for the calculation of the phase equilibrium of multicomponent mixtures if the binary interaction (and other necessary) parameters are known for each possible pair of components. If the necessary parameters of a pair of components are not known (e.g. because of the lack of measurement data) then they can be estimated by using so-called group contribution models (e.g. UNIFAC).

1.1.2. Homo- and heteroazeotropic mixtures

The mixtures with strong deviation from the ideal behaviour frequently form azeotropes. If a mixture of azeotropic composition is boiling, the composition of the equilibrium vapour phase is identical to that of the (overall) liquid composition. In this case the value of the relative volatility is one:

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{y_i/x_i}{y_j/x_j} = \frac{x_i/x_i}{x_j/x_j} = 1 \tag{1.18}$$

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Since the compositions of the two phases do not differ from each other, the mixture cannot be separated into their components by ordinary distillation. An azeotrope occurs in a homogeneous binary system if:

$$\frac{p_A^0}{p_B^0} = \frac{\gamma_B}{\gamma_A}$$

(1.19)

The behaviour strongly deviating from the ideal one can result in the limited miscibility of the components (Gmehling et al., 1994). In the most cases a heterogeneous (minimum boiling point) azeotrope is formed, that is, the azeotropic composition is in the two-liquid phase region. In this case the condensate forming from the vapour of azeotropic composition separates into two liquid phases. There are also some mixtures of limited miscibility, which form homogeneous azeotrope, that is, the azeotropic point is out of the heterogeneous region. There are also some examples for mixtures, which form maximum boiling point homoazeotrope despite their components are partially miscible.

In the following part the types of binary and ternary azeotropes are presented.

1.1.2.1. Types of binary azeotropes

I. Minimum boiling point homogeneous azeotrope (e.g. ethanol – water)

II. Minimum boiling point heterogeneous azeotrope (e.g. water – 1-butanol)

III. Maximum boiling point homogeneous azeotrope (e.g. acetone – chloroform)

IV. Minimum boiling point azeotrope in a partially miscible system
   (e.g. tetrahydrofuran – water)

V. Double azeotrope (e.g. benzene – hexafluorobenzene)

VI. Maximum boiling point homogeneous azeotrope in a partially miscible system
   (e.g. hydrogen chloride – water)

Fig. 1.1 shows for all types of binary azeotrope:

- the dew and boiling point pressure curves at constant temperature,

- the dew and boiling point temperature curves at constant pressure, and

- the vapour-liquid equilibrium composition curves.
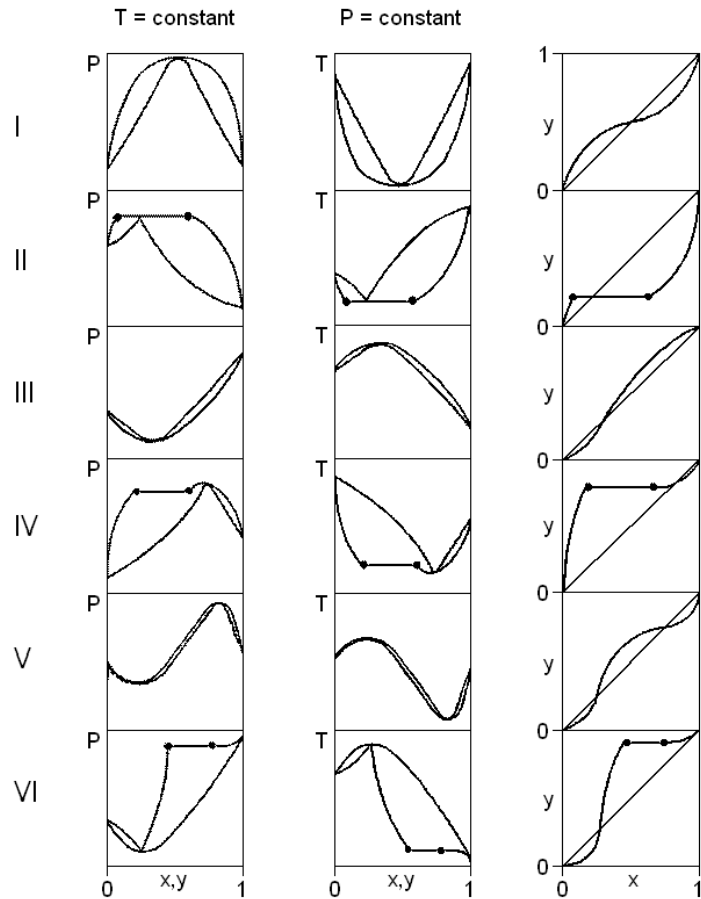
Fig. 1.1. Types of binary azeotropes

Similarly to the binary systems, azeotropy is observed also in the case of multicomponent mixtures. In these mixtures, beside the minimum and maximum boiling point azeotropes, so called saddle point azeotropes can also occur. For this type of mixtures the boiling point belonging to the azeotropic composition is between those of the lightest and heaviest components.

1.1.2.2. Types of ternary azeotropes

I. Minimum boiling point homogeneous azeotrope (e.g. benzene – cyclohexane – 2-propanol)

II. Minimum boiling point heterogeneous azeotrope (e.g. benzene – 2-propanol – water)

III. Maximum boiling point homogeneous azeotrope (e.g. hydrogen fluoride – hexafluoro-silicic acid – water)

IV. Homogeneous saddle point azeotrope (e.g. acetone – chloroform – methanol)

V. Minimum boiling point homogeneous azeotrope in a partially miscible system (e.g. ethyl acetate – ethanol – water)

Similarly to the binary azeotropes, where the azeotropic point cannot be crossed by ordinary distillation, in the case of ternary mixtures there are boundaries, which also cannot be crossed by ordinary distillation.

1.2. Different distillation methods

Distillation is the method the most frequently applied for the separation of liquid mixtures. It is based on the difference of the volatility of the components. The concentrations of the more volatile components in the vapour phase contacting intensively with the liquid phase are higher than in the liquid.

Rectification is a distillation process, during which the liquid is evaporated and then condensed several times. In this way higher purity can be reached than by simple distillation. In the engineering practice rectification is called also as distillation.

First the residue curves derived from the simple batch distillation and the residue curve maps are presented. Then the special distillation methods are presented for continuous cases. The extractive and the heteroazeotropic distillations are described in a more detailed form. It is followed by the ordinary batch distillation, and finally the batch extractive and heteroazeotropic distillation methods are presented.

1.2.1. Residue curves of the simple batch distillation

The residue curves have high importance for the determination of the separation sequence of azeotropic mixtures and for the feasibility studies (Doherty and Perkins, 1978). The residue curves defined first by Schreinemakers (1901) can be determined by experiments and calculations, as well. If a liquid mixture is filled into a heated vessel, it is heated onto the boiling point and it is continuously progressively evaporated, the composition of the pot residue ($\vec{x}(t)$) is measured and displayed in the concentration space (triangular diagram for a ternary mixture), then the path of the pot residue composition is the residue curve.

The residue curve of the simple batch distillation is determined by the initial charge composition and the vapour-liquid equilibrium conditions.

Assumptions:

- The composition of the vapour leaving ($\vec{y}^{*}(t)$) is in equilibrium with the current composition of the pot residue.
- The reflux ratio is zero.
- The pressure is constant.

On the basis of the total and component material balances the following differential equation describes the residue curve where U denotes the molar quantity of the residue:

$$\frac{d\vec{x}}{dU/U} = \vec{y}^{\,*} - \vec{x} \qquad\qquad (1.20)$$

If the dimensionless time is introduced as $dh = -dU/U$, the above equation can be written as:

$$\frac{d\vec{x}}{dh} = \vec{x} - \vec{y}^{\,*} \qquad\qquad (1.21)$$

The residue curves give the possible concentration profiles of a packed column if it is operated under total reflux. The profiles of a tray column can be also approached by residue curves but the distillation line is more precise suggested by Stichlmair and Fair (1998).

The system of the residue curves and distillation regions is called *residue curve map* (RCM). The structure of the RCM can be clearly characterised by the separatrices. Generally some typical residue curves are also displayed. For the determination of the separation sequence it is enough to know the approximate position of the simple distillation boundaries. For the scheme of the RCM the knowledge of the boiling points of the pure components and the binary and ternary azeotropic data (temperature, composition) are sufficient.

In Fig. 1.2 RCMs of three types of mixture is presented:

a. The residue curves of a zeotropic mixture move away from the vertex denoting the most volatile component (*A,* unstable node) and they approach vertex *C* (the heaviest component, stable node). The vertex of the intermediate boiling point component (*B*) is a saddle, which can be arbitrarily approached by the residue curves but they pass by it.

b. On the RCM of a ternary mixture containing only one minimum boiling point azeotrope there are an unstable (*AZ*) and a stable node (*C*), and two saddles (*A* and *B*), respectively.

c. The RCM of a ternary mixture, which contains three binary minimum boiling point azeotropes and also a ternary minimum one (as the ternary mixtures used for our calculations, simulations and experiments) is divided into three distillation regions by separatrices. These separatrices connect the ternary azeotropic point with the binary azeotropic ones. Each region has a different unstable node.
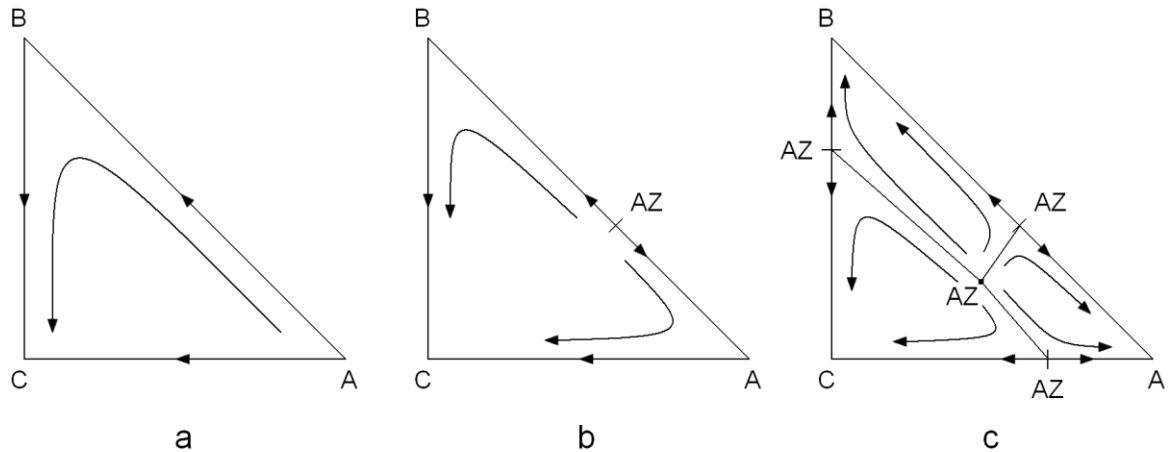
Fig. 1.2. Some ternary residue curve map types:

a. Zeotropic mixture

b. Mixture with one minimum binary azeotrope

c. Mixture with three minimum binary and a ternary minimum azeotrope

1.2.2. Special distillation methods

By using ordinary distillation there are two cases where appropriate separation cannot be reached:

- Mixtures forming azeotrope cannot be separated to their components.

- If the boiling points of the components are close (low relative volatility) the difference between the vapour and liquid compositions becomes small. It would need many steps consisting of evaporation and condensation (too high number of trays and reflux ratio), which would not be economic.

In these cases special distillation methods must be applied. In continuous mode they can be realised only in systems containing at least two columns.

A binary azeotropic mixture can be separated into their components without adding a third one (separating agent) in the following cases:

I. If the variation of pressure modifies significantly the azeotropic composition of a homoazeotropic mixture *pressure swing distillation* can be applied.

II. If the components are partially miscible and the azeotropic composition is in the heterogeneous composition range, the mixture can be separated by binary *heteroazeotropic distillation*. This process contains also liquid-liquid separation.

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III. If there is an adsorbent, which adsorbs selectively one of the components, *adsorptive distillation* can be applied (Marple and Foecking, 1956). Although in this case a third component is used but this method differs significantly from those where a solvent is added to the mixture because the separating agent is solid and it is not soluble in the mixture. Mujiburohman et al. (2006) studied the feasibility of the separation of isopropanol – water by continuous fixed adsorptive distillation. Their flowsheet consists of two distillation columns and an adsorber. The first column produces distillate whose IPA content remains slightly below that of the azeotrope. Then silica gel adsorbs selectively a part of the water content of the distillate. (The composition of the distillate gets through the azeotropic one.) Finally, the second column produces isopropanol in high purity.

If the methods mentioned above cannot be applied, a separating agent (entrainer) must be used. Depending on the effect of the entrainer, the following methods are distinguished (Lang, 2005):

I. Homoazeotropic distillation:

The entrainer (solvent) modifies favourably the relative volatility of the components without generating a second liquid phase. The homoazeotropic distillation method the most frequently applied is the *extractive distillation*. In this case the boiling point of the entrainer is much higher than those of the components to be separated, and it does not form any azeotrope with them (Benedict and Rubin, 1945).

II. Heteroazeotropic distillation:

The entrainer modifies favourably the relative volatility of the components with generating a second liquid phase. The entrainer forms at least one heteroazeotrope with the other components. This process contains also liquid-liquid separation.

III. Reactive distillation:

The entrainer reacts with one of the components in a reversible way.

IV. Salt-effect distillation:

The entrainer dissociates into ions and modifies the azeotropic composition in this way. In this case the separating agent is not evaporated.

Amongst the above methods in the industry the most widespread ones are the continuous extractive distillation and the heteroazeotropic distillation. These methods are presented in more details.

1.2.3. Continuous homoazeotropic distillation

When a distillation technology is developed for the separation of a binary azeotrope or a mixture of low relative volatility, first the applicable solvents must be the selected. Many publications deal with this question, e.g. Rodriguez-Donis et al. (2001).

Requirements for the solvents are the followings:

I. Selectivity:

The relative volatility of the original components must be changed favourably by the solvent, and the azeotrope must be broken if necessary.

II. Separability:

The products must be separable from the solvent and it must be also regenerated easily. Therefore the boiling point of the solvent applied is generally much higher than those of the other components.

III. Further requirements:

The solvent must have low freezing point and low viscosity. It must be thermally stable, environmentally friendly and cheap. It cannot be corrosive, toxic and reactive.

The industrial realisation of the continuous extractive distillation is done by a double-column system (*Fig. 1.3*).
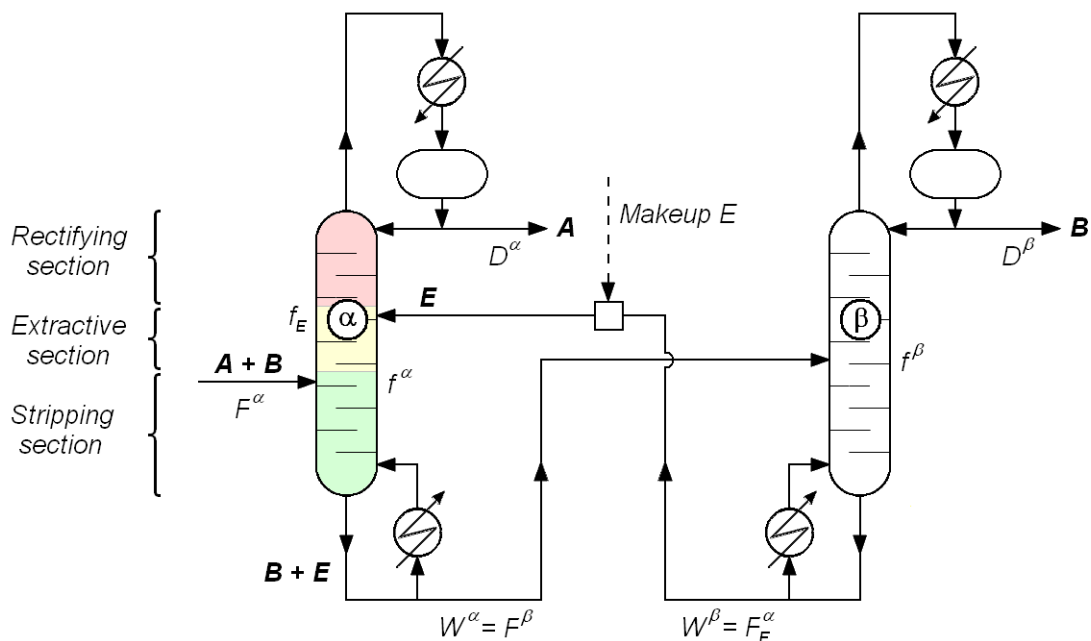
Fig. 1.3. Double-column system for continuous extractive distillation

The binary mixture $A - B$ arrives at the extractive column (Column α). At a higher tray (f_E) of this column regenerated solvent (E) is fed, which brakes the azeotrope. Above this tray, in the rectifying section the top product A is purified from E. The separation of A and B are performed in the presence of E of significant quantity in the extractive middle section and in the stripping lower section (f^α and the trays under that). The crossing of the azeotropic ratio happens in the extractive (or absorption) section. In the stripping section the liquid phase (bottom product) is purified from A. In the traditional Column β B is produced and E is regenerated simultaneously.

Stichlmair and Fair (1998) consider the extractive distillation as a hybrid process: for the separation of minimum boiling point azeotropes a combination of absorption and distillation, and for the separation of maximum boiling point azeotropes a combination of desorption and distillation, respectively.

Before the extractive column usually there is a preconcentrator column, whose product's composition is near to the azeotropic one. It operates without solvent. The advantage of the application of this column is that in the extractive column a smaller quantity of more concentrated mixture is processed, therefore the quantity of the solvent circulating in the system can be reduced. However the application of a third column also results in several drawbacks (e.g. higher investment cost, larger space requirement).

1.2.4. Continuous heteroazeotropic distillation

If the components of a mixture form a *heteroazeotrope,* or by the addition of an entrainer (E) a heteroazeotrope can be formed, it is possible to get through the azeotropic composition by decantation.

1.2.4.1. Processing of binary heteroazeotropic mixtures

If the feed is homogeneous, the system shown in *Fig. 1.4* is applied. (In this case the A-content of the feed is higher than in the A-rich equilibrium phase.) Column α produces A as bottoms and its top vapour has nearly azeotropic composition. After condensation it is led into a decanter where it splits into two liquid phases: the A-rich phase is fed back into Column α and the B-rich phase is the feed of Column β. It produces B as bottoms and its nearly azeotropic top product is also led into the decanter.

If the *A*-content of the feed is lower than in the equilibrium *B*-rich phase, the same configuration can be used. The only difference is that the feed arrives at Column β (producing *B*).

If the feed is heterogeneous, then it is fed into the decanter (*Fig. 1.5*, Fonyo and Fabry, 1998) and the columns are operated as strippers (Doherty and Malone, 2001).
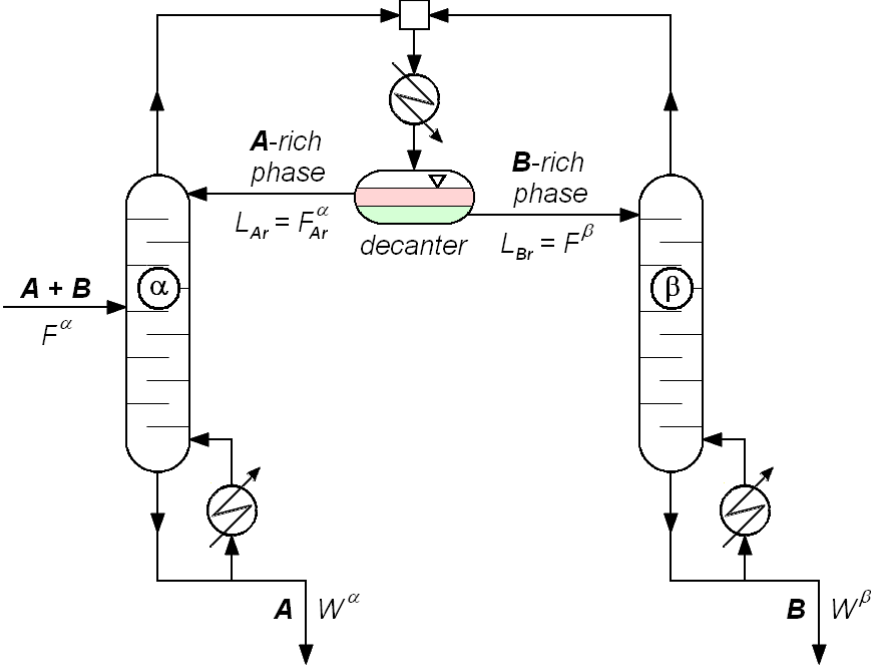
Fig. 1.4. Double-column system for continuous heteroazeotropic distillation (homogeneous feed)
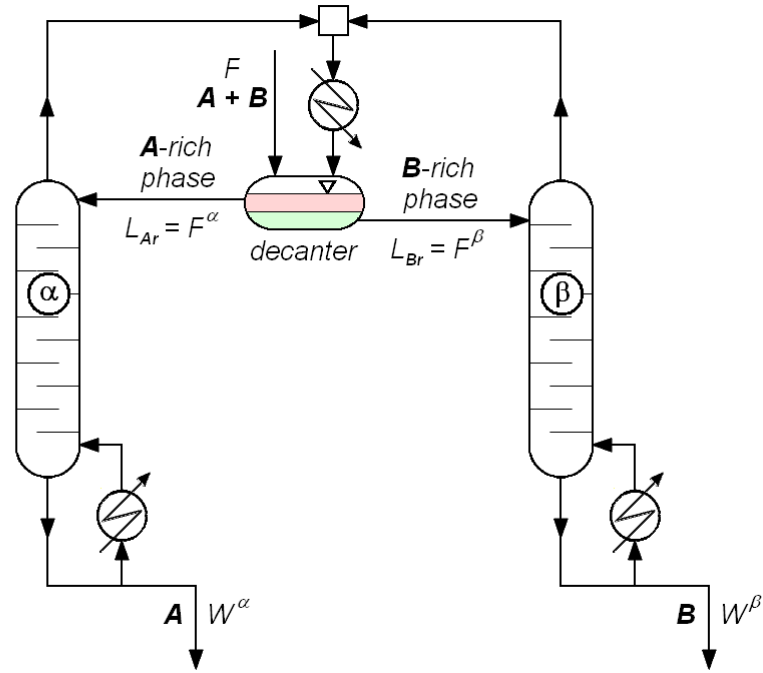
Fig. 1.5. Double-column system for continuous heteroazeotropic distillation
(heterogeneous feed)

1.2.4.2. Processing of binary homoazeotropic mixtures

The continuous heteroazeotropic distillation was realised first by Kubierschky (1915) who processed a homoazeotropic feed: he prepared pure ethanol from the mixture ethanol (A) – water (B) using benzene (E) as entrainer (Doherty and Malone, 2001). A three- and a two-column system were developed:

The **Three-Column System** (*Fig. 1.6*) consists of a preconcentrator column, an azeotropic one and an entrainer recovery column. This system is fed (F^0) in the *Preconcentrator column* (0), whose top product (D^0) has nearly binary azeotropic composition. Component B eliminated leaves as bottoms (W^0). D^0 is the feed (F^α) of the *Azeotropic column* (α). It produces top vapour of nearly ternary azeotropic composition, which is led into a decanter after condensation. The A-rich phase of the decanter holdup is refluxed (L^α), the E-rich one (D^α) is fed (F^β) into the *Entrainer recovery column* (β). A part of the E-rich phase is also refluxed if necessary. The distillate of Column β is fed back to Column α ($D^\beta = F_E^\alpha$), thus the E is recycled. B is produced as bottoms (W^β).
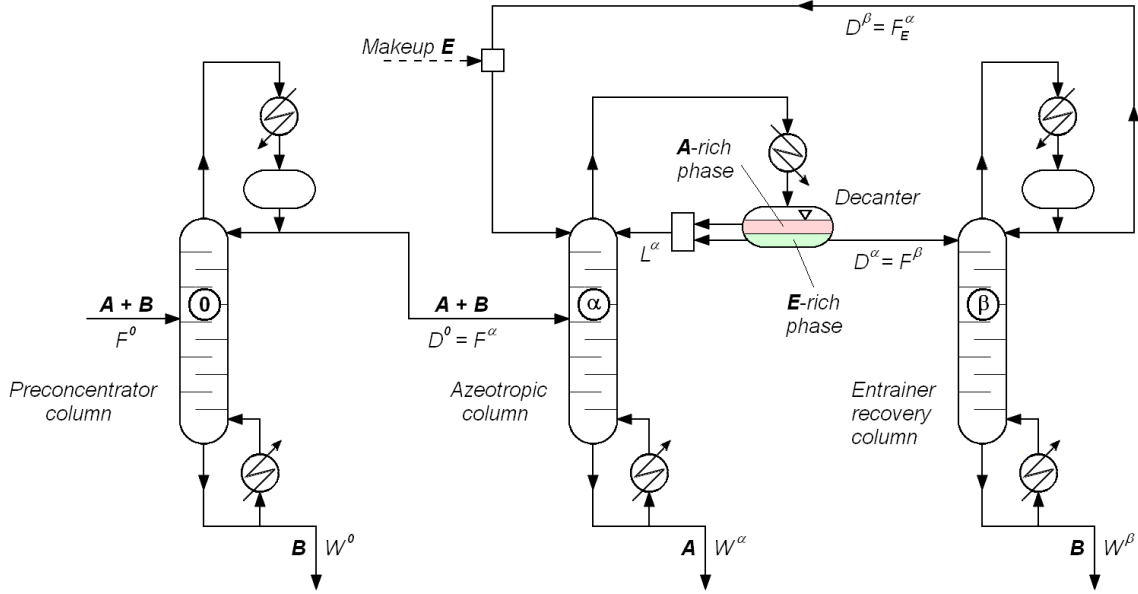
Fig. 1.6. Kubierschky Three-Column System for continuous heteroazeotropic distillation
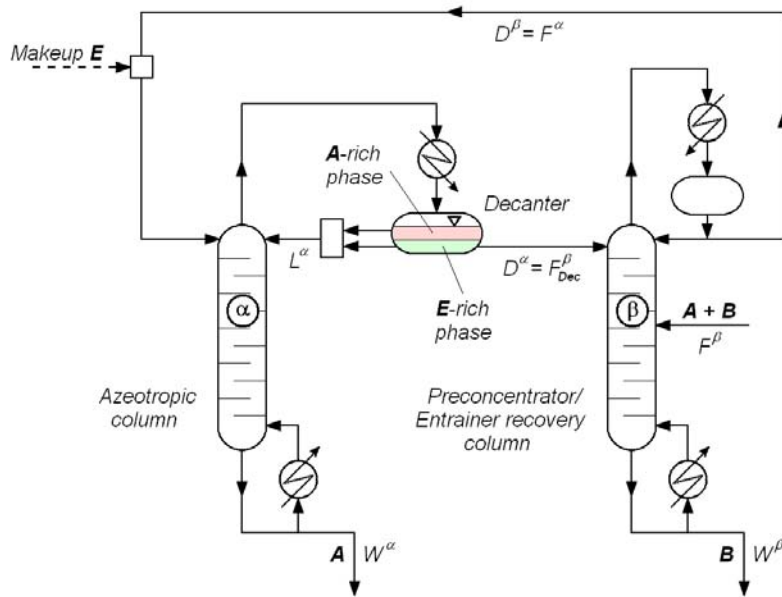
Fig. 1.7. Kubierschky Two-Column System for continuous heteroazeotropic distillation

In the **Two-Column System** (*Fig. 1.7*) one column serves as *Preconcentrator and Entrainer recovery column* (β). The stream to be processed is fed into this column (F^β). Its bottom product (W^β) is B and its top product, which is more concentrated in A than the feed is led into the *Azeotropic column* (α), whose only feed is this stream ($D^\beta = F^\alpha$). The bottoms of this column (W^α) is Product A. The nearly ternary azeotropic top vapour is condensed and led into a decanter. The A-rich phase of the decanter holdup is refluxed (L^α) and also a part of the *E-*

rich one if necessary. The E-rich phase ($D^\alpha = F_{DEC}^\beta$) is fed into Column β in order to recover E and produce B.

1.2.5. Homogeneous batch rectification (without separating agent)

In the pharmaceutical and fine chemical industries the quantity of the products is often low and they are changed frequently, therefore batch processes are widely applied (Mujtaba, 2004). It means that the quantities of the mixtures to be separated are often low, their compositions and the products desired vary frequently. Therefore it is worth to apply the batch rectification instead of the continuous distillation.

In this case the total quantity of the mixture (charge) is fed into the reboiler before the start and there is no liquid feed and withdrawal during the operation of the column. In this column there is no stripping section, only rectificating one (*Fig. 1.8*). The continuous column consists of two sections: above the feed location there is a rectificating section, under that there is a stripping one, respectively.

In a batch process the parameters (temperature, compositions) vary during the operation.

A further advantage of the batch processes is that more than two components can be produced (without side withdrawal) in a single equipment because the products of different compositions can be separated in time. Nevertheless, it is a drawback of the batch distillation that the volume of the reboiler must be larger and the control of the process is more difficult than for the continuous distillation.
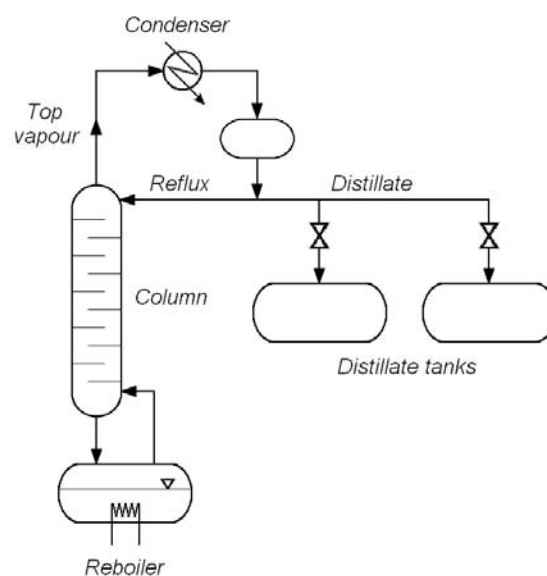
Fig. 1.8. Batch rectifier

1.2.5.1. Operational policies for the batch distillation *(presented for binary ideal mixture)*

I. Operation under constant reflux ratio (R = constant)

This is the simplest, most widespread operational policy. During the process the distillate becomes richer and richer in the more volatile component therefore its concentration in the reboiler decreases. This operation policy results in the decreasing of x_D with time.

II. Operation under constant distillate composition (x_D = constant)

The concentration of the more volatile component can be held at a constant value during the process by the gradual increase of the reflux ratio. This operational policy is called also *variable reflux mode* (Kim and Diwekar, 2001). In the last section of the process the reflux ratio must be extremely increased in order to ensure constant x_D, which reduces the economy of this operational policy.

III. Operation under optimal reflux ratio

This is a compromise between the above two operational policies. The reflux ratio remains between the reflux ratios of the two other policies. Neither R nor x_D remain constant with time. This policy is more economical than the two other ones. The determination of the optimal $R(t)$ is a complicated task, which can be solved on the basis of the *optimal control theory*.

IV. Cyclic operation

In this operational policy (Perry and Green, 1984) R alternates: a period of $R = \infty$ (until reaching the equilibrium state) is followed by another one of $R = 0$ (product withdrawal).

1.2.5.2. Unconventional column configurations for batch distillation

The batch distillation can be performed in unconventional column configurations, as well. The operation of these configurations was studied extensively but until now mainly by simulation.

Their operation is presented for the separation of ternary and quaternary mixtures. The sequence of the components by decreasing volatility is *A, B, C, D*. Kim and Diwekar (2001) distinguished the following configurations (*Fig. 1.9*):

I. Batch stripper,

II. Middle vessel column,

III. Multivessel column.

For each configuration at the bottom of the equipment heat is furnished, and heat is withdrawn at the top.
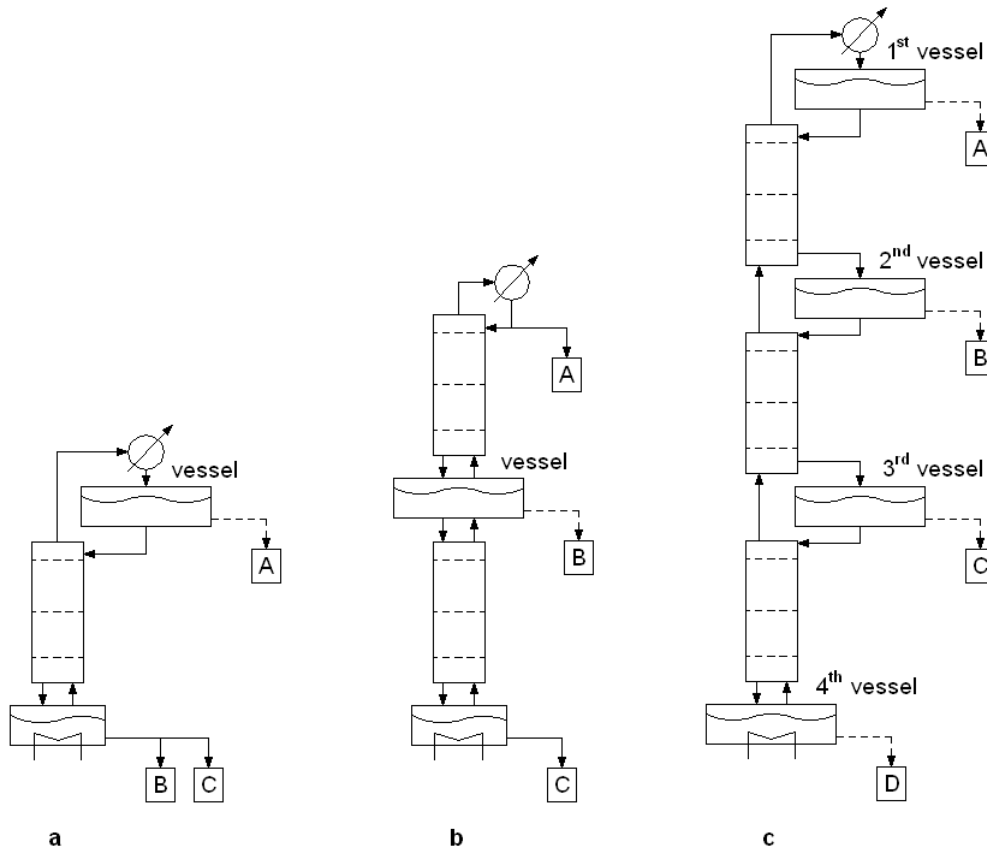
Fig. 1.9. Unconventional batch column configurations
a. batch stripper, b. middle vessel column, c. multivessel column

I. Batch stripper

In the **batch stripper** (*Fig. 1.9a*) the liquid vessel ensuring the feeding to the top tray of the column is located above the column. Therefore this configuration can be considered as a top vessel column (Lang, 2005). The charge is filled and the condensate is led into this top vessel. The product is withdrawn from the partial reboiler or from the bottom of the column in the case of total reboiler. Therefore first the heaviest component *C* then *B* can be produced. At the end of the process the lightest component *A* is enriched in the top vessel. Since in the product stream the heavier components are enriched, in the batch stripper the temperatures decrease with time contrary to the batch rectifier. The conception of the batch stripper is already presented in the classic book of Robinson and Gilliland (1950). Because of the inverted behaviour of the batch stripper compared with that of the batch rectifier, it is also called

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inverted batch column (e.g. Sorensen and Skogestad, 1996). The most important operational parameter of the batch stripping is the reboil ratio (equivalent to the reflux ratio).

II. Middle vessel column

The **middle vessel column** (Bortolini and Guarise, 1970; Hasebe et al., 1992, Davidyan et al., 1994) is the combination of the batch rectifier and batch stripper. The charge is filled into the vessel located between the two column sections (*Fig. 1.9b*). From the vessel the liquid of continuously varying composition is led to the top tray of the lower (stripping) column section. The liquid leaving the lowest tray of the upper (rectifying) column section and the vapour leaving the lower column section are led into the vessel. The vapour leaving the middle vessel arrives at the lowest tray of the upper column section. Hence the middle vessel can be considered as a tray of great, variable holdup. (In another variant the top vapour of the lower section can be led through a bypass directly to the bottom of the upper column section.) Product withdrawals are continuous at the top (*A*) and also at the bottom (*C*). At the end of the process in the middle vessel *B* is obtained.

III. Multivessel column

In the **multivessel column** the charge is divided between the vessels (*Fig. 1.9c*). The column is operated under total reflux, without product withdrawal. Until the end of the process each component is enriched in one of the vessels depending on the volatility order: the lightest component in the top vessel, the heaviest one in the lowest vessel, respectively. This configuration can be also operated with constant and varying holdup (Hasebe et al., 1997).

It must be noted that these promising unconventional column configurations are not widespread yet in the practice. Until now experimental results were published only in few cases (e.g. for the middle vessel column Barolo et al., 1998; Warter et al., 2004; for the multivessel column Wittgens and Skogestad, 2000).

Before the industrial application of these configurations several operational and control issues must be solved. Even the batch stripper seeming to be simple can be operated in a much more complicated way than the batch rectifier (Santoro, 1999). For the safe operation of a rectifier it is sufficient to ensure the stabilities of the reboiler heat duty and reflux ratio. There is no need for any control because the setting of the reboiler heat duty determines unambiguously the material (vapour) flow rate entering the column. However, for the batch stripper the inlet

stream and the heat duty must be set separately. Even if the reboil ratio is constant (which is the simpliest operational mode), the reboiler heat duty must be fit to the inlet material flow rate. If the heat duty is too low, the liquid holdup of the column can increase very high. In the case of too high heat duty the heating surface can dry out. The same problem can also occur in the lower section of the middle vessel column. For the solution of this problem Phimister and Seider (2000a) suggested liquid level control at the bottom of the column. However, this needs considerable liquid holdup there, which is disadvantageous from the point of view of the separation. On the other hand, the safe heating of a column cannot be easily realised in the case of low liquid holdup. By the multivessel column the problem of the holdup occurs increased because of the lack of the continuous product withdrawal.

1.2.6. Special batch distillation methods

The azeotropic mixtures can be separated into their pure components only by applying a special distillation method, such as pressure swing, extractive or heteroazeotropic distillation.

1.2.6.1. Batch pressure swing distillation

If the azeotropic composition of a *homoazeotropic mixture* is pressure sensitive, it can be separated without the addition of a separating agent by *pressure swing distillation*. The separation of the pressure sensitive minimum boiling azeotrope acetonitrile – water with semicontinuous and batch pressure swing distillation was investigated by simulation by Phimister and Seider (2000b) and pilot plant experiments by Repke et al. (2007). Two new double-column configurations (double-column batch rectifier and double-column batch stripper) were suggested by Modla and Lang (2008) by modifying the middle vessel column. Both systems were operated in open mode (with continuous withdrawal of products (distillate/bottoms)). Two versions of closed double-column systems for batch pressure swing distillation of binary homoazeotropic mixtures were investigated by Modla (2010).

1.2.6.2. Batch extractive distillation

The *batch extractive distillation* (BED) with the application of a heavy solvent in a batch rectifier was studied among others by Lang et al. (1994), Lelkes et al. (1998), and in non-conventional configurations (mainly in middle vessel column) among others by Safrit et al. (1995), Warter and Stichlmair (1999), Cui et al. (2002), Low and Sorensen (2002), Warter et al. (2004), and Steger et al. (2006). Steger et al. (2003) studied the feasibility of the BED of

minimum and maximum binary homoazeotropes in rectifying column with middle boiling entrainer. Steger et al. (2004) suggested a new configuration for the BED of maximum boiling point azeotropes. Steger et al. (2005) studied the BED in rectifier for minimum and maximum boiling point azeotropes by using heavy, light and intermediate entrainers.

Lang et al. (2006) suggested a new operational policy for the BED on the basis of industrial experiences obtained for the batch rectifier. Kotai et al. (2007) compared the BED with the hybrid process (absorption + distillation) suggested by Duessel and Stichlmair (1995). Acosta-Esquijarosa et al. (2006) studied experimentally and by simulation the separation of the mixture acetonitrile – water by a process which combines extraction and batch distillation consecutively: after the extraction done by butyl acetate the solvent-rich phase is distilled.

Rodriguez-Donis et al. (2001) described novel methods for heterogeneous BED to break azeotropes using an entrainer that is partially miscible with one of the components of the binary feed. The heterogeneous BED was investigated also by Van Kaam et al. (2008) for the system chloroform – methanol – water.

In the book of Luyben and Chien (2010), a whole chapter deals with the batch distillation of azeotropes. For the batch extractive distillation they studied the separation of two mixtures: acetone – methanol + water (by constant reflux policy), and isopropanol – water + dimethyl sulfoxide. For the latter mixture where the boiling point of the entrainer is much higher than that of the two other components varying reflux ratio and entrainer feed rate policies were also investigated.

1.2.6.3. Batch heteroazeotropic distillation

The *Batch Heteroazeotropic Distillation* (BHD) is an old method, widespread in the industry. Young (1902) was the first who applied the BHD successfully: he prepared pure ethanol from the mixture ethanol – water using benzene as entrainer.

To our best knowledge, the BHD has been performed in the industry only in (one-column) Batch Rectifiers (BR) equipped with a decanter (in open operation mode, with continuous distillate withdrawal).

A new general method for the calculation of the residue curves and for the determination of distillation regions of the BHD was suggested by Lang and Modla (2006), who extended the method of Pham and Doherty (1990). By this new method, besides the VLLE, the operational parameters, such as withdrawal of the *E*-lean or the *E*-rich phase or any combination of the two phases as distillate, are also taken into consideration.

In the BHD the separation methods of the hybrid process, the distillation and the liquid-liquid phase split are applied simultaneously. This operation mode is called Mode II by Skouras et al. (2005a,b). By Mode I the two separation methods are done sequentially. For Mode II there are two separation strategies as presented by Koehler et al. (1995) and Skouras et al. (2005a,b). By Strategy A (in the first dehydration step) the *E*-rich phase is totally, and by Strategy B only partially refluxed, respectively. Obviously for Strategy B more entrainer is needed since a considerable part of it is also withdrawn as distillate. Therefore it provides a competitive alternative to Strategy A only in the cases where the original ($A - B - E$ ternary) mixture already contains *E* in sufficient quantity. Lang and Modla (2006) suggested distinguishing two versions for both strategies of Mode II: (1) the *E*-lean phase is not refluxed and (2) where this phase is refluxed partially (in order to increase the reflux ratio, if necessary). The above operation modes and strategies are presented also by Luyben and Chien (2010). They studied the dehydration of acetic acid via BHD by using isobutyl acetate and vinyl acetate as entrainer. They also suggested overall control strategy for this process. They investigated the separation also in multivessel column but they did not recommend it because of its need for additional process instrumentation and process equipment.

The BR was investigated with variable decanter holdup by Rodriguez-Donis et al. (2002) and with continuous entrainer feeding by Modla et al. (2001, 2003) and Rodriguez-Donis et al. (2003), respectively. Skouras et al. (2005a,b) studied extensively the closed operation mode for the BR and also for multivessel columns. Rodriguez-Donis et al. (2005) studied the separation of the mixture n-hexane − ethyl acetate by using BHD with four different entrainers.

Skouras (2004) studied the separation of the mixture ethyl acetate − water − acetic acid in three unconventional BHD configurations (*Fig. 1.10*). Ethyl acetate and water form a heteroazeotrope but the other two pairs of components do not. The boiling point of the heteroazeotrope is lower than those of other components, therefore first vapour of this composition leaves.

Way of the separation:

For *multivessel column (a) with and (b) without vapour bypass* the separation is performed in the same manner.

I. In the startup step the heteroazeotrope is accumulated in the top vessel.

II. In the next step the top vessel is operated as a decanter: the organic phase refluxed into the column. The aqueous phase is accumulated in the top vessel, the ethyl acetate in the middle one and the acetic acid in the bottom vessel (reboiler), respectively.

The operation of the *two-vessel column (c)* (Lang, 2005) can be divided into four steps:

I. First in a startup period the heteroazeotrope accumulates in the top vessel.

II. Then the top vessel is operated as a decanter: the organic phase refluxed into the column and the aqueous phase is gradually accumulated in the top vessel.

III. Then the aqueous phase is withdrawn.

IV. The final step is practically a binary separation: ethyl acetate is accumulated in the top vessel and acetic acid in the bottom one, respectively.
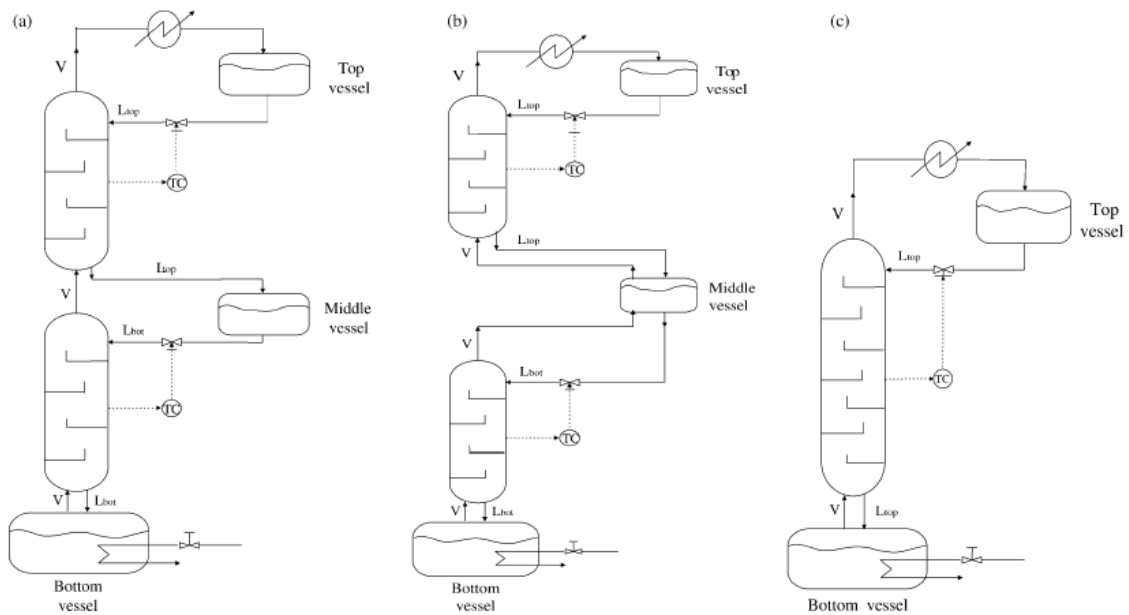
Fig. 1.10. Unconventional column configurations for BHD by Skouras (2004)

a. multivessel column with vapour bypass

b. multivessel column without vapour bypass

c. two-vessel column

Pommier et al. (2008) developed a specific software architecture based on the BatchColumn® simulator and on both Sequential Quadratic Programming and Genetic Algorithm for the optimisation of sequential batch columns and BHD in open mode. Huang and Chien (2008) studied the dehydration of acetic acid by BHD using different entrainers (isobutyl acetate, vinyl acetate, ethyl acetate) and configurations (BR and multivessel column).

CHAPTER 2

THEORETICAL STUDY
OF THE NEW CONFIGURATIONS

2. Theoretical study of the new configurations

A new Double-Column System for batch heteroazeotropic distillation then its generalised version are studied. For each configuration first its feasibility is investigated then its operation is modelled by rigorous simulation. On the basis of the results of both methods the configurations are compared with each other and with the Batch Rectifier equipped with a decanter.

2.1. Feasibility and computational study of the new Double-Column System

A new Double-Column System for batch heteroazeotropic distillation is studied and compared with the Batch Rectifier equipped with a decanter. First feasibility studies then rigorous simulations are done for both configurations, respectively.

2.1.1. Introduction

The goals of the work are

- to suggest a new Double-Column System (DCS) for the batch heteroazeotropic distillation,
- to investigate this configuration first by feasibility studies then by dynamic simulation based on a more detailed model,
- to compare its performance with that of the traditional BR.

For both configurations we investigated the simultaneous realisation of distillation and liquid-liquid phase split (Mode II). Furthermore we studied only the cases where one-phase streams are fed to the top of the column(s) from the decanter.

We compared the optimum operation of the two configurations. The total duration of the process was minimised (min(Δt)) by systematic simulation studies. Since the (total) heat duty was kept constant this means practically minimising the operation costs (min(C_{op})).

The calculations and the simulations were performed for a binary (1-butanol (*A*) – water (*B*)) and for a ternary heteroazeotropic mixture (isopropanol (*A*) – water (*B*) + benzene as entrainer (*E*)). For the simulation we used the dynamic simulator of CHEMCAD 5.6 (module CC-DCOLUMN, Chemstations, 2007).

2.1.2. The mixtures to be separated

2.1.2.1. Binary mixture 1-butanol – water

The vapour-liquid equilibrium curve (*Fig. 2.1*) and the boiling and dew curves (*Fig. 2.2*) show that the components form a (minimum boiling point) heteroazeotrope. The *A*-rich (organic phase) contains *B* in considerable quantity, however *A* is only slightly soluble in the *B*-rich (aqueous) phase. The activity coefficients are computed by using the NRTL model (Appendix 1).

The composition of the heteroazeotrope and those of the *A*-rich and *B*-rich phases are, respectively:

$$\vec{x}_{AZ} = [0.2562, 0.7438], \qquad \vec{x}_{AZ}^{Ar} = [0.568, 0.432], \qquad \vec{x}_{AZ}^{Br} = [0.012, 0.988]$$
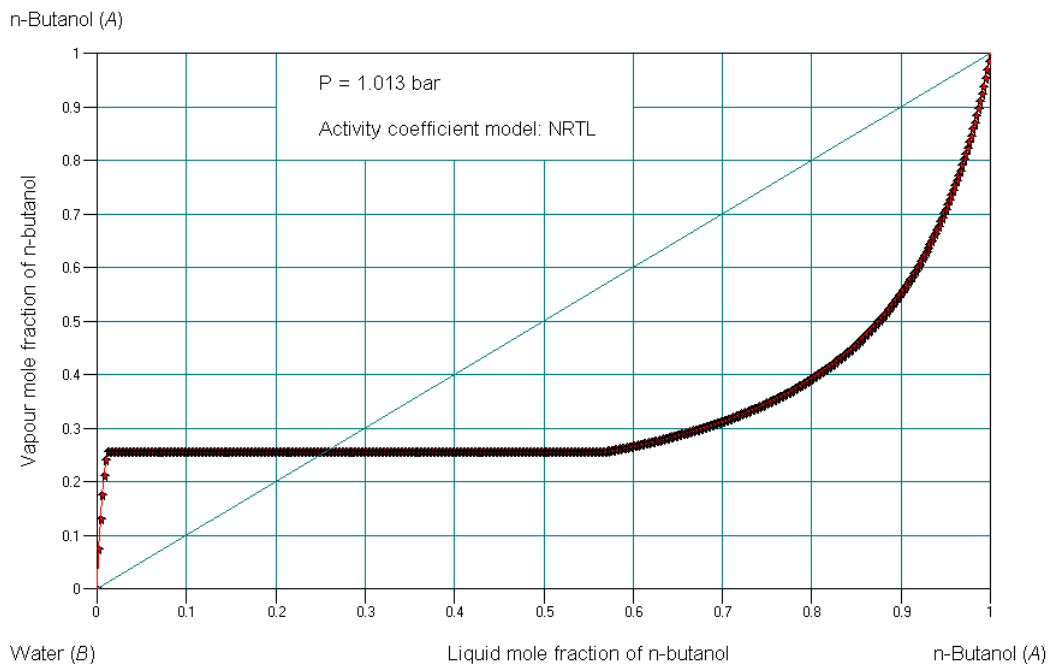
Fig. 2.1. Computed vapour-liquid equilibrium curve of the mixture 1-butanol – water
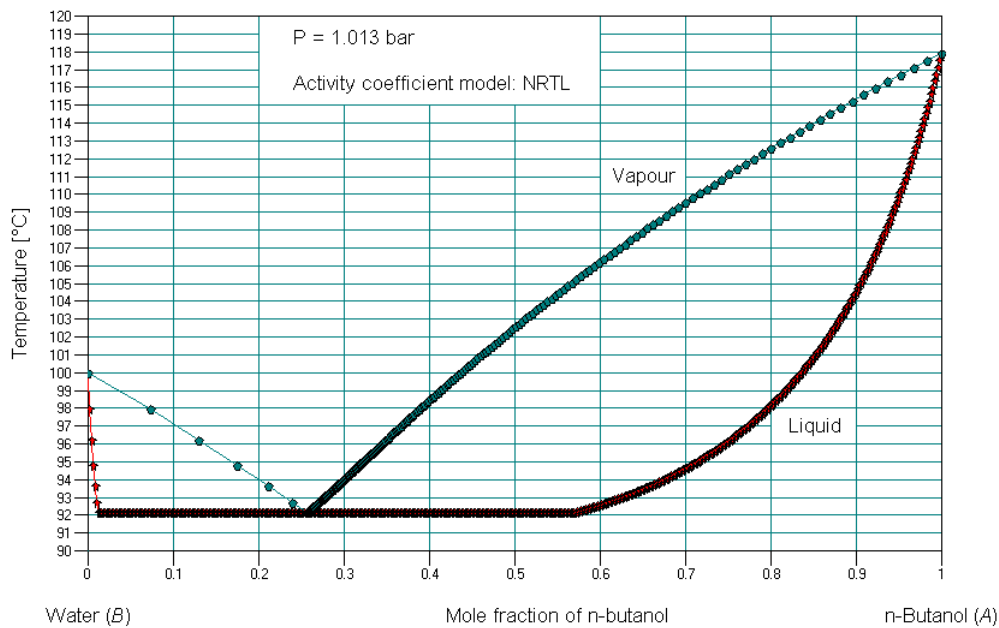
Fig. 2.2. Computed boiling and dew point curves of the mixture 1-butanol – water

2.1.2.2. Ternary mixture isopropanol – water – benzene

The vapour-liquid equilibrium curve (*Fig. 2.3*) and the boiling and dew curves (*Fig. 2.4*) show that the isopropanol and the water form a minimum boiling homoazeotrope. Therefore it is not possible to cross the azeotropic composition by ordinary distillation. In this case a separating agent (entrainer) must be added to the mixture. The entrainer chosen is benzene. The ternary mixture forms a ternary heteroazeotrope, which splits into an organic (*E*-rich) and an aqueous (*B*-rich) phase (*Fig. 2.5*). In the latter one the *B*/*A* ratio is much higher than in the $A - B$ azeotrope. The activity coefficients are computed by using the UNIQUAC model (Appendix 1).
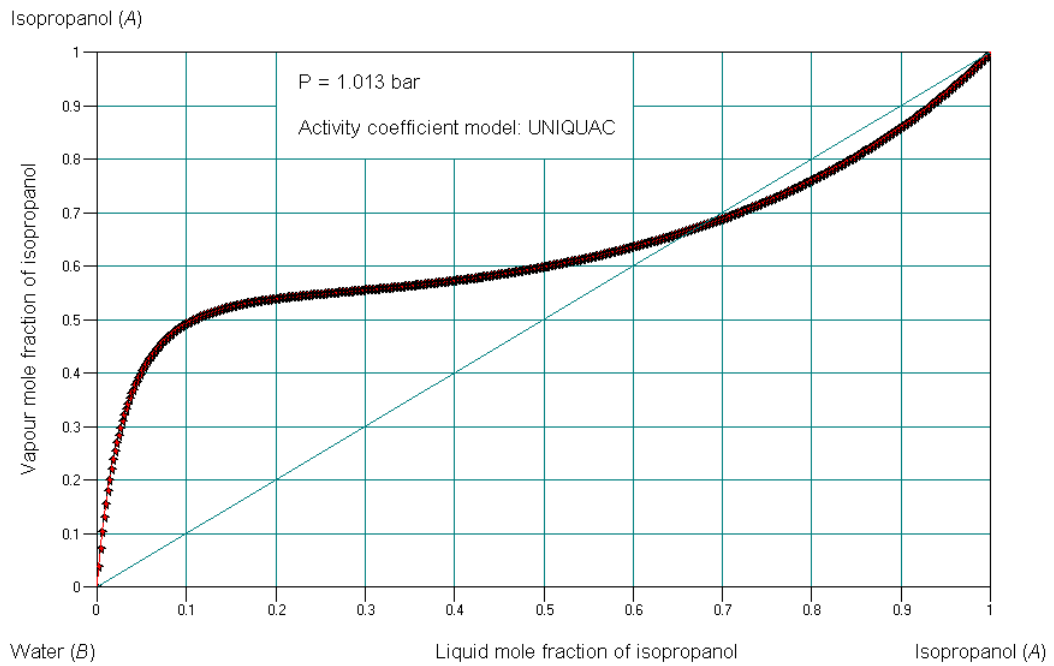
Fig. 2.3. Vapour-liquid equilibrium curve of the mixture isopropanol – water
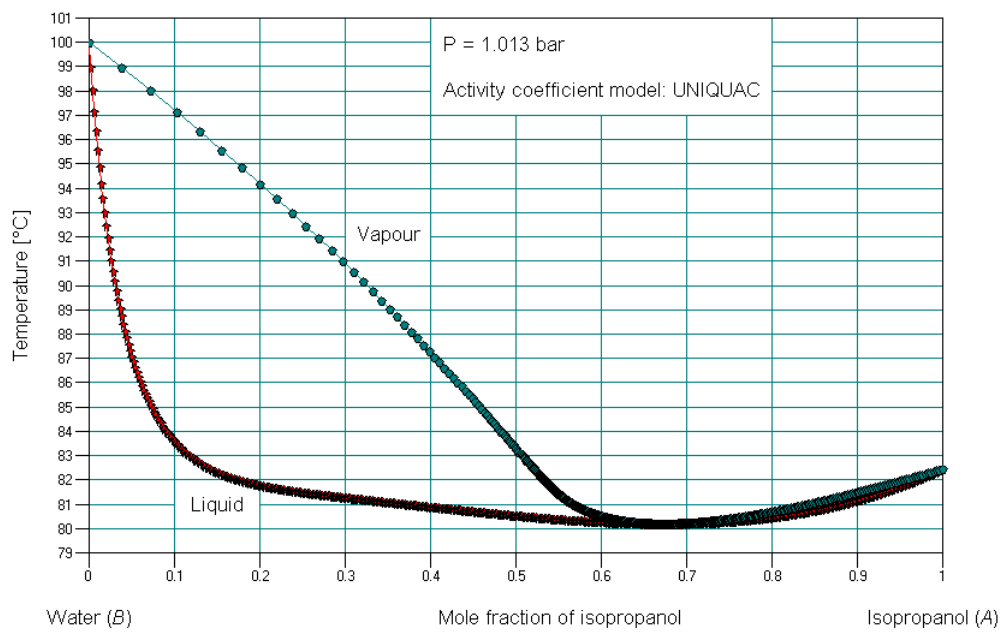
Fig. 2.4. Boiling and dew curves of the mixture isopropanol – water
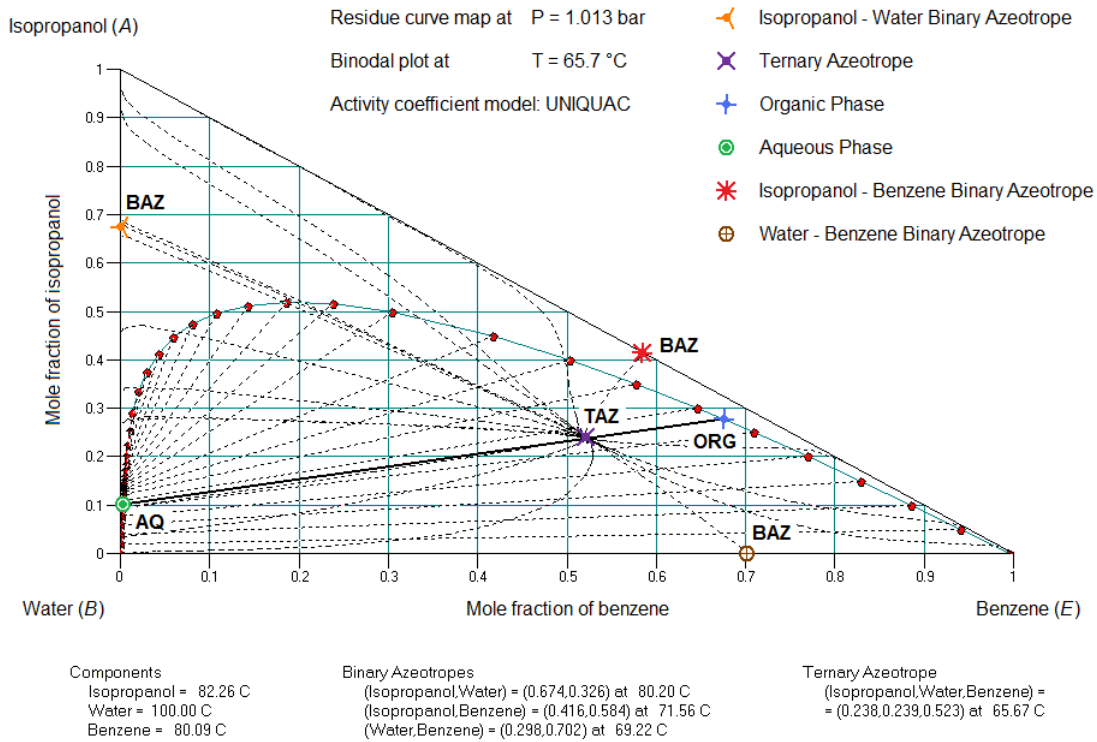
Fig. 2.5. Residue curve map and binodal plot of the mixture isopropanol – water + benzene

2.1.3. The column configurations studied

First the operation of the Batch Rectifier (BR) then that of the new Double-Column System (DCS) will be presented. For the sake of simplicity we assume maximal separation for both configurations, that is, in each column the top vapour has always azeotropic composition.

2.1.3.1. Batch Rectifier

First the separation of the binary then that of the ternary mixture is presented.

2.1.3.1.1. Separation of the binary mixture

If the charge is homogeneous, the whole charge is filled into the reboiler. If the feed (charge) composition $x_{ch,A}$ is in the heterogeneous region ($x_{AZ,A}^{Br} < x_{ch,A} < x_{AZ,A}^{Ar}$), it is worth to separate it by decantation into an A-rich ($x_{AZ,A}^{Ar}$) and a B-rich ($x_{AZ,A}^{Br}$) phase before the start of the distillation.

One production cycle consists of two distillation steps. We select the phase to be distilled in the first step so that the overall quantity of the two products in the first cycle be maximal. (In this case the quantity of the byproduct is minimal.) By assuming maximal separation from the

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material balances it can be derived (for pure products) that we have to distil the *A*-rich phase first if

$$x_{ch,A} > \frac{x_{AZ,A}^{Br}}{1-(x_{AZ,A}^{Ar} - x_{AZ,A}^{Br})}$$ (2.1)

The detailed derivation of the above inequality can be found in Appendix 2.

The steps of a production cycle are as follows:

Step 1. Production of A (Fig. 2.6a): The *A*-rich phase ($x_{AZ,A}^{Ar}$) of the heteroazeotrope ($x_{AZ,A}$) is refluxed and the *B*-rich one ($x_{AZ,A}^{Br}$) is withdrawn as distillate. The bottom residue is product *A*.

Step 2. Production of B (Fig. 2.6b): The *B*-rich phase(s) is (are) distilled. The *B*-rich phase of the azeotrope is refluxed and the *A*-rich one is withdrawn as distillate. The bottom residue is product *B*.

We can state that the main disadvantages of the BR are:
 - in one step only one pure component can be produced (in the residue),
 - the recovery is limited since the other component in the distillate is always saturated with
   this component.
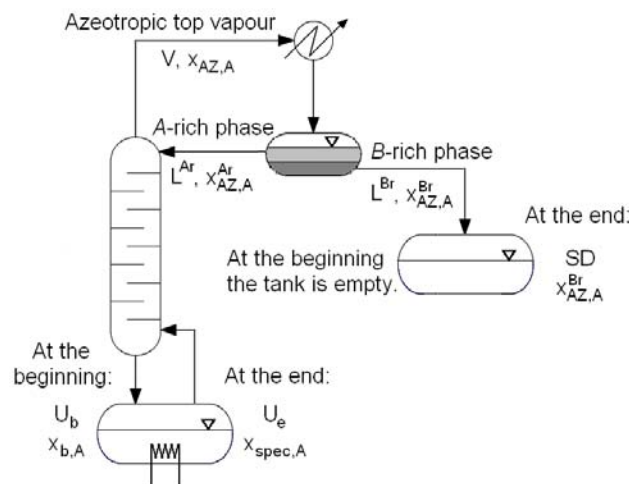
Fig. 2.6a. Batch Rectifier producing A from a binary mixture in Step 1
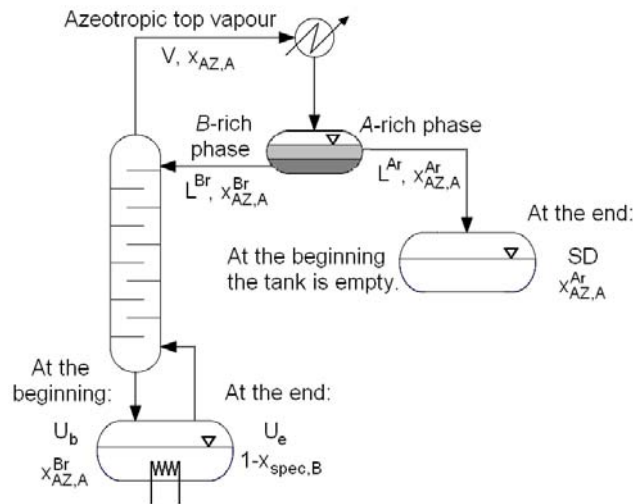
Fig. 2.6b. Batch Rectifier producing B from a binary mixture in Step 2

2.1.3.1.2. Separation of the ternary mixture

A homoazeotropic binary alcohol (*A*) − water (*B*) mixture is considered, which cannot be separated by ordinary rectification. Hence the addition of a third component (entrainer, *E*) is needed, usually in a small amount. *E* is partially miscible with *B* but totally miscible with *A*. The steps of a production cycle are as follows:

Step 0. Addition of *E* to the charge

Step 1. Production of A (Fig. 2.7a): The *E*-rich organic phase ($\overrightarrow{x}_{TAZ}^{Er}$) of the ternary azeotrope ($\overrightarrow{x}_{TAZ}$) is refluxed and the *B*-rich aqueous phase ($\overrightarrow{x}_{TAZ}^{Br}$) is withdrawn as distillate. The bottom residue is product *A*. The distillate is processed in Step 2.

Step 2. Removal of E (Fig. 2.7b): Removal of *E*: The *B*-rich phase of the azeotrope is refluxed and the *E*-rich phase is withdrawn as distillate. The bottom residue still contains some *A*.

Step 3. Purification of B from A (Fig. 2.7c): In this step a homogeneous mixture is processed, thus there is no need for a decanter. *A* is removed (from the bottom residue of Step 2) in the form of binary *A* − *B* homoazeotrope ($\overrightarrow{x}_{BAZ}$) in the distillate and the bottom residue is product *B*.
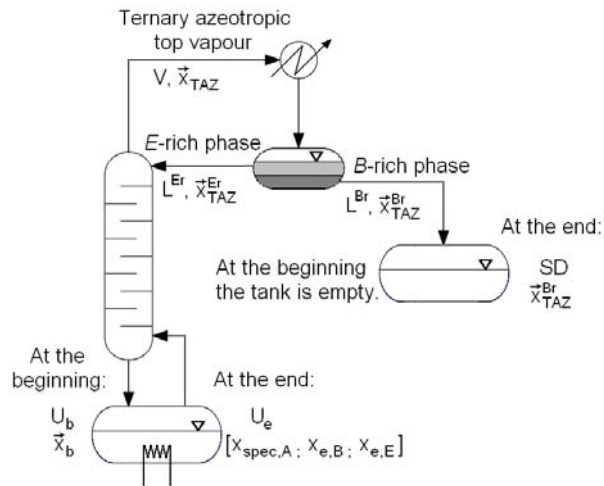
Fig. 2.7a. Batch Rectifier: production of A from mixture A–B+E in Step 1
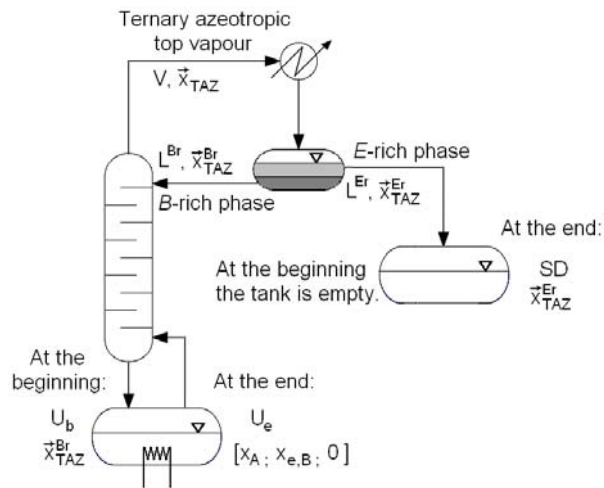
Fig. 2.7b. Batch Rectifier: removal of E in Step 2 (from the distillate of Step 1)
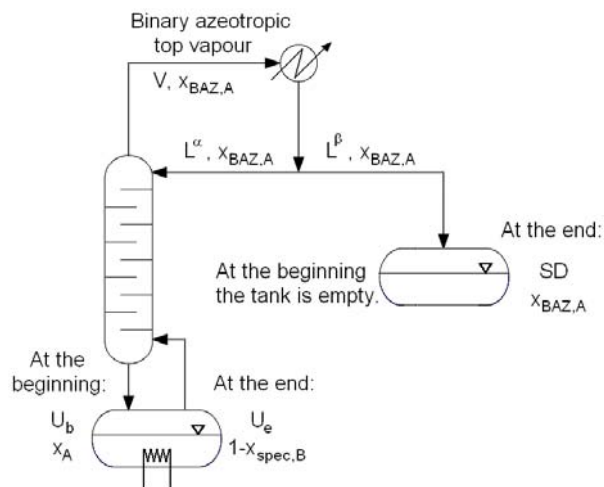
Fig. 2.7c. Batch Rectifier: production of B in Step 3 (from the residue of Step 2)

2.1.3.2. The new Double-Column System

The DCS is operated in closed mode (without continuous product withdrawal). The two columns are equipped with a single, common decanter. Two components are simultaneously produced as bottom residues.

2.1.3.2.1. Separation of the binary mixture (Fig. 2.8)

If the charge composition is in the heterogeneous region similarly to the BR it is worth to separate it by decantation. Contrary to the BR both phases are filled into the reboilers. The *A*-rich phase is filled in the reboiler of Column α (producing *A*) and a *B*-rich one to Reboiler β, respectively.

If the charge is homogeneous, mixtures of the same composition are loaded into the two reboilers. The top vapour of both columns is of azeotropic composition. The *A*-rich phase is sent to the top of Column α and the *B*-rich one is fed to the top of Column β. In one operation step we obtain product *A* of prescribed purity ($x_{spec,A}$) in Reboiler α and product *B* of prescribed purity ($x_{spec,B}$) in Reboiler β, respectively.
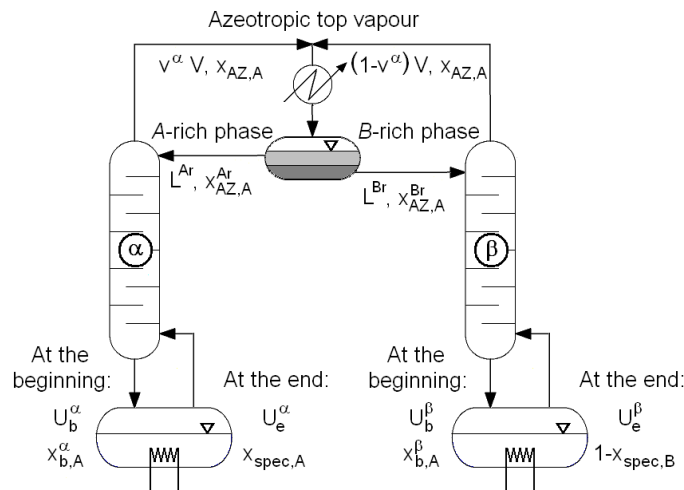
Fig. 2.8. Operation of the Double-Column System for the binary mixture

2.1.3.2.2. Separation of the ternary mixture (Fig. 2.9)

The homogeneous charge must be divided between the two reboilers. The entrainer, which is filled at the start only in the reboiler of Column α, circulates in the system. The top vapour of Column α is ternary azeotrope and that of Column β is binary azeotrope *A-B*. The *E*-rich phase is sent to the top of Column α and the *B*-rich one (containing negligible amount of *E*) is

fed to the top of Column β. It is unnecessary to fill E into Reboiler β because the B-rich phase of the decanter (mixture of the binary (A-B) and ternary azeotropes) contains more B than the binary azeotropic top vapour of Column β. That is B can be purified even without adding E.
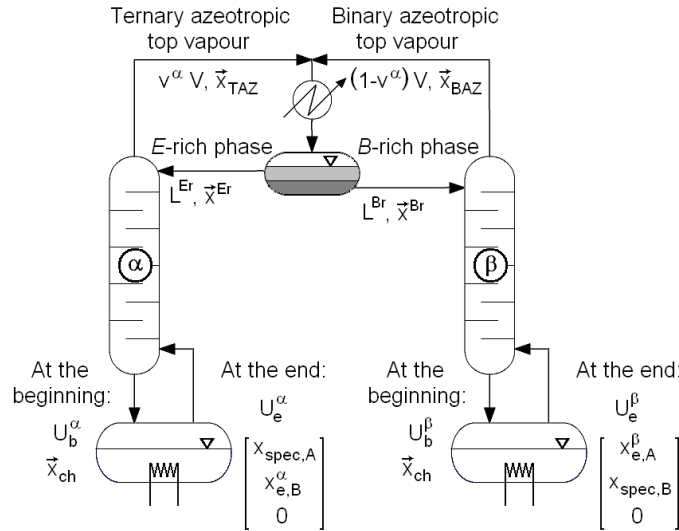
Fig. 2.9. Operation of the Double-Column System for the ternary mixture

2.1.4. Feasibility method

Our aim is to estimate the duration of the processes, the amount of the products and that of the byproducts. A simplified model was applied based on the following assumptions:
 - maximal separation (It means, that the molar compositions of the top vapour, distillate and reflux are constant.),
 - negligible hold-up on the trays and in the decanter,
 - constant molar overflow (It means, that all molar flow rates (distillate (SD), reflux (L), top vapour (V)) are constant.),
- one-phase liquid streams leave the decanter,
 - negligible duration of pumping between the operation steps (BR),
 - no entrainer loss (in the case of the ternary mixture).

The total (TMB) and component material (CMB) balance equations for one column and the decanter are analytically solved. For the DCS we assume that both products reach the prescribed purity at the same time, that is, the duration is minimal. The process time (τ) for both configurations and for the DCS the optimum division (v^{α}) of total molar vapour flow rate (V) between the two reboilers and that of the charge ($u^{\alpha} = U_b^{\alpha}/U_{ch}$) are calculated.

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2.1.4.1. Model equations for the Batch Rectifier

2.1.4.1.1. Separation of the binary mixture (Figs. 2.6a-b)

Integral material balances for the given step:

TMB:
$$U_b = U_e + SD \tag{2.11}$$

CMB:
$$U_b \cdot x_{b,i} = U_e \cdot x_{spec,i} + SD \cdot x_{e,i}^{SD} \tag{2.12}$$

      where i denotes the component produced in the given step,

      and SD is the molar quantity of the distillate.

Differential material balances for the column:

DTMB:
$$\frac{dU}{dt} = -V + L^{ir} \tag{2.13a}$$

Boundary conditions:
$$U(0) = U_b \tag{2.13b}$$

$$U(\tau) = U_e \tag{2.13c}$$

Hence
$$U_e = U_b + (-V + L^{ir}) \cdot \tau \tag{2.13}$$

where L^{ir} denotes the molar flow rate of the phase rich in component i leaving the decanter (the reflux).

DCMB:
$$\frac{d(U \cdot x_i)}{dt} = -V \cdot x_{AZ,i} + L^{ir} \cdot x_{AZ,i}^{ir} \tag{2.14a}$$

Boundary conditions:
$$(U \cdot x_i)(0) = U_b \cdot x_{b,i} \tag{2.14b}$$

$$(U \cdot x_i)(\tau) = U_e \cdot x_{spec,i} \tag{2.14c}$$

Hence
$$U_e \cdot x_{spec,i} = U_b \cdot x_{b,i} + (-V \cdot x_{AZ,i} + L^{ir} \cdot x_{AZ,i}^{ir}) \cdot \tau \tag{2.14}$$

Differential material balances for the decanter:

DTMB:
$$\frac{dU^{dec}}{dt} = V - L^{ir} - L^{jr} = 0 \tag{2.15}$$

DCMB:
$$\frac{d(U^{dec} \cdot x_i^{dec})}{dt} = V \cdot x_{AZ,i} - L^{ir} \cdot x_{AZ,i}^{ir} - L^{jr} \cdot x_{AZ,i}^{jr} = 0 \tag{2.16}$$

Known parameters:

- initial conditions: $U_b, x_{b,i}$

- purity specification (final condition): $x_{spec,i}$

- operating parameter: V

- phase equilibria conditions: $x_{AZ,i}, x^{ir}_{AZ,i}, x^{jr}_{AZ,i}$

Unknowns: $\qquad U_e, SD, x^{SD}_{e,i}, \tau, L^{ir}, L^{jr}$

Number of independent equations: 6 (2.11-16 without equations -a, -b and -c)

Number of unknowns: 6

Degree of freedom: 0

If we produce component A first, the known parameters have the following values:

Step 1. i = A, j = B; if the charge is homogeneous: $U_b = U_{ch}$, $x_{b,i} = x_{ch,A}$,

$\qquad\qquad$ if the charge is heterogeneous: $U_b = U^{Ar}_{AZ}$, $x_{b,i} = x^{Ar}_{AZ,A}$.

Step 2. i = B, j = A; if the charge is homogeneous: $U_b = SD$, $x_{b,i} = x^{Br}_{AZ,B}$,

$\qquad\qquad$ if the charge is heterogeneous: $U_b = SD + U^{Br}_{AZ}$, $x_{b,i} = x^{Br}_{AZ,B}$.

The solution of the set of Eqs. 2.11-16 is:

Duration of the step: $\quad \tau = \dfrac{(x^{ir}_{AZ,i} - x^{jr}_{AZ,i})(x_{e,i} - x_{b,i})}{(x^{ir}_{AZ,i} - x_{AZ,i})(x_{e,i} - x^{jr}_{AZ,i})} \cdot \dfrac{U_b}{V}$

Further results: $\qquad L^{ir} = \dfrac{x_{AZ,i} - x^{jr}_{AZ,i}}{x^{ir}_{AZ,i} - x^{jr}_{AZ,i}} \cdot V$, $\qquad L^{jr} = V - L^{ir}$,

$$U_e = \dfrac{x_{b,i} - x^{ir}_{AZ,i}}{x_{e,i} - x^{jr}_{AZ,i}} \cdot U_b, \qquad SD = U_{ch} - U_e, \qquad\qquad x^{SD}_{e,i} = x^{jr}_{AZ,i}$$

2.1.4.1.2. Separation of the ternary mixture

Step 1. *(Fig. 2.7a)*

It is supposed that product A does not contain E (it is contaminated only by B) and that the amount of E in the B-rich phase of the heteroazeotrope can be neglected.

Integral material balances:

TMB:
$$U_{ch} = U_e + SD \qquad (2.21)$$

CMB:
$$U_{ch} \cdot x_{ch,A} = U_e \cdot x_{spec,A} + SD \cdot x_{e,A}^{SD} \qquad (2.22)$$

Differential material balances for the column:

DTMB:
$$\frac{dU}{dt} = -V + L^{Er} \qquad (2.23a)$$

Boundary conditions:
$$U(0) = U_b \qquad (2.23b)$$

$$U(\tau) = U_e \qquad (2.23c)$$

Hence
$$U_e = U_{ch} + (-V + L^{Er}) \cdot \tau \qquad (2.23)$$

DCMB:
$$\frac{d(U \cdot x_A)}{dt} = -V \cdot x_{TAZ,A} + L^{Er} \cdot x_{TAZ,A}^{Er} \qquad (2.24a)$$

Boundary conditions:
$$(U \cdot x_A)(0) = U_{ch} \cdot x_{ch,A} \qquad (2.24b)$$

$$(U \cdot x_A)(\tau) = U_e \cdot x_{spec,A} \qquad (2.24c)$$

Hence
$$U_e \cdot x_{spec,A} = U_{ch} \cdot x_{ch,A} + (-V \cdot x_{TAZ,A} + L^{Er} \cdot x_{TAZ,A}^{Er}) \cdot \tau \qquad (2.24)$$

Differential material balances for the decanter:

DTMB:
$$\frac{dU^{dec}}{dt} = V - L^{Er} - L^{Br} = 0 \qquad (2.25)$$

DCMB:
$$\frac{d(U^{dec} \cdot x_A^{dec})}{dt} = V \cdot x_{TAZ,A} - L^{Er} \cdot x_{TAZ,A}^{Er} - L^{Br} \cdot x_{TAZ,A}^{Br} = 0 \qquad (2.26)$$

Known parameters:

- initial conditions: $U_{ch}, x_{ch,A}$

- purity specification (final condition): $x_{spec,A}$

- operating parameter: V

- phase equilibria conditions: $x_{TAZ,A}, x_{TAZ,A}^{Er}, x_{TAZ,A}^{Br}$

Unknowns: $U_e, SD, x_{e,A}^{SD}, \tau, L^{Er}, L^{Br}$

Number of independent equations: 6 (2.21-26 without equations -a, -b and -c)

Number of unknowns: 6

Degree of freedom: 0

The solution of the set of Eqs. 2.21-26 is:

Duration of the step:
$$\tau = \frac{(x_{TAZ,A}^{Er} - x_{TAZ,A}^{Br})(x_{spec,A} - x_{ch,A})}{(x_{TAZ,A}^{Er} - x_{TAZ,A})(x_{spec,A} - x_{TAZ,A}^{Br})} \cdot \frac{U_{ch}}{V}$$

Further results:
$$L^{Er} = \frac{x_{TAZ,A} - x_{TAZ,A}^{Br}}{x_{TAZ,A}^{Er} - x_{TAZ,A}^{Br}} \cdot V \ , \qquad L^{Br} = V - L^{Er} \ ,$$

$$U_e = \frac{x_{ch,A} - x_{TAZ,A}^{Er}}{x_{spec,A} - x_{TAZ,A}^{Br}} \cdot U_{ch} \ , \qquad SD = U_{ch} - U_e \ , \qquad x_{e,A}^{SD} = x_{AZ,A}^{Br}$$

Step 2. *(Fig. 2.7b)*

The top vapour has ternary azeotropic composition. At the end of the step only IPA-water binary mixture remains in the reboiler.

Integral material balances:

TMB: $$U_b = U_e + SD \qquad (2.31)$$

CMB: $$U_b \cdot x_{TAZ,E}^{Br} = SD \cdot x_{TAZ,E}^{Er} \qquad (2.32)$$

CMB: $$U_b \cdot x_{TAZ,A}^{Br} = U_e \cdot x_{e,A} + SD \cdot x_{TAZ,A}^{Er} \qquad (2.33)$$

Differential material balances for the column:

DTMB: $$\frac{dU}{dt} = -V + L^{Br} \qquad (2.34a)$$

Boundary conditions: $$U(0) = U_b \qquad (2.34b)$$

$$U(\tau) = U_e \qquad (2.34c)$$

Hence $$U_e = U_b + (-V + L^{Br}) \cdot \tau \qquad (2.34)$$

Differential material balances for the decanter:

DTMB: $$\frac{dU^{dec}}{dt} = V - L^{Er} - L^{Br} = 0 \qquad (2.35)$$

DCMB: $$\frac{d(U^{dec} \cdot x_A^{dec})}{dt} = V \cdot x_{TAZ,A} - L^{Er} \cdot x_{TAZ,A}^{Er} - L^{Br} \cdot x_{TAZ,A}^{Br} = 0 \qquad (2.36)$$

Known parameters:

- initial conditions: U_b

- operating parameter: V

- phase equilibria conditions: $\vec{x}_{TAZ}, \vec{x}_{TAZ}^{Er}, \vec{x}_{TAZ}^{Br}$

Unknowns: $\qquad U_e, SD, x_{e,A}, \tau, L^{Er}, L^{Br}$

Number of independent equations: 6 (2.31-36 without equations -a, -b and -c)

Number of unknowns: 6

Degree of freedom: 0

The solution of the set of Eqs. 2.31-36 is:

Duration of the step: $\qquad \tau = \dfrac{x_{TAZ,A}^{Er} - x_{TAZ,A}^{Br}}{x_{TAZ,A} - x_{TAZ,A}^{Br}} \cdot \dfrac{x_{TAZ,E}^{Br}}{x_{TAZ,E}^{Er}} \cdot \dfrac{U_b}{V}$

Further results: $\qquad L^{Er} = \dfrac{x_{TAZ,A} - x_{TAZ,A}^{Br}}{x_{TAZ,A}^{Er} - x_{TAZ,A}^{Br}} \cdot V , \qquad L^{Br} = V - L^{Er} ,$

$$U_e = \dfrac{x_{TAZ,E}^{Er} - x_{TAZ,E}^{Br}}{x_{TAZ,E}^{Er}} \cdot U_b , \qquad SD = U_e - U_b ,$$

$$x_{e,A} = \dfrac{x_{TAZ,E}^{Er} \cdot x_{TAZ,A}^{Br} - x_{TAZ,E}^{Br} \cdot x_{TAZ,A}^{Er}}{x_{TAZ,E}^{Er} - x_{TAZ,E}^{Br}}$$

Step 3. *(Fig. 2.7c)*

In this step only *A* and *B* are present, the top vapour is the homoazeotrope. There is no need for a decanter.

Integral material balances:

TMB: $\qquad\qquad\qquad\qquad U_b = U_e + SD \qquad\qquad\qquad (2.41)$

CMB: $\qquad\qquad\qquad U_b \cdot x_I = U_e \cdot (1 - x_{spec,2}) + SD \cdot x_{BAZ,A} \qquad (2.42)$

Differential material balances for the column:

DTMB: $\qquad\qquad\qquad \dfrac{dU}{dt} = -V + \dfrac{R}{1 + R} \cdot V \qquad (2.43a)$

Boundary conditions: $\qquad U(0) = U_b \qquad\qquad (2.43b)$

$$U(\tau) = U_e \qquad\qquad (2.43c)$$

Hence
$$U_e = U_b - \frac{1}{1+R} \cdot V \cdot \tau \qquad (2.43)$$

Known parameters:

- initial conditions: $U_b, x_{b,A}$

- purity specification (final condition): $x_{spec,B}$

- operating parameter: V

- phase equilibria conditions: $x_{BAZ,A}$

Unknowns: $\qquad U_e, SD, \tau, R$

Number of independent equations: 3 (2.41-43 without equations -a, -b and -c)

Number of unknowns: 4

Degree of freedom: 1

Let us consider R as an operational parameter.

The solution of the set of Eqs. 2.41-43 is:

Duration of the step:
$$\tau = \frac{x_{b,A} - (1 - x_{spec,B})}{x_{BAZ,A} - (1 - x_{spec,B})} \cdot (1 + R) \cdot \frac{U_b}{V}$$

Further results:
$$U_e = \frac{x_{BAZ,A} - x_{b,A}}{x_{BAZ,A} - (1 - x_{spec,B})} \cdot U_b, \quad SD = U_e - U_b$$

2.1.4.2. Model equations for the Double-Column System

The model equations are presented first for the separation of the binary mixture and then for that of the ternary one.

2.1.4.2.1. Separation of the binary mixture (Fig. 2.8)

Integral material balances for the whole system (for the whole process):

TMB:
$$U_b^\alpha + U_b^\beta = U_{ch} \qquad (2.51)$$

$$U_e^\alpha + U_e^\beta = U_{ch} \qquad (2.52)$$

CMB:
$$U_b^\alpha \cdot x_{b,A}^\alpha + U_b^\beta \cdot x_{b,A}^\beta = U_{ch} \cdot x_{ch,A} \qquad (2.53)$$

$$U_e^\alpha \cdot x_{spec,A} + U_e^\beta \cdot (1 - x_{spec,B}) = U_{ch} \cdot x_{ch,A} \qquad (2.54)$$

Differential material balances for Column α:

DTMB:
$$\frac{dU^{\alpha}}{dt} = -v^{\alpha} \cdot V + L^{Ar} \qquad (2.55a)$$

Boundary conditions:
$$U^{\alpha}(0) = U_b^{\alpha} \qquad (2.55b)$$

$$U^{\alpha}(\tau) = U_e^{\alpha} \qquad (2.55c)$$

Hence
$$U_e^{\alpha} = U_b^{\alpha} + (-v^{\alpha} \cdot V + L^{Ar}) \cdot \tau \qquad (2.55)$$

DCMB:
$$\frac{d(U^{\alpha} \cdot x_A^{\alpha})}{dt} = -v^{\alpha} \cdot V \cdot x_{AZ,A} + L^{Ar} \cdot x_{AZ,A}^{Ar} \qquad (2.56a)$$

Boundary conditions:
$$(U^{\alpha} \cdot x_A^{\alpha})(0) = U_b^{\alpha} \cdot x_{b,A}^{\alpha} \qquad (2.56b)$$

$$(U^{\alpha} \cdot x_A^{\alpha})(\tau) = U_e^{\alpha} \cdot x_{spec,A} \qquad (2.56c)$$

Hence
$$U_e^{\alpha} \cdot x_{spec,A} = U_b^{\alpha} \cdot x_{b,A}^{\alpha} + (-v^{\alpha} \cdot V \cdot x_{AZ,A} + L^{Ar} \cdot x_{AZ,A}^{Ar}) \cdot \tau \quad (2.56)$$

Differential material balances for the decanter:

DTMB:
$$\frac{dU^{dec}}{dt} = V - L^{Ar} - L^{Br} = 0 \qquad (2.57)$$

DCMB:
$$\frac{d(U^{dec} \cdot x_A^{dec})}{dt} = V \cdot x_{AZ,A} - L^{Ar} \cdot x_{AZ,A}^{Ar} - L^{Br} \cdot x_{AZ,A}^{Br} = 0 \qquad (2.58)$$

Known parameters:

- initial conditions: U_{ch}

- purity specification (final condition): $x_{spec,A}, x_{spec,B}$

- operating parameter: V

- phase equilibria conditions: $x_{AZ,A}, x_{AZ,A}^{Ar}, x_{AZ,A}^{Br}$

Unknowns:
$$U_b^{\alpha}, U_b^{\beta}, U_e^{\alpha}, U_e^{\beta}, v^{\alpha}, \tau, L^{Ar}, L^{Br}$$

If the charge is heterogeneous: $x_{b,A}^{\alpha} = x_{AZ,A}^{Ar}$ and $x_{b,A}^{\beta} = x_{AZ,A}^{Br}$.

Number of independent equations: 8 (2.51-58 without equations -a, -b and -c)

Number of unknowns: 8

Degree of freedom: 0

If the charge is homogeneous: $x^{\alpha}_{b,A} = x^{\beta}_{b,A} = x_{ch,A}$, thus Eq. 2.53 is identical to Eq. 2.51, hence one of the unknowns $(U^{\alpha}_{b}, U^{\beta}_{b}, v^{\alpha})$ must be specified. In the calculations later presented U^{α}_{b} is specified.

Number of independent equations: 7

Number of unknowns: 8

Degree of freedom: 1

The solution of the set of Eqs. 2.51-58 is:

Duration of the step:
$$\tau = \frac{\Delta(U^{\alpha} \cdot x^{\alpha}_{A}) - \Delta U^{\alpha} \cdot x_{AZ,A}}{x^{Ar}_{AZ,A} - x_{AZ,A}} \cdot \frac{1}{L^{Ar}}$$

where $\Delta U^{\alpha} = U^{\alpha}_{e} - U^{\alpha}_{b}$ and $\Delta(U^{\alpha} \cdot x^{\alpha}_{A}) = U^{\alpha}_{e} \cdot x_{spec,A} - U^{\alpha}_{b} \cdot x^{\alpha}_{b,A}$.

Optimum division of the charge:
$$U^{\alpha}_{b} = \frac{x_{ch,A} - x^{Br}_{b,A}}{x^{Ar}_{b,A} - x^{Br}_{b,A}} \cdot U_{ch}$$

$$U^{\beta}_{b} = U_{ch} - U^{\alpha}_{b}$$

Optimum division of the vapour flow rate:
$$v^{\alpha} = \frac{\Delta(U^{\alpha} \cdot x^{\alpha}_{A}) - \Delta U^{\alpha} \cdot x^{Ar}_{AZ,A}}{\Delta(U^{\alpha} \cdot x^{\alpha}_{A}) - \Delta U^{\alpha} \cdot x_{AZ,A}} \cdot \frac{L^{Ar}}{V}$$

Further results:
$$L^{Ar} = \frac{x_{AZ,A} - x^{Br}_{AZ,A}}{x^{Ar}_{AZ,A} - x^{Br}_{AZ,A}} \cdot V, \quad L^{Br} = V - L^{Ar},$$

$$U^{\alpha}_{e} = \frac{x_{ch,A} - (1 - x_{spec,B})}{x_{spec,A} - (1 - x_{spec,B})} \cdot U_{ch}, \quad U^{\beta}_{e} = U_{ch} - U^{\alpha}_{e}$$

2.1.4.2.2. Separation of the ternary mixture (Fig. 2.9)

Initially only Reboiler α contains E. We neglect the content of E of the B-rich phase. Hence there is no E in Column β whose top vapour is A-B binary azeotrope.

Integral material balances for the whole system:

TMB:
$$U^{\alpha}_{b} + U^{\beta}_{b} = U_{ch} \tag{2.61}$$

$$U^{\alpha}_{e} + U^{\beta}_{e} = U_{ch} \tag{2.62}$$

CMB:
$$U_{ch} \cdot x_{ch,A} = U^{\alpha}_{e} \cdot x_{spec,A} + U^{\beta}_{e} \cdot (1 - x_{spec,B}) \tag{2.63}$$

Differential material balances for Column α:

DTMB:
$$\frac{dU^{\alpha}}{dt} = -v^{\alpha} \cdot V + L^{Er} \qquad (2.64a)$$

Boundary conditions:
$$U^{\alpha}(0) = U_{b}^{\alpha} \qquad (2.64b)$$

$$U^{\alpha}(\tau) = U_{e}^{\alpha} \qquad (2.64c)$$

Hence
$$U_{e}^{\alpha} = U_{b}^{\alpha} + (-v^{\alpha} \cdot V + L^{Er}) \cdot \tau \qquad (2.64)$$

DCMB:
$$\frac{d(U^{\alpha} \cdot x_{A}^{\alpha})}{dt} = -v^{\alpha} \cdot V \cdot x_{TAZ,A} + L^{Er} x_{A}^{Er} \qquad (2.65a)$$

Boundary conditions:
$$(U^{\alpha} \cdot x_{A}^{\alpha})(0) = U_{b}^{\alpha} \cdot x_{ch,A} \qquad (2.65b)$$

$$(U^{\alpha} \cdot x_{A}^{\alpha})(\tau) = U_{e}^{\alpha} \cdot x_{spec,A} \qquad (2.65c)$$

Hence
$$U_{e}^{\alpha} \cdot x_{spec,A} = U_{b}^{\alpha} \cdot x_{ch,A} + (-v^{\alpha} \cdot V \cdot x_{TAZ,A} + L^{Er} \cdot x_{A}^{Er}) \cdot \tau \quad (2.65)$$

Differential material balances for the decanter:

DTMB:
$$\frac{dU^{dec}}{dt} = V - L^{Er} - L^{Br} = 0 \qquad (2.66)$$

DCMB:
$$\frac{d(U^{dec} \cdot x_{E}^{dec})}{dt} = V \cdot x_{TAZ,E} - L^{Er} \cdot x_{E}^{Er} = 0 \qquad (2.67)$$

Overall composition of the liquid in the decanter:
$$\vec{x}_{ov} = v^{\alpha} \cdot \vec{x}_{TAZ} + (1 - v^{\alpha}) \cdot \vec{x}_{BAZ} \qquad (2.68)$$

Composition of the *E*-rich phase leaving the decanter:
$$x_{A}^{Er} = f_{1}(\vec{x}_{ov}) \qquad (2.69)$$

$$x_{E}^{Er} = f_{2}(\vec{x}_{ov}) \qquad (2.70)$$

Known parameters:

- initial conditions: $U_{ch}, x_{ch,A}$

- purity specification (final condition): $x_{spec,A}, x_{spec,B}$

- operating parameter: V

- phase equilibria conditions: $\vec{x}_{TAZ}, \vec{x}_{BAZ}$

Unknowns: $U_{b}^{\alpha}, U_{b}^{\beta}, U_{e}^{\alpha}, U_{e}^{\beta}, v^{\alpha}, \tau, L^{Er}, L^{Br}, x_{A}^{Er}, x_{E}^{Er}, \vec{x}_{ov}$

Number of independent equations: 10 (2.61-70 without equations -a, -b and -c)

Number of unknowns: 11

Degree of freedom: 1

Eqs. 2.69 and 2.70 describe the composition of the *E*-rich phase of the heterogeneous ternary mixture in the decanter. The compositions of the liquid phases depend on the overall composition and on the location of the solubility curve (*Fig. 2.10*). Although the overall composition depends linearly on v^α (Eq. 2.68) but the solubility curve is highly non-linear. Because of the complexity of the activity coefficient models used for the description of the liquid-liquid equilibrium this set of equations cannot be solved analytically, only numerically. Hence v^α is considered as an operational parameter which makes possible to calculate separately the composition of the liquid phases (Eqs. 2.68-70) from the Eqs. 2.61-67.

The solution of the set of Eqs. 2.61-67 is:

Duration of the step:
$$\tau = \frac{U_e^\alpha \cdot (x_{spec,A} - x_{ch,A})}{L^{Er} \cdot (x_A^{Er} - x_{ch,A}) + v^\alpha \cdot V \cdot (x_{ch,A} - x_{TAZ,A})}$$

Optimum division of the charge:
$$U_e^\alpha = \frac{x_{ch,A} - (1 - x_{spec,B})}{x_{spec,A} - (1 - x_{spec,B})} \cdot U_{ch}$$

$$U_e^\beta = U_{ch} - U_e^\alpha$$

Further results:
$$L^{Er} = \frac{x_{TAZ,E}}{x_E^{Er}} \cdot v^\alpha \cdot V, \qquad L^{Br} = V - L^{Er},$$

$$U_b^\alpha = U_e^\alpha + (v^\alpha \cdot V - L^{Er}) \cdot \tau, \qquad U_b^\beta = U_{ch} - U_b^\alpha$$
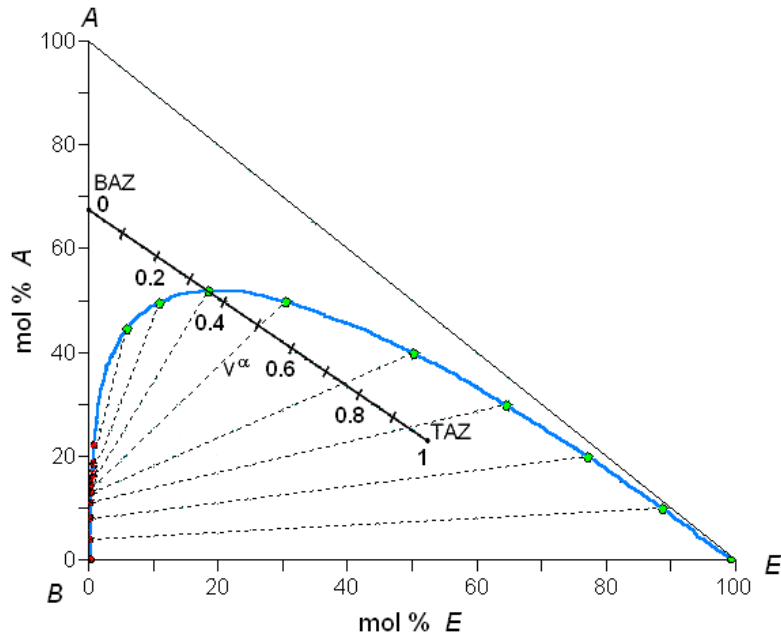
Fig. 2.10. Composition of the liquid in the decanter as the function of the relative vapour flow rate of Column α (mixture: isopropanol – water + benzene)

2.1.5. Calculation results of the feasibility studies

The heat duty is proportional to the vapour flow rate. The total vapour flow rate of the DCS is taken equal to that of the BR ($V = 20\,kmol/h$) in order to have the same operating costs for the DCS and BR. For the DCS we determine the optimum division of the charge between the two reboilers (and the division of the total vapour flow rate belonging to it). In all cases the amount of charge is 100 kmol and the specified purity ($x_{spec,i}$) is 99.5 mol% for both products.

2.1.5.1. Distillation of a binary mixture (1-butanol (A) – water (B))

The composition of the heteroazeotrope and those of the *A*-rich and *B*-rich phases are, respectively:

$$\vec{x}_{AZ} = [0.2562, 0.7438], \qquad \vec{x}_{AZ}^{Ar} = [0.568, 0.432], \qquad \vec{x}_{AZ}^{Br} = [0.012, 0.988]$$

All possible cases are studied: two homogeneous charges (one rich in *A* and the other rich in *B*) and a heterogeneous one.

2.1.5.1.1. A homogeneous charge rich in A ($\vec{x}_{ch} = [0.9, 0.1]$)

I. Batch Rectifier

In Step 1 *A*, in Step 2 *B* is produced (*Table 2.1a*).

II. Double-Column System

We determine τ and v^{α} for different ratios of division of the charge U_b^{α}/U_{ch} (*Figs. 2.11-12*). The best operational policy (*Table 2.1a*) is when the total amount of the charge is fed into Reboiler α ($U_b^{\alpha}/U_{ch} = 1$).
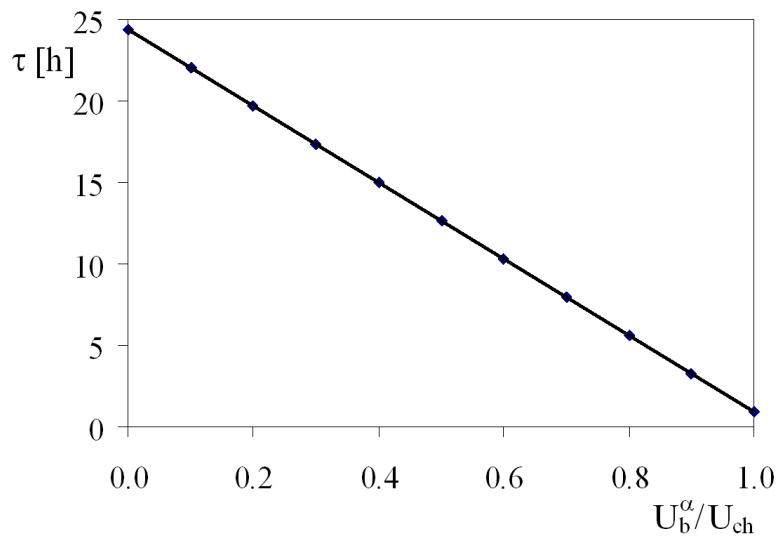
Fig. 2.11. Duration of the process for different charge divisions (simplified model, mixture: 1-butanol – water)
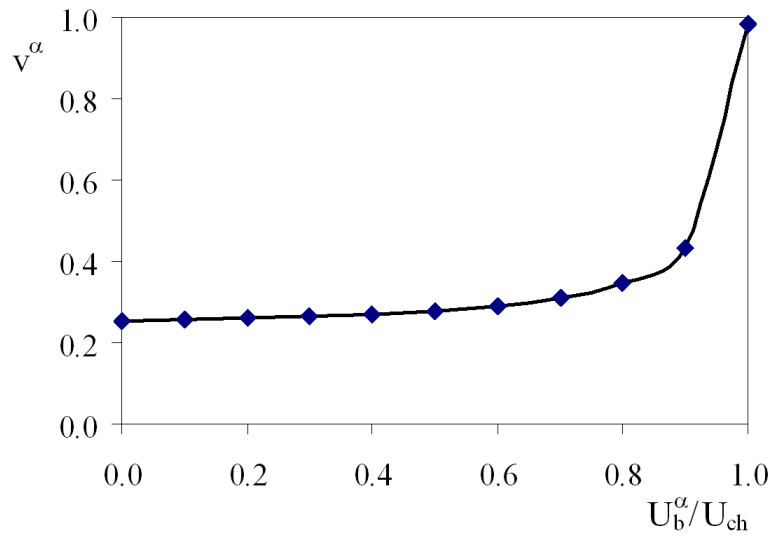
Fig. 2.12. Relative vapour flow rate of Column a for different divisions of the charge (simplified model, mixture: 1-butanol – water)

		BR			DCS	
		Step 1	Step 2	Total	Column α	Column β
Division of charge	kmol	-	-	-	100	0
Division of vapour flow rate	-	-	-	-	0.9844	0.0156
Duration	hour	0.862	0.014	0.876	0.880	
Product *A*	kmol	90.336	0.000	90.336	90.404	0.000
Product *B*	kmol	0.000	9.544	9.544	0.000	9.596
Byproducts	kmol	-	0.120	0.120	0.000	
Byproduct composition	mol% *A*	-	56.80	56.80	-	

Table 2.1a. Results for the binary mixture of homogeneous charge composition, rich in A (simplified model)

The duration of the cycle is nearly equal for the two configurations (if we neglect the duration of pumping between the two steps of the BR).

In the case of DCS by the best policy the whole amount of *A* is already in Reboiler α at the start and only *B* must be eliminated from it. The reason of the small value of v^{β} is that the *B*-rich phase flowing from the decanter into Column β has already very high *B*-content

$\left(x_{AZ,B}^{Br} = 0.988 \right)$. Hence only a small amount of A must be removed in the form of azeotrope for the purification of B. The main advantage of the DCS is that there is no byproduct at all.

The ratio of the duration of the two steps of the BR ($\tau^{(1)}/\tau^{(2)} = 61.57$) is close to that of vapour flow rates of the two columns of DCS ($v^\alpha/v^\beta = 63.10$), which shows that energy demand of the production of both components is nearly the same for the two configurations.

2.1.5.1.2. A homogeneous charge rich in B ($\vec{x}_{ch} = [0.01, 0.99]$)

I. Batch Rectifier

In Step 1 B, in Step 2 A is produced (*Table 2.1b*).

II. Double-Column System

We determined τ and v^α for different divisions of the charge. By the best operational policy (*Table 2.1b*) the total amount of the charge is fed into Reboiler β.

		BR			DCS	
		Step 1	Step 2	Total	Column α	Column β
Division of charge	kmol	-	-	-	0	100
Division of vapour flow rate	-	-	-	-	0.2538	0.7462
Duration	hour	0.101	0.034	0.135	0.136	
Product A	kmol	0.000	0.502	0.502	0.505	0.000
Product B	kmol	99.112	0.000	99.112	0.000	99.495
Byproducts	kmol	-	0.386	0.386	0.000	
Byproduct composition	mol% A	-	1.12	1.12	-	

Table 2.1b. Results for the binary mixture of homogeneous charge composition, rich in B (simplified model)

The duration of the cycle is nearly equal in the two cases.

Energy demand of the production of each component is again nearly the same for the two configurations ($\tau^{(1)}/\tau^{(2)} = 2.97$, $v^\beta/v^\alpha = 2.94$). The optimum division of the charge can be explained similarly as in the case of the previous charge composition.

2.1.5.1.3. A heterogeneous charge

Before the distillation the charge of composition $\vec{x}_{ch} = [0.3, 0.7]$ is separated by decantation into an A-rich ($U^{Ar} = 51.8\,kmol$) and a B-rich ($U^{Br} = 48.2\,kmol$) phases.

I. Batch Rectifier

In Step 1 the A-rich phase is distilled (by taking into consideration Inequality 2.1) and A is produced (as residue). In Step 2 the product is B (*Table 2.1c*).

II. Double-Column System

The preliminary decantation provides the division of the charge which determines the value of v^α. Hence only one solution exists (*Table 2.1c*).

		BR			DCS	
		Step 1	Step 2	Total	Column α	Column β
Division of charge	kmol	-	-	-	51.8	48.2
Division of vapour flow rate	-	-	-	-	0.9530	0.0470
Duration	hour	2.006	0.100	2.106	2.141	
Product A	kmol	29.298	0.000	29.298	29.798	0.000
Product B	kmol	0.000	69.823	69.823	0.000	70.202
Byproducts	kmol	-	0.879	0.879	0.000	
Byproduct composition	mol% A	-	56.80	56.80	-	

Table 2.1c. Results for the binary mixture of heterogeneous charge composition (simplified model)

The duration of the cycle is nearly equal in the two cases.

Energy demand of the production of each component is nearly the same for the two configurations ($\tau^{(1)}/\tau^{(2)} = 20.1$, $v^\alpha/v^\beta = 20.3$) like in the previous cases.

2.1.5.2. Distillation of a ternary mixture (isopropanol (A) – water (B) + benzene (E))

Binary azeotropic charge ($\vec{x}_{ch} = \vec{x}_{BAZ} = [0.674, 0.326, 0]$) is separated by the application of an entrainer. The composition of the ternary IPA – water + benzene heteroazeotrope and those of its E-rich and B-rich phases are, respectively:

$$\vec{x}_{TAZ} = [0.238, 0.239, 0.523], \quad \vec{x}_{TAZ}^{Er} = [0.277, 0.048, 0.675], \quad \vec{x}_{TAZ}^{Br} = [0.103, 0.894, 0.003]$$

I. Batch Rectifier

Calculation results are shown in *Table 2.2*.

II. Double-Column System

We determine τ and U_b^{α}/U_{ch} for different relative vapour flow rates of Column α (*Figs. 2.13-14*). Calculation results for the best operational policy are shown in *Table 2.2*.
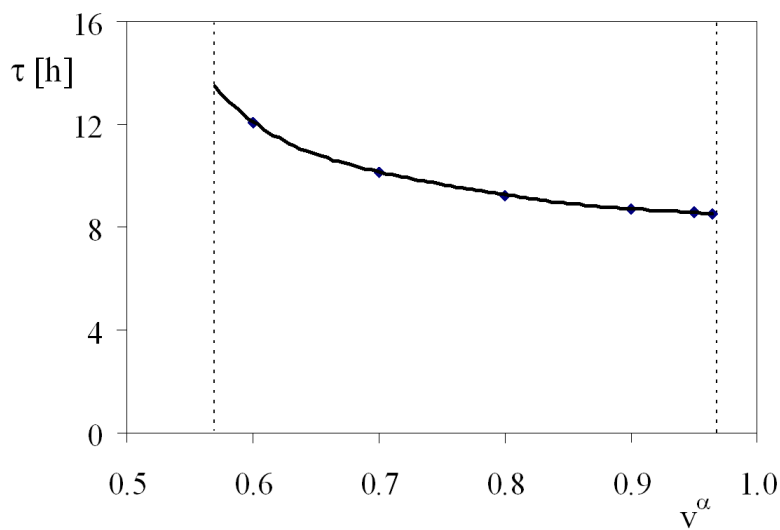
Fig. 2.13. Duration of the process for different divisions of the charge (simplified model, mixture: isopropanol – water + benzene)
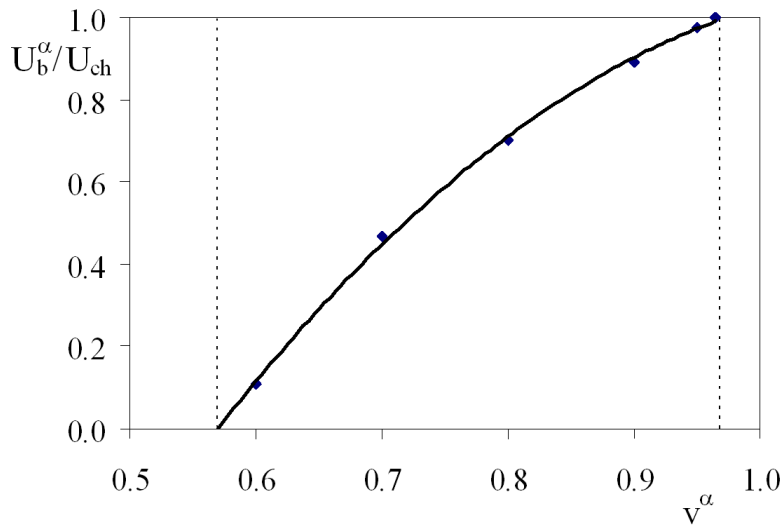
*Fig. 2.14. Relative vapour flow rate of Column α for different divisions of the charge
(simplified model, mixture: isopropanol – water + benzene)*

		BR				DCS	
		Step 1	Step 2	Step 3	Total	Column α	Column β
Division of charge	kmol	-	-	-	-	99.81	0.19
Division of vapour flow rate	-	-	-	-	-	0.9650	0.0350
Duration	hour	8.055	0.010	0.261	8.326	8.494	
Product A	kmol	64.001	0.000	0.000	64.001	67.576	0.000
Product B	kmol	0.000	0.000	30.723	30.723	0.000	32.424
Byproducts	kmol	-	0.160	5.224	5.384	0.000	
Byproduct composition	-	-	TAZ	BAZ	-	-	

Table 2.2. Results for the ternary mixture (simplified model)

The duration of cycle is nearly equal in the two cases. The amount of the final byproduct is more than 5 % of the charge for the BR, whilst there is no byproduct at all by the DCS. The energy demand of the production of each component is nearly the same for the two configurations.

The ratio of the duration of production of *A* and that of *B*: $\dfrac{\tau^{(1)}}{\tau^{(2)} + \tau^{(3)}} = 29.7$

The ratio of vapour flow rates of the two columns for the DCS: $v^{\beta}/v^{\alpha} = 27.6$

2.1.6. Simulation method

When making detailed simulation calculations we already take into consideration (contrary to the feasibility studies):

 - the variation of the composition and the flow rate of the streams with time,

 - that the separation is not maximal,

 - the liquid holdup of the trays and that of the decanter,

 - the entrainer loss (for the ternary mixture).

The following simplifying assumptions are always applied:

 - theoretical trays,

 - constant volumetric liquid holdup on the trays and in the decanter,

 - negligible vapour holdup,

 - negligible duration of pumping between the two steps (BR).

On the basis of the calculational experiences another simplifying assumption was applied in order to reduce the computational time:

- two liquid phases appear only in the decanter, in the other parts of the configuration there is only one liquid phase.

Hence VLLE calculations were made for the decanter only, and in the other parts of the configuration VLE calculations were performed.

The model equations to be solved are well-known (e.g. Mujtaba, 2004):

I. Non-linear differential equations (material balances, heat balances)

II. Algebraic equations (VLE and LLE relationships, summation equations, hold-up and physical property models)

For describing phase equilibria NRTL (for the binary mixture) and UNIQUAC (for the ternary mixture) models are applied. For the solution of the above equations the dynamic simulator of ChemCad 5.6 (program CC-DCOLUMN) is applied. Column sections are modelled by the module DYNAMIC COLUMN, reboilers and the (vertical cylindrical flat bottom) decanter by the DYNAMIC VESSEL, respectively (*Figs. 2.15-16*). Besides these units the flow-sheet still contains HEAT EXCHANGERs (condensers), MIXERs and DIVIDERs (stream splitters). The ChemCad models built-up make possible to lead any liquid

phases into any columns, hence all configurations are suitable for the production of all components without modification and arbitrary reflux policy can be realised. Furthermore they are suitable also for two liquid phase reflux which is not applied in this work.

Since in the columns only VLE is calculated, the run time is shorter and the simulations can converge easier than in the case when VLLE would be taken into account in all ChemCAD modules.
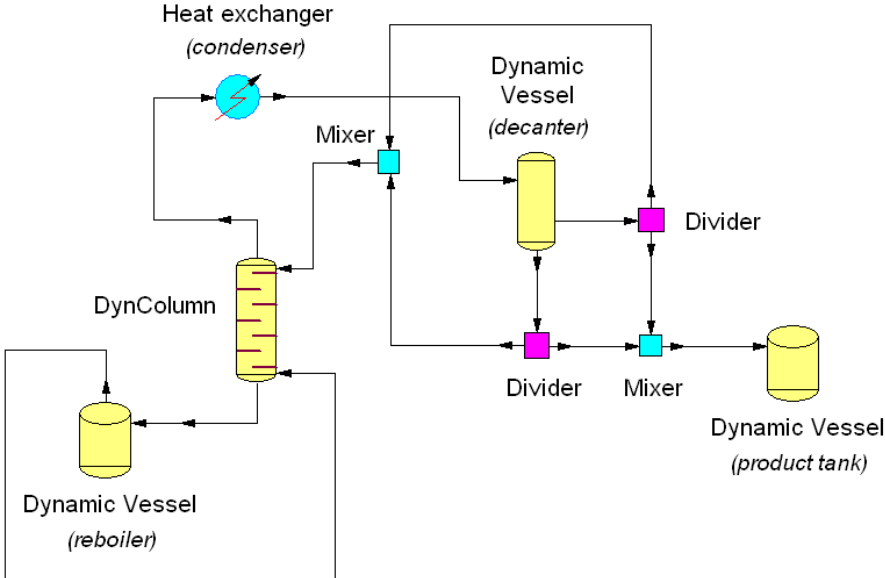
Fig. 2.15. ChemCad model of the Batch Rectifier equipped with a decanter
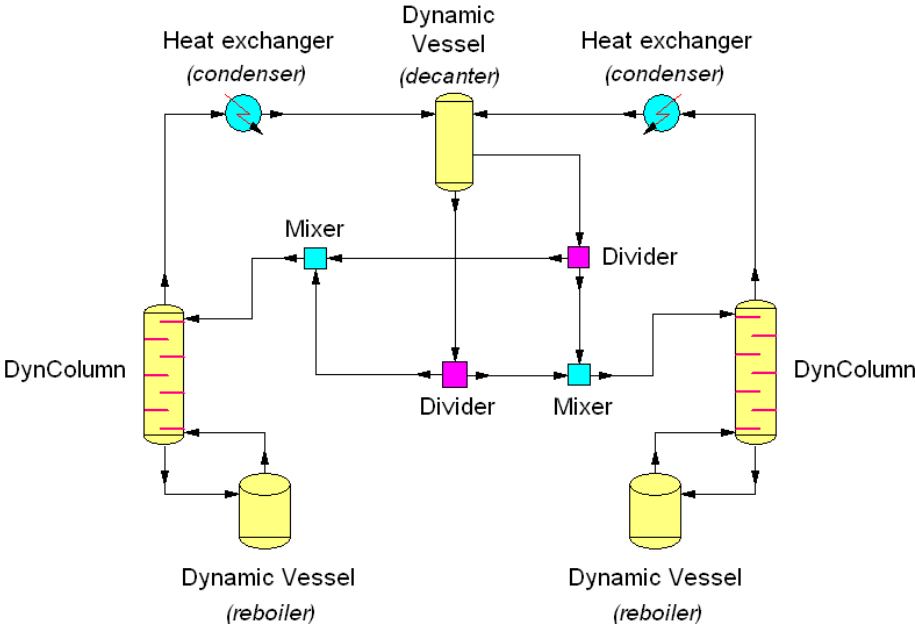
Fig. 2.16. ChemCad model of the new Double-Column System

2.1.7. Simulation results

We investigate the separation of the same mixtures with the same compositions as in the case of feasibility studies. The sequence of the production of the components by the BR is also identical to that applied in the course of feasibility studies.

In each case the total number of theoretical stages (N) (without the condenser, decanter and reboiler) is 10 for both configurations. The separation is performed at atmospheric pressure. Both reflux and distillate (BR) are homogeneous. In the decanter ($D=0.5m$) the volume of liquid phases are prescribed constant (after the start-up). The ratio of the volumes of the two phases is equal to that of the binary/ternary heteroazeotrope. The holdup of the trays is taken ~ 1 % of the initial liquid volume in the reboiler of the given column. In each case the amount of charge (U_{ch}) is 100 kmol and the prescribed purity of both products is 99.5 mol%. The calculations are started with dry trays and empty decanter.

For both configurations there is an optimum amount of entrainer for which the (total) duration of the production cycle is minimal. For the DCS the duration of the distillation in the two columns can be also influenced by the division of the total number of trays (N^{α}/N), total heat duty (Q^{α}/Q), and the amount of charge (U_b^{α}/U_{ch}). For each configuration we publish the results only for the optimum case with minimum duration.

2.1.7.1. Distillation of a binary heteroazeotropic mixture

2.1.7.1.1. A homogeneous charge rich in A

The total heat duty (Q) is 10 MJ/min in each case. (For the given charge composition the vapour flow rate is approximately 20 kmol/h.) The charge volume is 8.360 m^3. First the BR then the DCS is studied, finally the two configurations are compared.

I. Batch Rectifier

In Step 1 A is produced as bottom residue (*Table 2.3a*). (When in Step 1 we tried to produce B we did not reach the prescribed purity at all.) Step 2 is very short since the amount of distillate (B-rich phase) in Step 1 is very low (7.3 mol% of the charge) and the A-content of this distillate, which must be removed in Step 2, is also very low (1.2 mol %).

II. Double-Column System (*Table 2.3a*)

In Column α of the DCS the heat duty and the amount of liquid to be distilled is much higher than in the other column due to the high content of *A* of the charge and because the *B*-rich phase purified in Column β hardly contains *A*.

		BR			DCS	
		Step 1	Step 2	Total	Column α	Column β
Division of charge	kmol	-	-	-	99.1	0.9
Heat duty	MJ/min	10	10	-	9.4	0.6
Tray holdup	dm^3	80	2	-	80	10
Duration	hour	3.85	0.04	3.89	4.23	
Product *A*	kmol	81.336	0.000	81.336	85.521	0.000
Product *B*	kmol	0.000	6.776	6.776	0.000	4.419
Distillate	kmol	7.282	0.000	0.000	0.000	
Distillate composition	mol% *A*	1.13	-	-	-	
Column holdup	kmol	8.387	0.017	8.404	7.065	
Column holdup composition	mol% *A*	98.02	-	-	58.31	
Decanter holdup	kmol	2.995	0.489	3.484	2.995	
Decanter holdup composition	mol% *A*	25.62	20.20	-	25.62	
Byproducts	kmol	11.382	0.506	11.888	10.060	

Table 2.3a. Optimum parameters and results for the binary mixture of homogeneous charge composition, rich in A (detailed model; $N^\alpha = N^\beta = 5$)

Comparing the two different configurations we can state that

-The duration of the process is shorter by 8% for the BR.

-However for the BR the amount of by-products is higher by 15%.

-The recovery of *A* is higher for the DCS (94.5 % instead of 89.9 %).

The results of the feasibility studies and the rigorous simulation are also compared on the basis of *Tables 2.1a* and *2.3a*:

- In both cases almost the whole charge is filled into Reboiler β.

- For both methods the heating (or vapour flow rate) of Column α is much higher than that of Column β.

- By both methods the durations for the two configurations are the same but there are considerable differences between the durations determined by the two methods.

- The product quantities are similar. The main reason of the slight differences is that in the feasibility studies the holdup of the decanter and columns were neglected, therefore there was no loss.

2.1.7.1.2. A homogeneous charge rich in B

The total heat duty: $Q = 16\,MJ/min$ in each case. (For the given charge composition the vapour flow rate is approximately 20 kmol/h, as in the feasibility studies.) The charge volume is 1.874 m^3.

I. Batch Rectifier

In the BR *B* is produced in Step 1 as bottom residue (*Table 2.3b*). (If in Step 1 we try to produce *A* the prescribed purity cannot be reached at all.) Since in the charge the amount of *A* is very low the bottom residue reaches the prescribed purity of *B* before filling up the decanter. (The majority of *A* appears in the column hold-up.) Since the amount of distillate in Step 1 is zero there is no need for Step 2.

II. Double-Column System (*Table 2.3b*)

In the DCS (similarly to the BR) *A* of prescribed purity cannot be produced at all, *A* accumulates in the hold-up. In Column α the heat duty and the amount of liquid to be distilled is much lower than in the other column due to the low content of *A* in the charge.

		BR			DCS	
		Step 1	Step 2	Total	Column α	Column β
Division of charge	kmol	-	-	-	1.5	98.5
Heat duty	MJ/min	16	-	-	0.86	15.14
Tray holdup	dm^3	20	-	-	10	80
Duration	hour	0.15	-	0.15	0.18	
Product A	kmol	0.000	-	0.000	0.000	0.000
Product B	kmol	97.083	-	-	4.043	92.482
Distillate	kmol	0.000	-	-	0.000	
Distillate composition	mol% A	-	-	-	-	
Column holdup	kmol	0.375	-	0.375	0.942	
Column holdup composition	mol% A	-	-	-	3.45	
Decanter holdup	kmol	2.542	-	2.542	2.533	
Decanter holdup composition	mol% A	20.06	-	-	19.94	
Byproducts	kmol	2.917	-	2.917	3.475	

Table 2.3b. Optimum parameters and results for the binary mixture of homogeneous charge composition, rich in B (detailed model; $N^\alpha = N^\beta = 5$)

Comparing the two different configurations we can state that

- The duration of the process is almost the same for the two different configurations (BR: 0.15 h, DCS: 0.18 h).
- The recovery of B is similar for the BR (97.57 %) and DCS (97.01 %).
- The DCS produces somewhat more byproducts because of its higher volumetric column holdup (BR: 200 dm^3, DCS: 450 dm^3).

The results of the feasibility studies and rigorous simulation are also compared on the basis of *Tables 2.1b* and *2.3b*. This comparison led similar results as in the case of the charge rich in *A*:

- In both cases almost the whole charge is filled into Reboiler β.
- For both methods the heating of Column β is much higher than that of Column α but there is a considerable difference between the values determined by the two methods.

- The duration is short in both cases because the charge composition is close to the prescribed purity of component *B*.
- The product quantities are similar.

2.1.7.1.3. A heterogeneous charge

The total heat duty is $Q = 12 MJ / min$ in each case. (For the given charge composition the vapour flow rate is approximately 20 kmol/h.) The volume of the charge is 3.988 m³.

Before the distillation the charge is separated into two liquid phases:

A-rich: $U_b^\alpha = 51.8 \, kmol$, $x_A = 0.568$ B-rich: $U_b^\beta = 48.2 \, kmol$, $x_A = 0.012$

I. Batch Rectifier

In the BR both components could be produced in Step 1. If *A* is produced first we get better results (*Table 2.3c*, where the results of the other sequence are given in brackets). Step 2 is very short since the amount of distillate (*B*-rich phase) in Step 1 is low (20.4 mol% of the charge) and the *A*-content of this distillate, which must be removed in Step 2, is very low (1.2 mol%).

II. Double-Column System (*Table 2.3c*)

In the DCS the heat duty of Column α (95.6 %) is much higher than in the other column due to the high content of *B* (43.2 mol%) whilst the *B*-rich phase purified in Column β hardly contains *A* (1.2 mol%). In this case the charge must be divided almost half-and-half between the two reboilers.

		BR			DCS	
		Step 1	Step 2	Total	Column α	Column β
Division of charge	kmol	-	-	-	51.8	48.2
Heat duty	MJ/min	12	12	-	11.47	0.53
Tray holdup	dm^3	30	10	-	30	10
Duration	hour	3.15 (0.13)	0.18 (3.20)	3.33 (3.33)	3.50	
Product A	kmol	24.948 (0.000)	0.000 (25.374)	24.948 (25.374)	26.948	0.000
Product B	kmol	0.000 (46.210)	65.851 (0.000)	65.851 (46.210)	0.000	65.449
Distillate	kmol	20.360 (0.000)	0.000 (20.688)	0.000 (20.688)	0.000	
Distillate composition	mol% A	1.13 (-)	- (1.13)	- (1.13)	-	
Column holdup	kmol	3.497 (0.247)	0.246 (2.743)	3.743 (2.990)	4.608	
Column holdup composition	mol% A	- (-)	- (-)	- (-)	45.23	
Decanter holdup	kmol	2.995 (1.743)	2.463 (2.995)	5.458 (4.738)	2.995	
Decanter holdup composition	mol% A	25.62 (20.87)	20.62 (25.62)	- (-)	25.62	
Byproducts	kmol	6.492 (1.990)	2.709 (26.426)	9.201 (28.416)	7.603	

Table 2.3c. Optimum parameters and results for the binary mixture of heterogeneous charge composition (detailed model; $N^\alpha = N^\beta = 5$ *)*

Comparing the two different configurations we can conclude that

- The duration of the process is slightly shorter (by 5%) for the BR.

- However for the BR the amount of by-products is higher (9.2 % vs. 7.6 %).

- The recovery of A is higher for the DCS (89.4 % instead of 82.7 %).

The results of the feasibility studies and the rigorous simulation are also compared on the basis of *Tables 2.1c* and *2.3c*:

- For both methods the heating of Column α is much higher than that of Column β and the values of the division of total vapour flow rate and the division of total heat duty were almost the same.

- The durations determined by the two methods differ but in both cases the duration for the BR and that of the DCS was nearly equal.

- The product quantities are similar.

2.1.7.2. Distillation of a binary homoazeotrope by using an entrainer

2.1.7.2.1. Isopropanol – water with benzene as entrainer

The total heat duty is $Q = 12MJ/min$ in each case. (For the given charge composition the vapour flow rate is approximately 20 kmol/h.) The volume of the charge is 5.690 m^3.
The prescribed levels of the decanter: *B*-rich phase: 0.0384 m, *E*-rich phase: 0.6 m.

I. Batch Rectifier

For the BR the optimum amount of *E* by which the duration of Step 1 (determining primarily the duration of the production cycle) is minimal: 4.2 kmol (0.371 m^3). In Step 1 *A* is produced (*Table 2.4*). The duration of this step is much longer than that of Step 2. Though the amount of distillate (*B*-rich phase) in Step 1 is not too low (36.4 mol% of the charge) but the *E*-content of this distillate, which must be removed (together with *A*) in Step 2, is very low (0.35 mol%). In Step 2 *B* is purified not only from *E* but also from *A* in the form of binary azeotrope *A-B* whose *A*-content is relatively high.

II. Double-Column System

For the ternary mixture three variations of the DCS are studied (*Table 2.4*).

- DCS-1: $N^\alpha + N^\beta = 10$, volumetric liquid tray holdup in Column α (and β): 1% of the volume of the initial charge of Reboiler α (and β).

- DCS-2: $N^\alpha = N^\beta = 10$, volumetric liquid tray holdup in Column α/β: 1% of the volume of the initial charge of Reboiler α (or β).

- DCS-3: $N^\alpha = N^\beta = 10$, The overall liquid tray holdup is equal to that of the DCS-1, the ratio of the tray holdups in the two columns are equal to the ratio of the volumes of the initial charges in the two reboilers.

For the DCS-1 the optimum division of the total number of trays is rather unequal. (In all binary cases studied formerly the influence of the division of the trays was slight on the results.) For all the three variations the optimum amount of *E*: 3.9 kmol. The whole amount of *E* is filled in Reboiler α. The division of the heat duty is very similar in each case. The relative heat duty of Reboiler α (92 %) is much higher than that of the other reboiler. The *A*-content of the top vapour of Column β is relatively high. In these cases 77% of the charge must be filled in Reboiler α. Among the three variations the least advantageous is the DCS-2 since its total holdup is greater than that of the other ones. The performance of DCS-1 and DCS-3 is nearly the same. The durations are almost identical for them and the recovery of *A* is also nearly equal. In DCS-1 somewhat more *B* and less byproducts are produced.

Comparing the two different configurations we can conclude that
 - The duration of the process is slightly shorter for the DCS.
 - The recovery of both components is somewhat higher for the DCS.
In *Fig. 2.17*. the evolution of liquid compositions in the reboilers is shown for both configurations. In the BR the two components produced are purified in the reboiler sequentially, in two operation steps (*Fig. 2.17a*). Step 2 consists of two parts: In the first one the benzene leaves the reboiler (*Fig. 2.17b*) then *B* is purified from *A*. These parts correspond to Step 2 & 3 of the operation of BR described in the Chapter 2.1.3. However, in the DCS the two components can be simultaneously produced in one step (*Fig. 2.17c*).
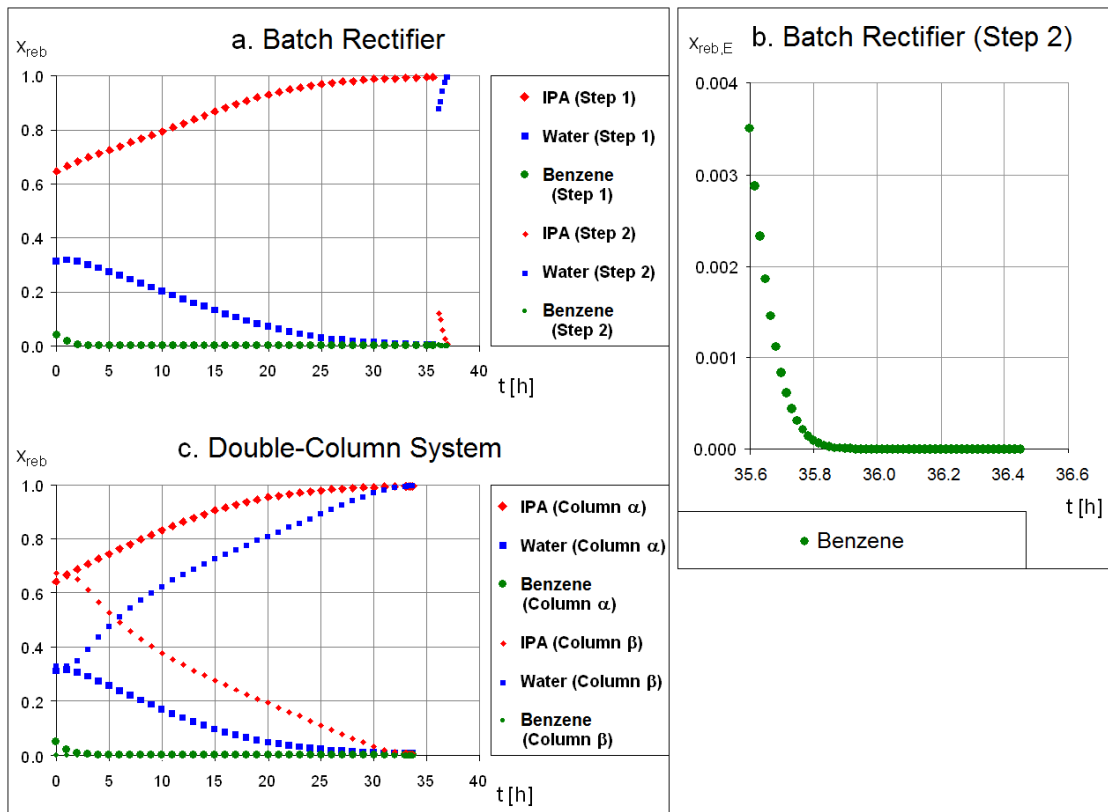
Fig. 2.17. The evolution of liquid compositions in the reboiler(s)

(mixture: isopropanol – water + benzene)

a. Batch Rectifier (Step 1 & 2)

b. Batch Rectifier (Step 2 for E)

c. Double-Column System (DCS-1, Reboilers α & β)

		BR			DCS-1		DCS-2		DCS-3	
		Step 1	Step 2	Total	Column α	Column β	Column α	Column β	Column α	Column β
Division of charge	kmol	-	-	-	77.0	23.0	77.0	23.0	77.0	23.0
Heat duty	MJ/min	12	12	-	11.03	0.97	11.10	0.90	11.05	0.95
Number of trays	-	10	10	-	8	2	10	10	10	10
Tray holdup	dm^3	60	10	-	47	13	47	13	31	9
Entrainer	kmol	4.2	0.0		3.9	0.0	3.9	0.0	3.9	0.0
Duration	hour	35.60	0.85	36.45	34.0		35.0		33.7	
Product A	kmol	55.972	0.000	55.972	58.700	0.000	57.517	0.000	59.449	0.000
Product B	kmol	0.000	23.586	23.586	0.000	29.320	0.000	23.990	0.000	26.062
Distillate	kmol	36.434	10.230	10.230	0.000		0.000		0.000	
Distillate composition	mol% A	11.94	40.89	-	-		-		-	
	mol% B	87.71	56.25	-	-		-		-	
Column holdup	kmol	10.187	2.378	12.565	14.260		20.773		16.775	
Column holdup composition	mol% A	67.18	-	-	58.42		45.78		45.23	
	mol% B	0.83	-	-	19.26		38.87		35.84	
Decanter holdup	kmol	1.607	0.240	1.847	1.620		1.620		1.614	
Decanter holdup composition	mol% A	31.99	11.23	-	33.69		33.68		32.96	
	mol% B	21.90	88.77	-	22.38		22.38		22.16	
Byproducts	kmol	11.794	12.848	24.642	15.880		22.393		18.389	

Table 2.4. Optimum parameters and results for the mixture isopropanol – water + benzene (detailed model)

2.1.7.2.2. Isopropanol – water with cyclohexane as entrainer

Since the benzene is carcinogenic in the industrial practice it is replaced by other solvents if it is possible. One possible solvent is the cyclohexane, which forms also a ternary heteroazeotrope with the mixture isopropanol – water. The ternary azeotropic composition and temperature are close to those of the ternary mixture containing benzene (Appendix 1). The ternary heteroazeotrope splits into an organic (rich in cyclohexane (E)) and an aqueous (B-rich) phase (*Fig. 2.18*). In the latter one the B/A ratio is much higher than in the $A - B$ azeotrope. The activity coefficients are computed by using the UNIQUAC model (Appendix 1).
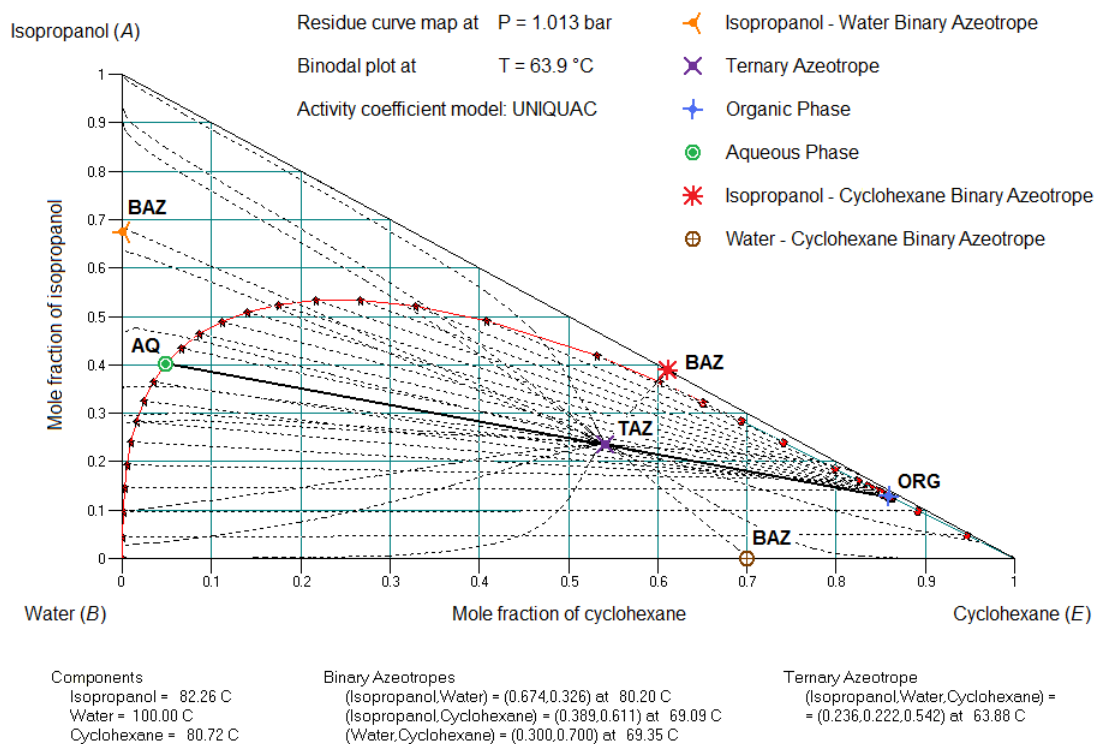
Fig. 2.18. Residue curve map and binodal plot of the mixture

isopropanol – water + cyclohexane

The total heat duty is $Q = 12\,MJ\,/\,min$ in each case. The composition of the charge is that of the binary homoazeotrope isopropanol – water: $x_{ch,A} = 67.4\,mol\%$. Its total volume is 5.690 m^3. The prescribed liquid levels in the decanter (from the bottom of the vessel): B-rich phase: 0.134 m, E-rich phase: 0.6 m. The separations are performed at atmospheric pressure.

I. Batch Rectifier

The number of theoretical trays in the column is 10. For the BR the optimum amount of E by which the duration of Step 1 (determining primarily the duration of the production cycle) is minimal: 3.8 kmol (0.408 m^3). In Step 1 A is produced (*Table 2.5*). The duration of this step is much longer than that of Step 2. Though the amount of distillate (*B*-rich phase) in Step 1 is not too low (37.9 mol% of the charge) but the *E*-content of this distillate, which must be removed (together with *A*) in Step 2, is very low (0.42 mol%). At the beginning of Step 2 the concentration of E decreases quickly in the reboiler (*Fig. 2.19*), and later on E disappears from top vapour (*Fig. 2.20*) as well. The concentration of A continuously decreases in the reboiler during the whole step.

II. Double-Column System

Two variations of the DCS are studied (*Table 2.5*).

- DCS-1: $N^\alpha + N^\beta = 10$, volumetric liquid tray holdup in Column α (and β): 1% of the volume of the initial charge of Reboiler α (and β).

- DCS-2: $N^\alpha = N^\beta = 10$, volumetric liquid tray holdup in Column α (and β): 1% of the volume of the initial charge of Reboiler α (or β).

For DCS-1 the optimal division of the total number of trays between the two columns is unequal: $N^\alpha=7$, $N^\beta=3$. In this case the optimal total quantity of E is 4.4 kmol and its 91% is filled into Reboiler α. The heat duty of Reboiler α (84.5 %) is much higher than that of the other reboiler. In this case 57% of the charge must be filled into the reboiler of Column α.

The increase of the number of trays of both columns to that of the BR (DCS-2) does not improve considerably the performance of the system. This can be partially explained by the increase of column holdups.

Comparing the two different configurations it can be concluded that

 -The duration of the process is shorter for the DCS.

 -The recovery of both components is higher for the DCS.

The evolution of liquid compositions in the reboilers for both configurations is shown in *Fig. 2.19*, that of top vapour compositions in *Fig. 2.20.*, respectively.

The similarity of the shapes of the curves in *Figs. 2.19* and *2.17* shows that the steps of the processing of the mixture isopropanol – water by using cyclohexane as entrainer in BR and

DCS are the same as by using benzene. *Figs. 2.20a* and *c* show that the top vapour compositions are nearly constant and not very different from the ternary azeotropic one during the process except for Step 2 in the case of BR when *E* is eliminated from Product *B*.

		BR			DCS (1)		DCS (2)	
		Step 1	Step 2	Total	Col. α	Col. β	Col. α	Col. β
Number of trays	-	10	10	10	7	3	10	10
Division of charge	kmol	-	-	-	57	43	55	45
Heat duty	kW	200	200	-	169.0	31.0	168.3	31.7
Tray holdup	dm^3/tray	60	10	-	35	25	35	25
Entrainer	kmol	3.8	0.0	3.8	4.0	0.4	4.0	0.4
Duration	hour	36.83	1.07	37.9	28.5		28.8	
Product *A*	kmol	50.75	0.00	50.75	59.33	0.00	58.78	0.00
Product *B*	kmol	0.00	21.30	21.30	0.00	25.46	0.00	26.16
Recovery of *A*	%	74.89	-	74.89	87.53	-	86.74	-
Recovery of *B*	%	-	65.10	65.10	-	77.89	-	79.97
Distillate	kmol	37.90	3.35	3.35*	0.00		0.00	
Distillate composition	mol% *A*	17.07	53.44	-	-		-	
	mol% *B*	82.51	43.09	-	-		-	
	mol% *E*	0.42	3.47	-	-		-	
Column holdup	kmol	13.28	10.49	23.77	17.68		17.50	
Column holdup composition	mol% *A*	75.24	34.41	-	44.12		47.41	
	mol% *B*	1.50	65.21	-	34.00		30.38	
	mol% *E*	23.16	0.38	-	21.88		22.21	
Decanter holdup	kmol	1.87	2.76	4.63	1.94		1.96	
Decanter holdup composition	mol% *A*	25.24	35.13	-	26.34		26.80	
	mol% *B*	44.61	64.76	-	46.45		46.95	
	mol% *E*	30.15	0.11	-	27.21		26.25	
Byproducts	kmol	15.15	16.60	31.76	19.61		19.46	

Table 2.5. Optimal parameters and results (mixture: isopropanol – water + cyclohexane)

* The distillate of Step 1 is processed in Step 2 therefore this is not a byproduct.
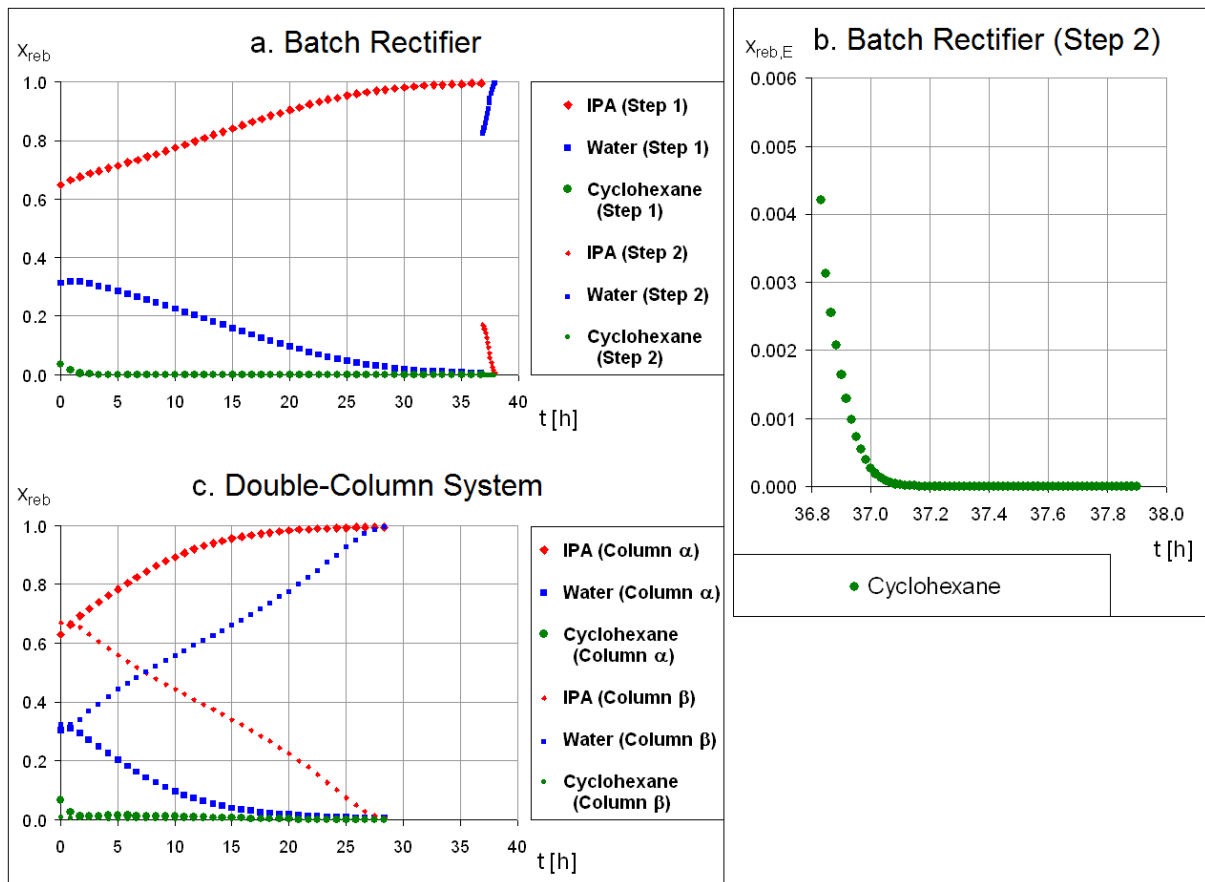
Fig. 2.19. The evolution of liquid compositions in the reboiler(s)

(mixture: isopropanol – water + cyclohexane)

a. Batch Rectifier (Step 1 & 2)

b. Batch Rectifier (Step 2 for E)

c. Double-Column System (DCS (1), Reboilers α & β)
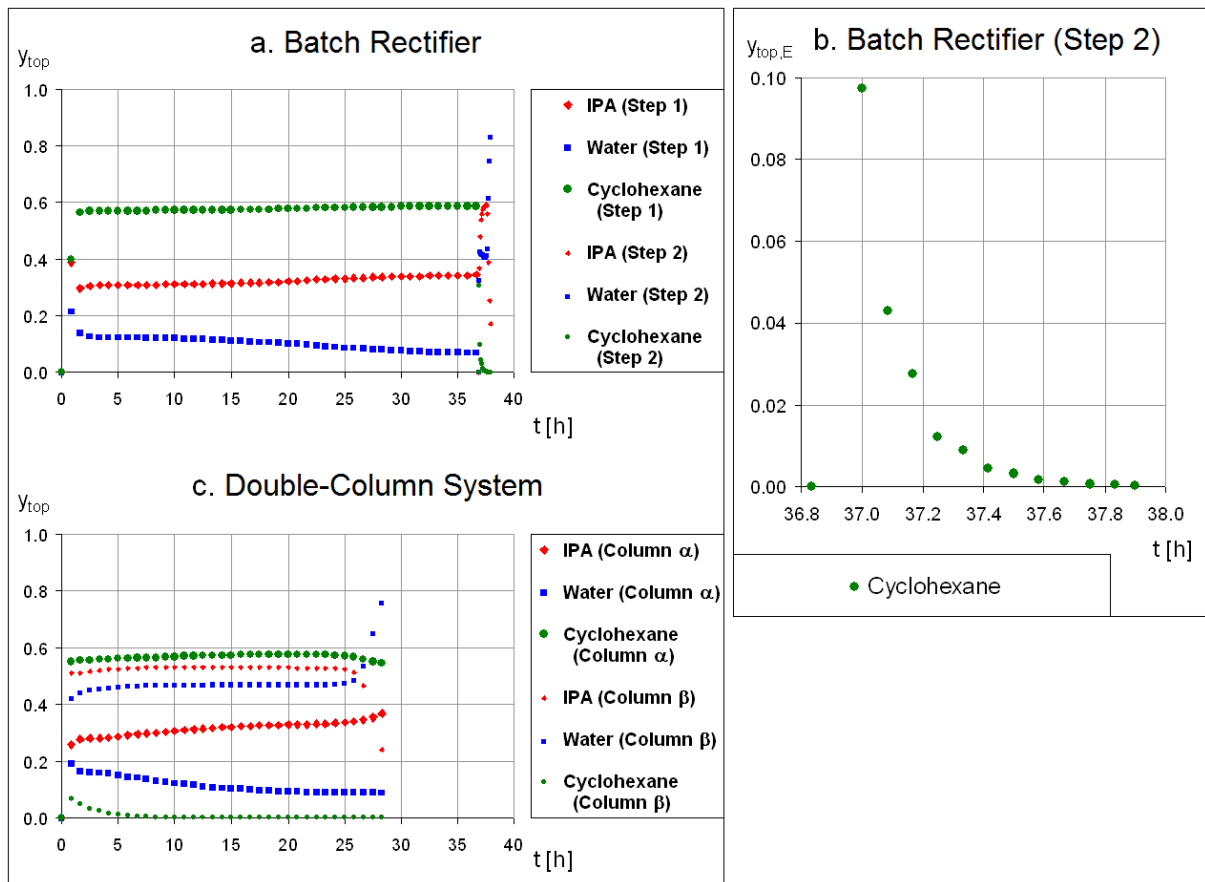
Fig. 2.20. The evolution of the top vapour composition(s)

(mixture: isopropanol – water + cyclohexane)

a. Batch Rectifier (Step 1 & 2)

b. Batch Rectifier (Step 2 for E)

c. Double-Column System (DCS (1), Reboilers α & β)

2.2. Feasibility and computational study of the new Generalised Double-Column System

By the generalisation of the DCS we get a much more flexible configuration for BHD. In this chapter the Generalised Double-Column System (GDCS) is studied and compared with the DCS. First feasibility studies are performed for the GDCS then rigorous simulations are done for both configurations, respectively.

2.2.1. Introduction

Our goals are:

- to study the feasibility of the separation of a homoazeotropic mixture isopropanol (*A*) – water (*B*) by applying cyclohexane or n-hexane as entrainer (*E*) in a Generalised Double-Column System (*Fig. 2.21*) by a simplified model,

- to study the effect of the new operation parameters (f^α, f^β, R^β) on the duration of the process,

- to compare the performance of the new GDCS with that of the original DCS by rigorous simulation.

In the GDCS Column β has a separate condenser. It is operated with homogeneous reflux (with arbitrary reflux ratio). The distillate of both columns can be fed into any tray of the other column.
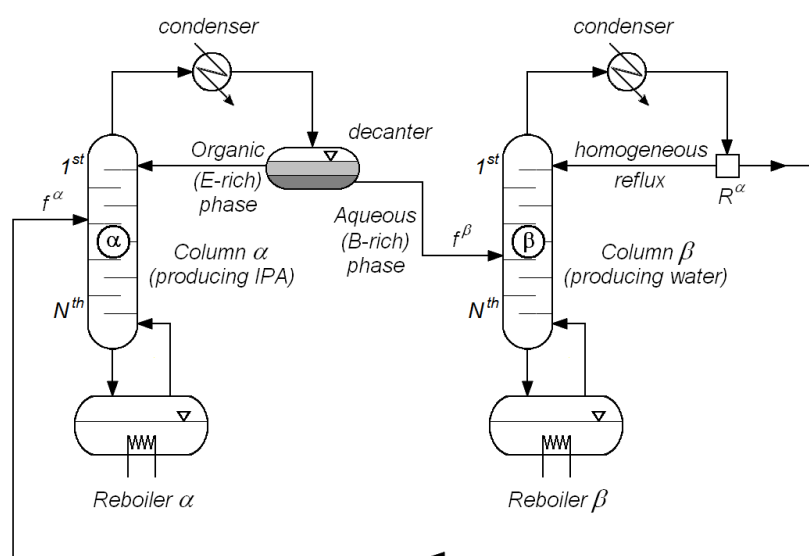
Fig. 2.21. Scheme of the GDCS

2.2.2. Description of the new configuration

We extended the original DCS. In the new generalised configuration (*Fig. 2.21*):

 - the distillate of Column β can be fed into any (f^{α}) plate (or the decanter) of Column α (not only into the decanter as by the DCS),

 - the aqueous phase of the decanter can be fed into any (f^{β}) plate of Column β (not only to the top of the column),

 - Column β can be operated with homogeneous reflux (reflux ratio: R^{β}).

The operation of the new configuration is as follows:

First the charge is divided between the reboilers then entrainer is added into Reboiler α. The composition of the top vapour of Column α is near to the ternary azeotropic one, that of Column β is near to the binary azeotropic one, respectively. The heterogeneous condensate of Column α is fed into a decanter. The light (organic, *E*-rich) phase is refluxed, the heavy (aqueous, *B*-rich) one is fed into Column β. The homogeneous condensate of Column β is partially refluxed. Its other part is fed into Column α. At the end of the process Product *A* is obtained in Reboiler α and Product *B* in Reboiler β, respectively.

The three new degrees of freedom, compared to the original DCS, make possible a more flexible operation. By the GDCS the decanter is fed only by the ternary heteroazeotrope (TAZ) and not by its mixture with the binary *A-B* homoazeotrope (BAZ). Therefore the compositions of the equilibrium phases (ORG and AQ) are farther from each other than by the DCS, that is, sharper liquid-liquid separation can be reached (longer tie line, *Fig. 2.22*). The condensate of Column β – whose *A*-content is higher than that of the *B*-rich phase coming from the decanter – is partially refluxed. Consequently the *A*-content of the top vapour β can be higher than by the original DCS.
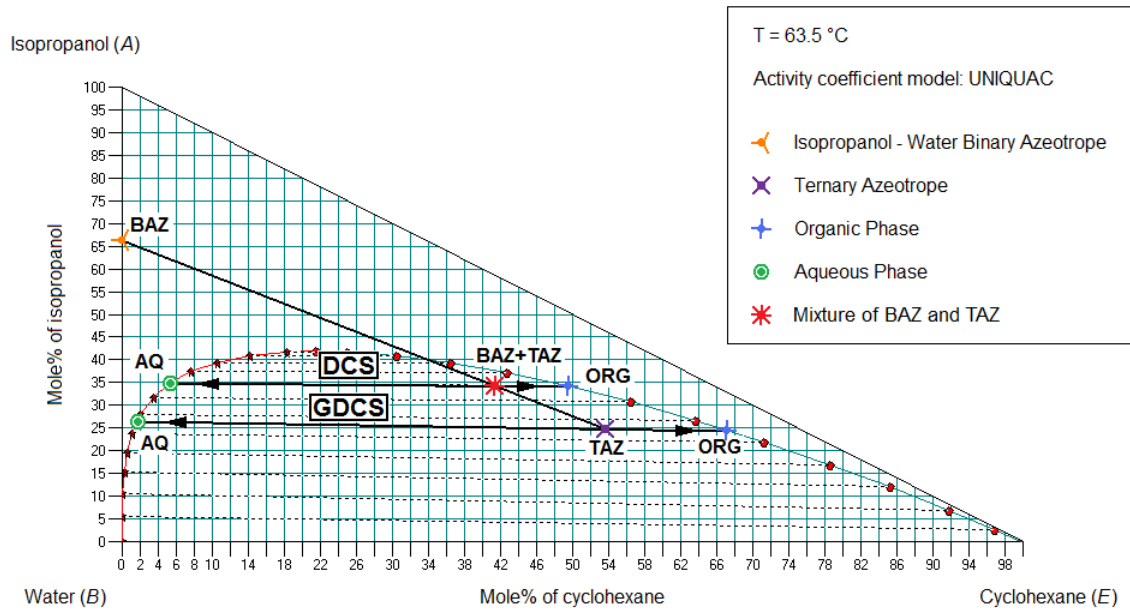
Fig. 2.22. Comparison of the split of the decanter feed for both configurations

(mixture: isopropanol – water + cyclohexane)

2.2.3. Feasibility study

In this chapter the feasibility of the separation in the GDCS is studied by a simplified method.

2.2.3.1. Method of the feasibility study

We apply a simplified model for the description of the distillation of the mixture *A-B*: the integral total and partial (for *A*) material balances are solved (*Eqs. 2.80-82*).

The simplifying assumptions are the same as for the DCS (Chapter 2.1.4). In this case the total separation means that the composition of the top vapour of Column α is supposed to be TAZ, and BAZ for Column β, respectively.

Model equations:

Component material balance for the whole process:

$$U_{ch} \cdot x_{ch,A} = U_e^\alpha \cdot x_{A/prodA} + (U_{ch} - U_e^\alpha) \cdot (1 - x_{B/prodB}) \qquad (2.80)$$

Integral total material balance for Column α:

$$U_e^\alpha = u^\alpha \cdot U_{ch} - \frac{v^\alpha}{1+R^\alpha} \cdot V \cdot t + \frac{1-v^\alpha}{1+R^\beta} \cdot V \cdot t \qquad (2.81)$$

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Integral component material balance for Column α:

$$U_e^\alpha \cdot x_{A/prodA} = u^\alpha \cdot U_{ch} \cdot x_{ch,A} - \frac{v^\alpha}{1+R^\alpha} \cdot x_{AQ,A}^{TAZ} \cdot V \cdot t + \frac{1-v^\alpha}{1+R^\beta} \cdot x_A^{BAZ} \cdot V \cdot t \qquad (2.82)$$

2.2.3.2. Input data

- Molar quantity of the charge: $U_{ch} = 100\ kmol$

- Composition of the charge [A, B, E]: $\vec{x}_{ch} = [0.662, 0.338, 0] = \vec{x}^{BAZ}$

- Prescribed purities in mole fraction: $x_{A/prodA} = x_{B/prodB} = 0.99$

- Total vapour flow rate: $V = 20 kmol/h$

- Division of the charge: $u^\alpha = U_b^\alpha / U_{ch} = 0.6$

- Reflux ratios: $R^\alpha = 3.79$ (determined by the liquid-liquid split), $R^\beta = 1/2$

2.2.3.3. Results

The three unknown variables are easily calculated from Eqs. 2.80-82:

- Molar quantity of Product A: $U_e^\alpha = 66.53 kmol$

- Division of the vapour flow rate: $v^\alpha = V^\alpha / V = 0.740$

- Duration: $t = 1052 min$

The prescribed purities $x_{e,A}^\alpha = x_{A/prodA}$ can be reached. Hence the separation with the new configuration proves to be feasible. The value of v^α is a good starting point for the determination of the optimal division of the heat duty during the further investigations.

2.2.4. Introduction to the rigorous simulations

First the influence of the new operational parameters is studied then the two configurations are compared. The simplifying assumptions and the model equations are the same as for the DCS (Chapter 2.1.6). The phase equilibria are described by the UNIQUAC model. For the description of VLE and LLE different sets of binary interaction parameters (BIPs) are used for the sake of the more accurate modelling (Appendix 1). In the decanter LLE is described by BIPs determined from LLE measurement results. For the solution of the equations of our models the dynamic flowsheet simulator of ChemCAD (CC-DCOLUMN) is applied as in the former studies. *Fig. 2.23* shows the ChemCAD-model of the GDCS. (*Fig. 2.24* shows a

simplified version of the DCS compared with *Fig. 2.16* in which the model makes possible heterogeneous reflux for both columns. Since this option is not used the model can be simpler.)
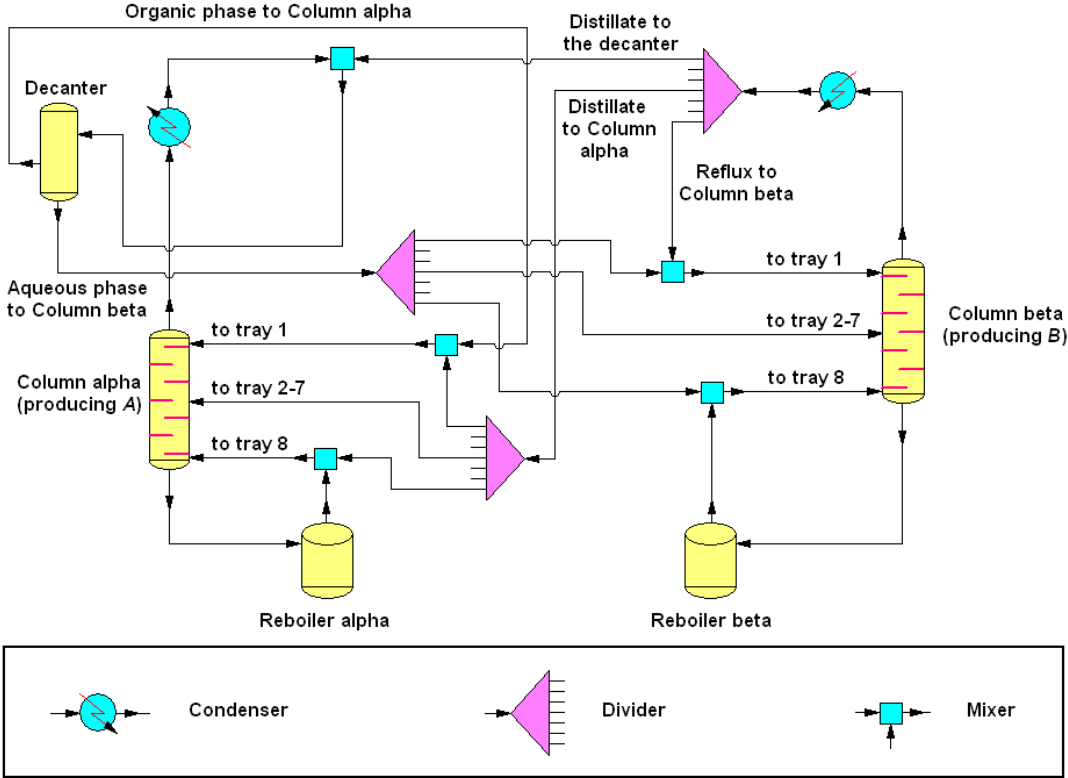
Fig. 2.23. ChemCAD-model of the GDCS
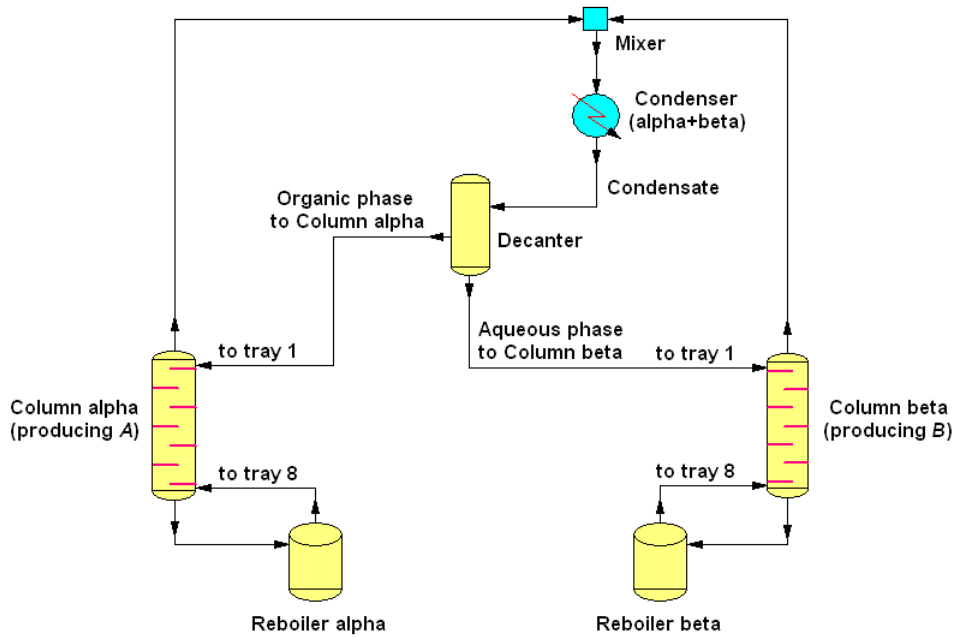
Fig. 2.24. Simplified ChemCAD-model of the DCS

2.2.5. Influence of the operational parameters

By applying rigorous simulation we studied the effect of the supplementary operation parameters ($f^{\alpha}, f^{\beta}, R^{\beta}$) on the energy demand of the process which is proportional to the duration. This study is performed for three different charge compositions (20, 40 and 66.2 mol% of *A*) and for the cyclohexane entrainer. During the sensitivity analysis only one of the new parameters is varied, the other two remain at their basic values.

2.2.5.1. Input data

Fixed parameters:

- Molar quantity of the charge: $U_{ch} = 100\,kmol$

- Composition of the charge: a. $\vec{x}_{ch,a} = [\,0.2, 0.8, 0\,]$

        b. $\vec{x}_{ch,b} = [\,0.4, 0.6, 0\,]$

        c. $\vec{x}_{ch,c} = \vec{x}_{BAZ} = [\,0.662, 0.338, 0\,]$

- Division of the charge: $u^{\alpha} = 0.6$

- Initial molar quantity of *E* in Reboiler α: $U_{b,E}^{\alpha} = 0.5\,kmol$

- Prescribed purity of the products: $x_{A/prodA} = x_{B/prodB} = 0.99$

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- Number of trays: $N^\alpha = N^\beta = 8$

- Tray holdup: $U_{HU}^\alpha = U_{HU}^\beta = 0.5\,kmol/tray$

- Decanter holdup: $U_{HU}^{dec} = 0.106\,m^3$

- Total heat duty of the reboilers: $Q = 12\,MJ/min = 200kW$

- Division of the heat duty (on the basis of preliminary calculations):

$$q^\alpha = Q^\alpha / Q = \frac{9.5\,MJ/min}{12\,MJ/min} = 0.792$$

The basic values of the parameters are chosen on the basis of the following considerations:

- f^α: If its value is high the distillate of Column β pollutes the A product because of its high B content (30-40 mol%). Therefore f^α must be low: $f^\alpha = 3$.

- f^β: If its value is low the aqueous phase increases the B content of the top vapour of Column β because of its high B content (approx. 70 mol%), although the aim is the removal of A. If it is high a lot of A is transferred into Reboiler β, which is advantageous for the production of B. Therefore f^β must be high: $f^\beta = 6$.

- R^β: If its value is high a lot of A returns to Column β, the production of B is slow. If N^β is high enough (e.g. $N^\beta = 8$) the BAZ composition can be reached also with low R^β. In this case A leaves Column β faster, too. Therefore R^β must be low: $R^\beta = 1/2$.

2.2.5.2. Results

2.2.5.2.1. Feed tray location in Column α (Fig. 2.25a-c)

This parameter f^α has influence mainly on the duration of the production of A (t^α). We get the shortest t^α when the distillate of Column β is fed into the decanter. When $f^\alpha = 1$ (top tray) the composition of the top vapour of Column α is out of the heterogeneous region therefore there is no liquid-liquid split in the decanter which makes the separation infeasible. From the 2nd tray the separation is feasible again but a further increase of f^α results in the increase of t^α. If $f^\alpha > 4$, the prescribed purity cannot be reached.

If the distillate of Column β is fed into the decanter, the duration of the production of B (t^β) is much longer than in the cases when it is fed into Column α because the distillate of Column β changes significantly the liquid composition in the decanter and the difference between the compositions of the two liquid phases is smaller (the tie line is shorter). When $f^\alpha = 1$ then for the two first charge compositions t^β is shorter than in the case when $f^\alpha = 2$ and for the third composition it is longer. From $f^\alpha = 2$ to 4-5 the increase of f^α does not result in any significant variation of t^β. After that t^β starts decreasing.

We can state that, for the sake of the minimum duration, the distillate of Column β must be fed into one of the upper trays except for the top tray to avoid decantation problems.
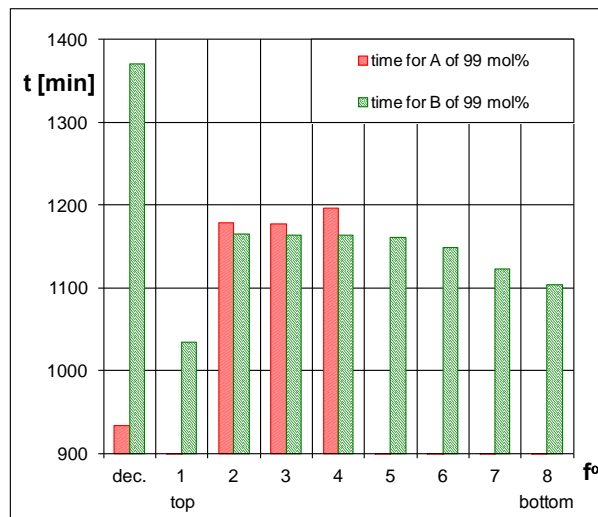
Fig. 2.25a. Effect of f^α on t^α and t^β ($x_{ch,A} = 0.2$, E: cyclohexane)

(The total duration is the shortest if $f^\alpha = 3$.)
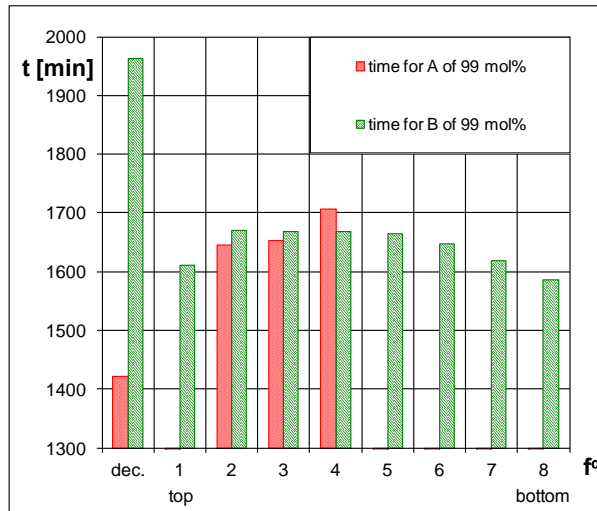
Fig. 2.25b. Effect of f^{α} on t^{α} and t^{β} ($x_{ch,A} = 0.4$, E: cyclohexane)

(The total duration is the shortest if $f^{\alpha} = 3$.)
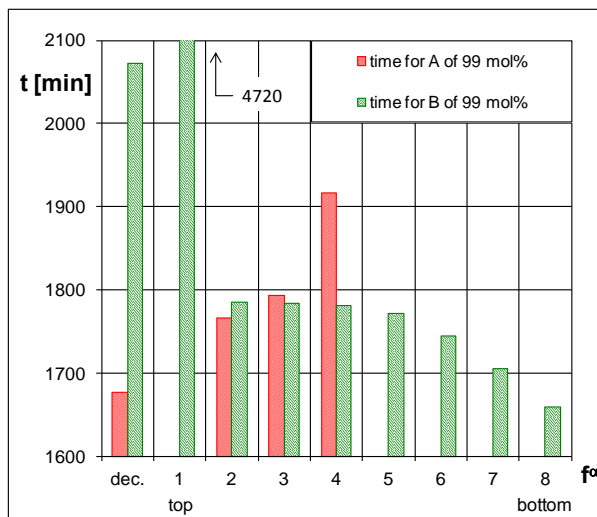
Fig. 2.25c. Effect of f^{α} on t^{α} and t^{β} ($x_{ch,A} = 0.662$, E: cyclohexane)

(The total duration is the shortest if $f^{\alpha} = 2$.)

2.2.5.2.2. Feed tray location in Column β (Fig. 2.26a-c)

This parameter has influence mainly on t^{β}. The increase of f^{β} results in considerable decrease of t^{β}. Its effect on t^{α} is slight and depends on the charge composition. For $x_{ch,a} = 0.2$ the increase of f^{β} results in a slight decrease of t^{α}, for $x_{ch,a} = 0.4$ there is not any effect and for $x_{ch,a} = 0.662$ t^{α} slightly increases.

We can state that the distillate of Column β must be fed into one of the lower trays.

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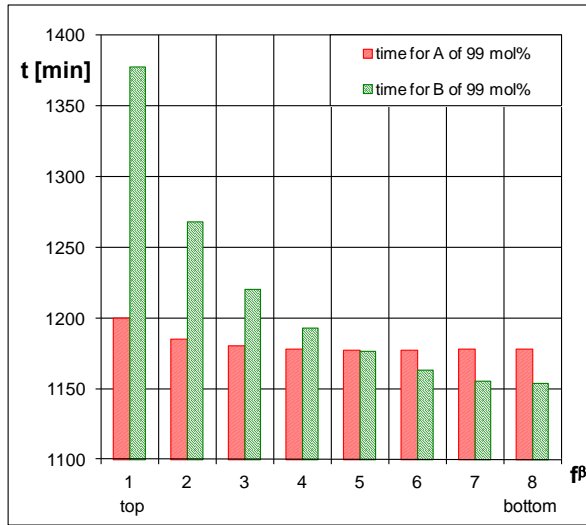
Fig. 2.26a. Effect of f^β on t^α and t^β ($x_{ch,A} = 0.2$, E: cyclohexane)

(The total duration is the shortest at $f^\beta = 5-8$.)
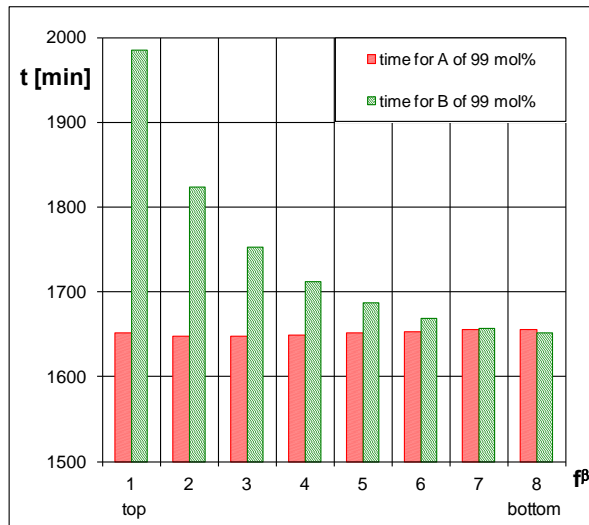
Fig.2.26b. Effect of f^β on t^α and t^β ($x_{ch,A} = 0.4$, E: cyclohexane)

(The total duration is the shortest at $f^\beta = 7-8$.)
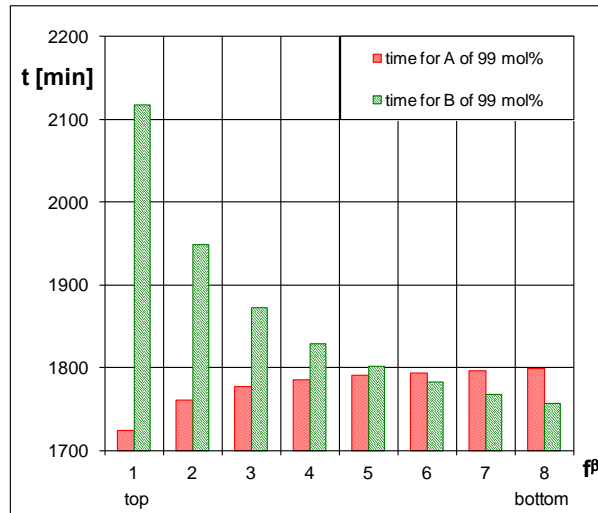
Fig. 2.26c. Effect of f^β on t^α and t^β ($x_{ch,A}$ = 0.662, E: cyclohexane)

(The total duration is the shortest at $f^\beta = 6$.)

2.2.5.2.3. Reflux ratio of Column β (Fig. 2.27a-c)

This parameter has strong influence on the duration of the production of both products, especially on t^β. The increase of R^β results in the increase of t^β and in the decrease of t^α. The purification of *B* needs less energy. Therefore the heat duty of Column β can be much less than that of Column α. Hence the flow rate of the top vapour β is much less than that of Column α, which results in a slighter effect of the flow rate of Distillate β (and R^β) on t^α. Therefore the absolute value of the slope of $t^\alpha(R^\beta)$ is much lower than that of $t^\beta(R^\beta)$.

We can state that it is worth applying a low reflux ratio in Column β ($R^\beta < 1$).
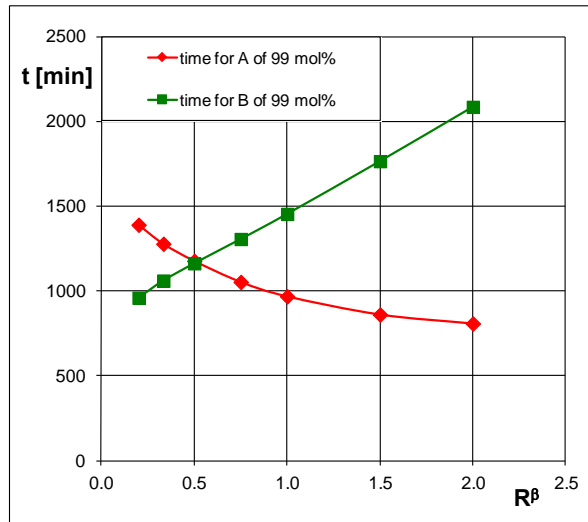
Fig. 2.27a. Effect of R^β on t^α and t^β ($x_{ch,A} = 0.2$, E: cyclohexane)

(The total duration is the shortest at $R^\beta = 0.5$.)
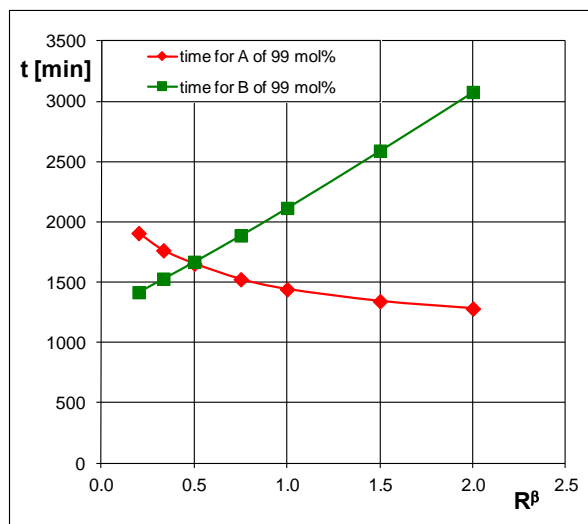
Fig. 2.27b. Effect of R^β on t^α and t^β ($x_{ch,A} = 0.4$, E: cyclohexane)

(The total duration is the shortest at $R^\beta = 0.5$.)
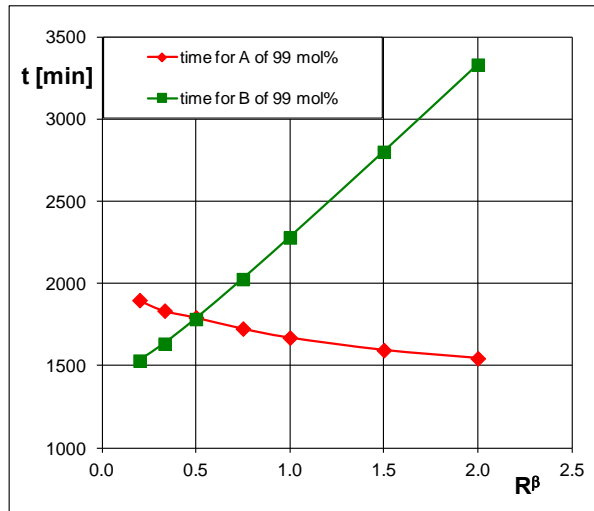
Fig. 2.27c. Effect of R^β on t^α and t^β ($x_{ch,A} = 0.662$, E: cyclohexane)

(The total duration is the shortest at $R^\beta = 0.5$.)

2.2.6. Comparison of the configurations

2.2.6.1. Method of the study

By applying rigorous simulation we compare the GDCS with the original DCS. In this study u^α, q^α and $U^\alpha_{b,E}$ are also variables beside $f^\alpha, f^\beta, R^\beta$. The fixed parameters are the same $\left(U_{ch}, \vec{x}_{ch}, x_{A/prodA}, x_{B/prodB}, N^\alpha, N^\beta, U^\alpha_{HU}, U^\beta_{HU}, Q\right)$ as in the study of the influence of the new operational parameters (Chapter 2.2.5). Before the comparison the optimal values of the variable parameters are determined for both configurations and for each charge composition. The objective function is the minimum duration of the process, the minimisation is performed by the downhill simplex method (Nelder and Mead, 1965, detailed in Appendix 3).

2.2.6.2. Domains of the variable parameters

- Feed tray location in Column α: $1 \le f^\alpha \le 8$ or the decanter

- Feed tray location in Column β: $1 \le f^\beta \le 8$

- Reflux ratio of Column β: $0 \le R^\beta < 1$

  The study of the effect of R^β showed that the duration is much higher than the optimum if $R^\beta \ge 1$.

- Initial division of the charge: $0.05 \le u^\alpha \le 0.95$

  (None of the reboilers can be empty at the beginning.)

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- Division of the heat duty: $0 < q^\alpha < 1$

- Initial molar quantity of E in Reboiler α: $0.5 \leq U_{b,E}^\alpha \leq 5\,kmol$

In the decanter the prescribed liquid levels of the two phases always guarantee the ternary azeotropic overall composition for the liquid holdup. In this case the holdup of the decanter must always contain 0.5 kmol of cyclohexane (or 0.65 kmol of n-hexane).

At the end of the process, entrainer can occur:

- in the decanter: 0.5 kmol,

- in Column α in the liquid holdup: max. $8 \times 0.5\,kmol = 4\,kmol$,

- in Reboiler α (in Product A): max. 0.5 kmol.

In Column β and Reboiler β practically there is no entrainer because of the low entrainer content of the aqueous phase fed into Column β. In each distillation system the amount of entrainer cannot be more than 5 kmol.

2.2.6.3. Results for the cyclohexane as entrainer

The optimum values of the operational parameters for both configurations are presented in *Table 2.6*. In the cases of the GDCS, the feed tray location of Column α is always one of the upper trays but not the top tray. The feed tray location of Column β is always the lowest tray and R^β is always low. For both configurations the major part of the charge must be fed into Reboiler β. The amount of the entrainer is always the possible minimum. The heat duty of Reboiler β is always higher than that of the other reboiler. The durations (*Fig. 2.28*) and the specific energy demands of the products (*Fig. 2.29*) are compared. In the cases studied the duration of the GDCS is always shorter (for each charge composition) and the specific energy demands of the products are also lower (for both components A and B and for each charge composition) than with the original DCS.

Mole fraction of A in the charge	Column configuration	Variable parameters					
		f^α	f^β	R^β	u^α	$U^\alpha_{b,E}$	q^α
		-	-	-	%	kmol	%
0.2	GDCS	3	8	0.05	5	0.5	70.7
	DCS	decanter	1	0	5	0.5	67.7
0.4	GDCS	3	8	0.16	7	0.5	66.8
	DCS	decanter	1	0	30	0.5	72.0
0.662 (BAZ)	GDCS	2	8	0.36	10	0.5	60.4
	DCS	decanter	1	0	18	0.5	54.4

Table 2.6. Optimum values of the variable operational parameters (E: cyclohexane)
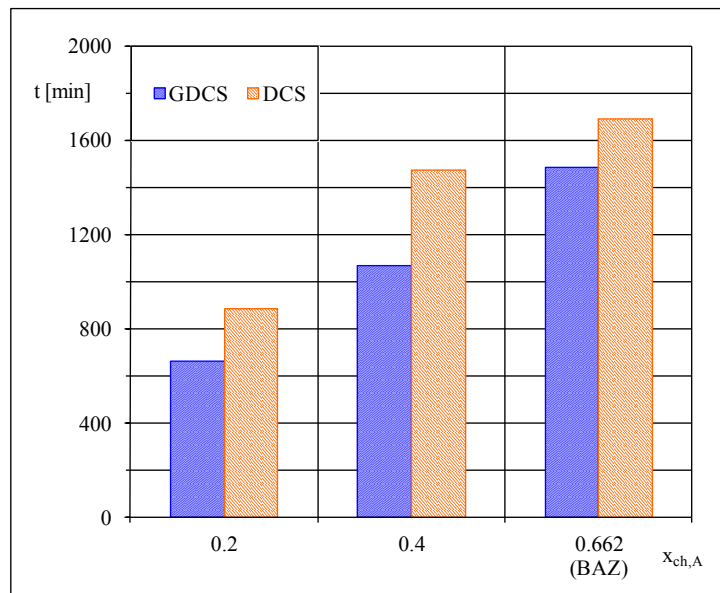
Fig. 2.28. Minimum duration for each configuration (E: cyclohexane)
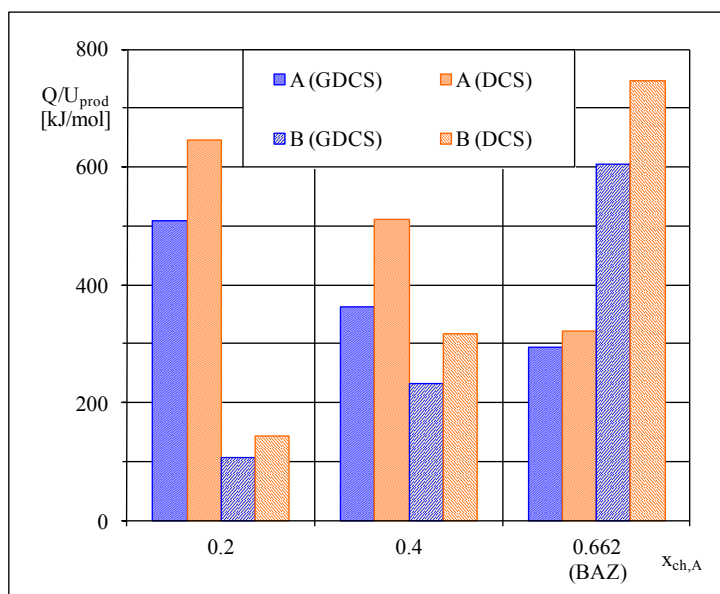
Fig. 2.29. Specific energy demand for each product and configuration

(E: cyclohexane)

2.2.6.4. Results for the n-hexane as entrainer

The comparison of the GDCS and the DCS is repeated by applying another entrainer (n-hexane), which seems to be more advantageous for the heteroazeotropic distillation of the mixture isopropanol – water than the cyclohexane (Subsection 2.2.6.6). The phase equilibria are described by the UNIQUAC model (parameters are given in Appendix 1). The optimum values of the operational parameters are shown in *Table 2.7*. The results are similar to those obtained for the cyclohexane. (The optimal feed tray location of Column β is always the lowest tray and R^{β} is always low.) However, for the GDCS the optimum feed tray of Column α is always Tray 1. Reboiler α must be charged in just all cases at the minimum level. The amount of the entrainer is always somewhat lower (by 14-27%) for the original DCS than for the GDCS. In each case the amount of the entrainer is higher than for the cyclohexane. The heat duty of Reboiler α is always higher for both configurations but the division of heat duty is more balanced than for the cyclohexane.

The duration of the GDCS is shorter for each charge composition (*Fig. 2.30*). The energy demands of both products are always lower by the GDCS than those by the DCS, except for one case (for *A* in the case of the charge containing 20 mol% *A*, *Fig. 2.31*).

Mole fraction of A in the charge	Column configuration	Variable parameters					
		f^{α}	f^{β}	R^{β}	u^{α}	$U^{\alpha}_{b,E}$	q^{α}
		-	-	-	%	kmol	%
0.2	GDCS	1	8	0.55	5	3.84	63.8
	DCS	decanter	1	0	5	3.30	64.8
0.4	GDCS	1	8	0.25	5	3.70	60.2
	DCS	decanter	1	0	5	2.92	56.8
0.662 (BAZ)	GDCS	1	8	0.42	5	3.88	55.2
	DCS	decanter	1	0	8	3.40	53.6

Table 2.7. Optimum values of the variable operational parameters (E: n-hexane)
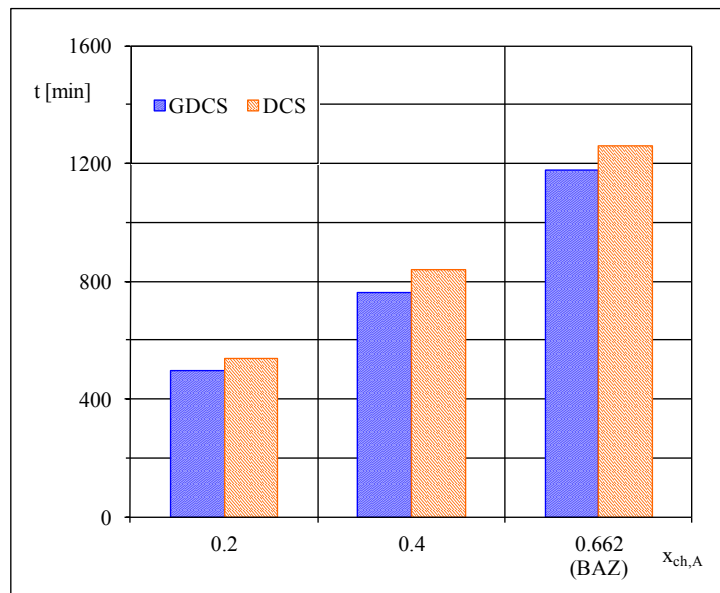
Fig. 2.30. Minimum duration for each configuration (E: n-hexane)
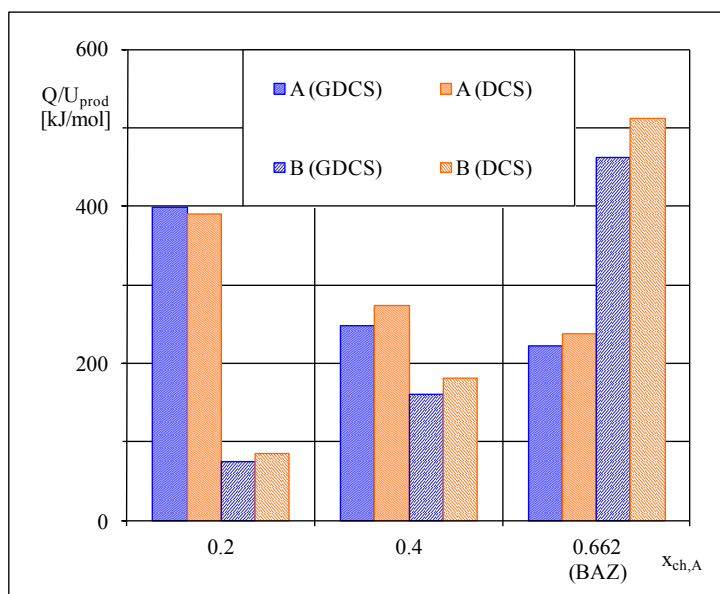
Fig. 2.31. Specific energy demand for each product and configuration (E: n-hexane)

2.2.6.5. Evolution of the reboiler liquid compositions

The still paths of the two different configurations are similar (*Figs. 2.32-33*). In Column α the still path begins in the interior of the triangle due to the *E*-addition. (In *Fig. 2.32*: in the homogeneous region, in *Fig. 2.33*: in the heterogeneous one) The *E* content of the initial holdup of Reboiler α is removed quickly therefore the still path approaches quickly the edge *A-B*. It turns toward the vertex *A* then approaches it closely. The purification of the reboiler liquid holdup is getting slower. In Column β the still path begins on the edge *A-B* and it remains on it. The purification starts slowly then it becomes faster and at the end it slows down again close to vertex *B*.
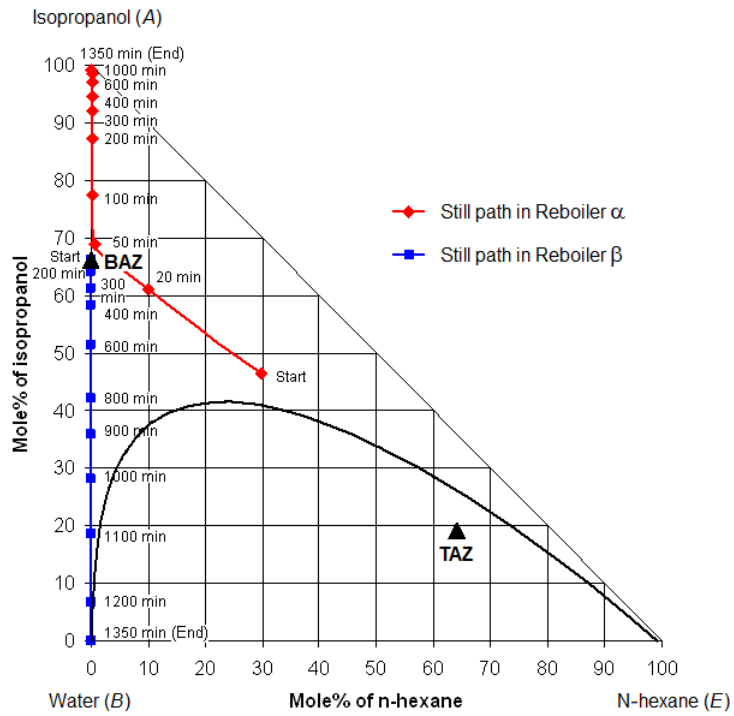
Fig. 3.32. Still paths for the DCS (charge: 66.2 mol% of A (BAZ composition), E: n-hexane)
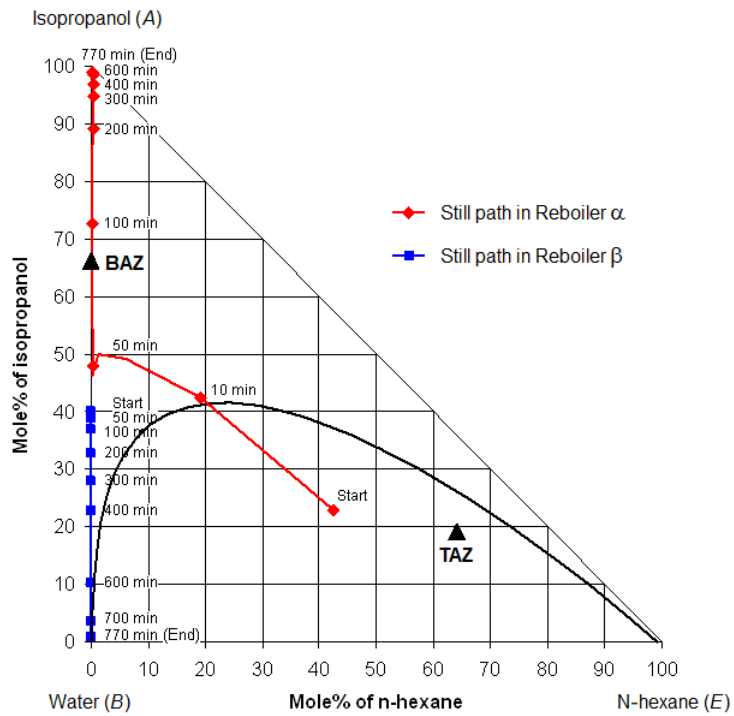
Fig. 2.33. Still paths for the GDCS (charge: 40 mol% of A, E: n-hexane)

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2.2.6.6. Comparison of the performances of the different entrainers

The binodal plots of the mixtures $A - B - E$ (*Fig. 2.34a* for the cyclohexane, *Fig. 2.34b* for the n-hexane) show the liquid-liquid phase splitting of the TAZ, its isopropanol content, and the length of the tie line passing through the TAZ point. The limit molar ratio of BAZ and TAZ between the homogeneous and heterogeneous phases is also displayed. Below this value the BAZ – TAZ mixture is heterogeneous otherwise homogeneous.

In *Table 2.8* the separating efficiency of the cyclohexane and n-hexane are compared on the basis of different properties depending on VLLE conditions. These properties are calculated also for benzene although it is not used in the study of the GDCS. The n-hexane seems to be more favourable than the cyclohexane and in the majority of the cases also than the benzene, respectively (which is not preferred because of its harmful effects on the health and environment despite its efficiency):

i. The IPA content of the TAZ is lower.

ii. The tie line passing through the TAZ is longer.

iii. The division of IPA between the organic and aqueous phases is more favourable.

iv. High ratio of the mole fractions of water and isopropanol in the ternary azeotrope $\left(\dfrac{x_{TAZ,B}}{x_{TAZ,A}} \right)$ is more favourable. For the more efficient separation it is better if in the aqueous phase of the ternary azeotrope withdrawn from Column α the mole fraction ratio of B and A $\left(\dfrac{x_{TAZ,B}^{AQ}}{x_{TAZ,A}^{AQ}} \right)$ is also the high. By the multiplication of these ratios a selectivity index can be defined:

$$SI = \frac{x_{TAZ,B}}{x_{TAZ,A}} \cdot \frac{x_{TAZ,B}^{AQ}}{x_{TAZ,A}^{AQ}} \tag{2.90}$$

v. Higher $R^{\alpha} = \dfrac{n_{TAZ}^{ORG}}{n_{TAZ}^{AQ}}$ can be ensured by refluxing only the organic phase.

vi. In the case of the DCS the condensate remains in the heterogeneous region at higher BAZ/TAZ ratio.

vii. The difference of the densities of the two liquid phases ($\Delta\rho$) is much higher.
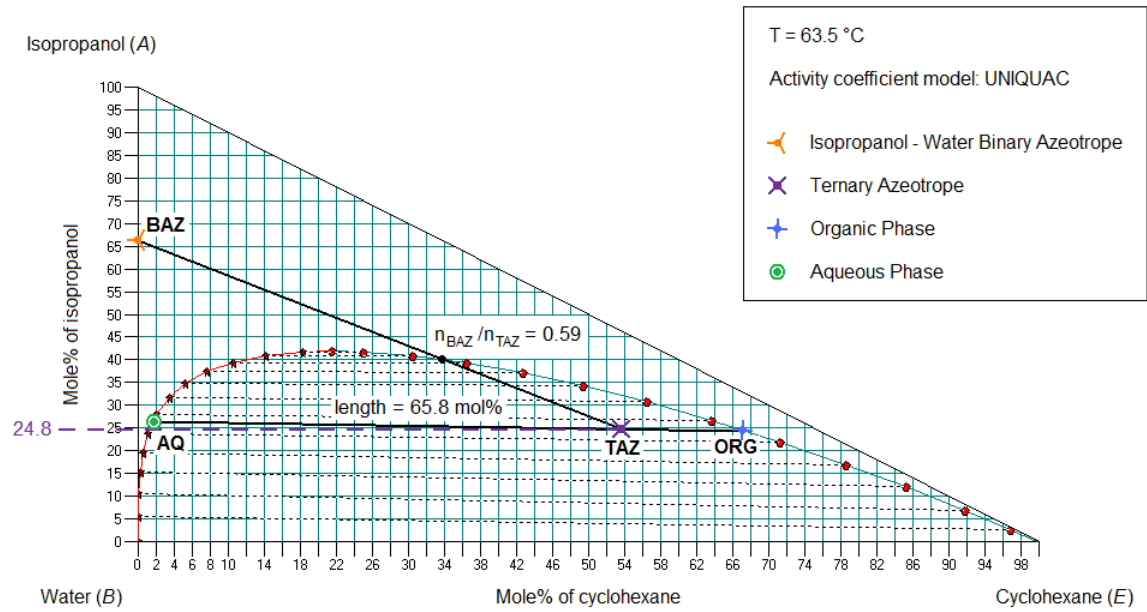
Fig. 2.34a. Binodal plot of the mixture isopropanol – water + cyclohexane at T_{TAZ}^{BP}

The binodal plot of the mixture A – B – cyclohexane shows the liquid-liquid splitting of the TAZ, its isopropanol content, and the length of the tie line passing through the TAZ point.
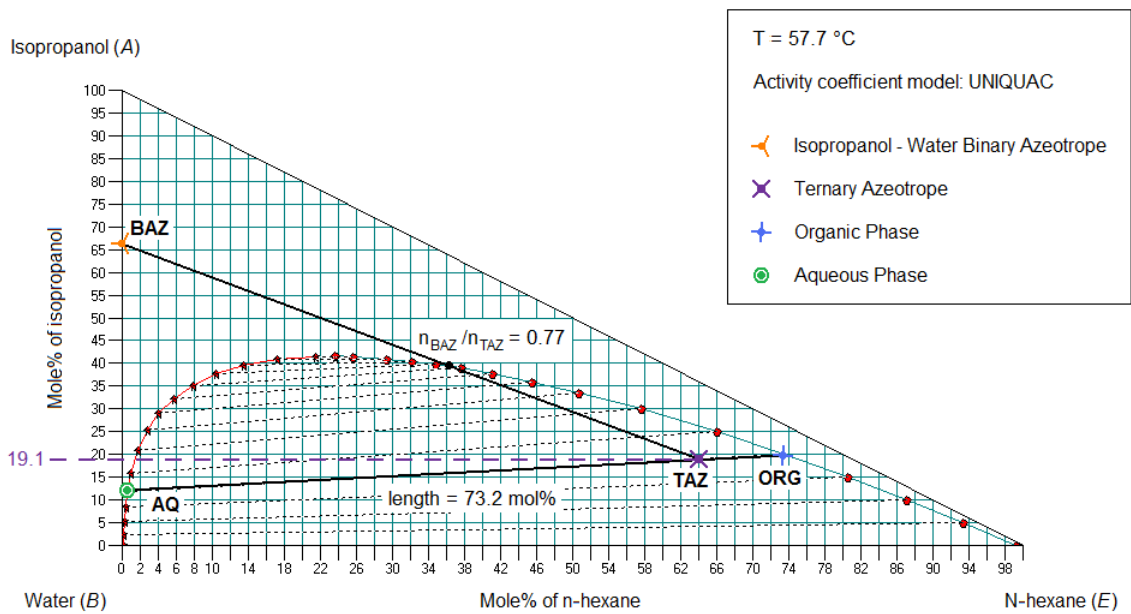
Fig. 2.34b. Binodal plot of the mixture isopropanol – water + n-hexane at T_{TAZ}^{BP}

The binodal plot of the mixture A – B – n-hexane shows the liquid-liquid splitting of the TAZ, its isopropanol content, and the length of the tie line passing through the TAZ point.

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	i	ii	iii	iv	v	vi	vii
	$x\%_{TAZ,A}$	$l_{TAZ\text{-}line}$	$\dfrac{n^{ORG}_{TAZ,A}}{n^{AQ}_{TAZ,A}}$	SI	R^{α}	max. $\dfrac{n_{BAZ}}{n_{TAZ}}$	$\Delta\rho$
	mol%	mol%	-	-	-	-	kg/m^3
Cyclohexane	24.8	65.8	3.57	2.43	3.79	0.59	83
N-hexane	**19.1**	**73.2**	**11.58**	**6.44**	**6.86**	**0.77**	**232**
Benzene	*23.8*	*69.4*	*2.71*	*8.76*	*3.43*	*1.81*	*70*

Table 2.8. Comparison of the entrainers

The simulation results correspond to the expectations: by using n-hexane as entrainer all results are more favourable than in the case of cyclohexane (*Table 2.9*):

- the duration is always much shorter,

- the amounts of both products are significantly higher (except for that of *A*, from the charge containing 20 mol% of *A*, in the GDCS).

For the GDCS in the case of binary azeotropic charge composition the distribution of each component is shown in *Table 2.10*. For the n-hexane the amount of *A* in Reboiler α and the amount of *B* in Reboiler β are higher at the end of the process than for the cyclohexane. These components remain in a smaller amount in the decanter.

Mole frac. of *A* in the charge	Column config.	t		$U^{\alpha}_{e,A}$		$U^{\beta}_{e,B}$		U_{byprod}	
		min		kmol		kmol		kmol	
		CHX	NHX	CHX	NHX	CHX	NHX	CHX	NHX
0.2	GDCS	660	**495**	**15.59**	14.92	74.48	**78.98**	10.43	**9.94**
	DCS	884	**538**	16.40	**16.57**	73.71	**76.75**	10.39	**9.98**
0.4	GDCS	1063	**762**	35.10	**36.81**	55.03	**57.03**	10.37	**9.86**
	DCS	1469	**840**	34.57	**36.95**	55.57	**55.99**	10.36	**9.98**
0.662 (BAZ)	GDCS	1485	**1176**	60.74	**63.59**	29.44	**30.50**	10.32	**9.79**
	DCS	1688	**1260**	63.05	**63.91**	27.17	**29.55**	10.28	**9.94**

Table 2.9. Comparison of the results for different entrainers

Comp.	Reboiler α (kmol)		Reboiler β (kmol)		Column α (kmol)		Column β (kmol)		Decanter (kmol)	
	CHX	NHX	CHX	NHX	CHX	NHX	CHX	NHX	CHX	NHX
A	60.13	62.95	0.28	0.30	2.45	2.27	1.33	1.17	0.38	0.16
B	0.08	0.28	29.16	30.20	0.08	0.13	2.68	2.83	0.54	0.17
E	0.53	0.36	0.00	0.00	1.48	1.61	0.00	0.00	0.58	0.66
Total	60.74	63.59	29.44	30.50	4.00	4.01	4.00	4.00	1.50	0.99

Table 2.10. Distribution of each component at the end of the process between the holdups of

the reboilers, the columns, and the decanter ($\vec{x}_{ch} = \vec{x}^{BAZ}$)

2.3. Conclusions

We suggested a new Double-Column System (DCS) for heterogeneous batch distillation. The system is operated in closed mode without continuous product withdrawal. This configuration was investigated by feasibility studies based on a simplified model (assumption of maximal separation, neglect of hold-up) and by dynamic simulation (based on a detailed model) by using a professional simulator (CC-DCOLUMN). The performance of this new DCS was compared with the traditional Batch Rectifier (BR). For the new configuration we determined the minimal operational time. The calculations and the simulations were performed for the heteroazeotropic mixture 1-butanol – water and for the ternary heteroazeotropes isopropanol – water + benzene or cyclohexane (entrainer). For both configurations we determined the optimal quantity of entrainer to be applied and for the new double-column system (DCS) the optimal divison of the entrainer, the charge and the total heat duty providing the minimal operational time for the different configurations. The new configuration proved to be feasible and competitive with the conventional BR. For the binary mixture DCS gave similar and for the ternary one better performance than the BR. Its main benefit is that it produces less byproducts to be separated later.

Then we studied the separation of the minimum homoazeotropic mixture isopropanol – water by applying cyclohexane and n-hexane as entrainer in a new Generalised Double-Column batch heteroazeotropic distillation System (GDCS). This configuration has three supplementary operational parameters comparing with the original DCS: the feed tray location of the distillate of Column β in Column α (f^{α}), the feed tray location of the aqueous phase of the decanter in Column β (f^{β}) and the reflux ratio in Column β (R^{β}). These

parameters provide the possibility of a more flexible and more efficient operation like that of the original Double-Column System (DCS).

First the feasibility of the GDCS was studied by a simplified method by using only the integral material balances. The separation by the GDCS proved to be feasible.

Then the influence of the supplementary operational parameters of the GDCS was studied by rigorous simulation. This study made clear the choice of the values of the operational parameters: the distillate of Column β must be fed into one of the upper plates of Column α, the aqueous phase from the decanter must be fed into one of the lower plates of Column β, and the reflux ratio of Column β must be low ($R^\beta < 1$).

After that the minimum duration of the process was determined for the GDCS and for the original DCS and their performances were compared (duration, specific energy demands of the products). By the downhill simplex method the optimum values of the operational parameters were also determined. The above investigations were done for three different charge compositions and for both entrainers. In every case shorter duration was obtained for the GDCS. The specific energy demands of the products were also lower in almost all cases.

Finally the performances of the entrainers were compared. On the basis of the VLLE conditions the n-hexane is more advantageous than the cyclohexane. This is also confirmed by the simulation results, as well: for n-hexane the duration is always shorter, the amounts of the products are in the majority of the cases higher and the total amount of the byproducts is always lower for both configurations.

CHAPTER 3

EXPERIMENTAL STUDY
OF THE NEW CONFIGURATIONS

3. Experimental study of the new configurations

In this chapter the experimental validation of the Double-Column System and that of its generalised version (GDCS) is presented. First laboratory experiments were done for the separation of a binary heteroazeotropic mixture in a simple small size equipment operated as BR and DCS. Then a pilot plant was used for the same separation as DCS. After this experiment the separation of a binary homoazeotropic mixture by using an entrainer was studied in the equipment operated as BR and GDCS.

3.1. Laboratory experiments for a binary mixture

In this chapter the separation of the heteroazeotropic mixture 1-butanol (*A*) – water (*B*) is studied experimentally in the new (DCS) and in the traditional configurations (BR) and their performances are compared by posterior simulation.

3.1.1. Description of the laboratory equipment

The BR and the DCS (*Fig. 3.1*) consist of the same laboratory means. Most of them are made of glass: boiling vessels (spherical flasks of volume 1000 ml (Reboiler α) and 2000 ml (Reboiler β) with three necks), columns, decanter and condenser. For both flasks there are electric heating mantles in convenient size. The nominal electric performances of the heating mantles are 300 W and 450 W, respectively. The two columns have the same parameters: both of them are double-walled, the height of the packing (H) is 1 m, the internal diameter (D) is 30 mm. The packing consists of Raschig rings made of glass whose average external diameters and heights (d_p) are approximately 7 mm. Both columns are thermally isolated by foamed plastic mantle.

The volumetric liquid holdup of the decanter is 55 ml and it is also thermally isolated.

The condenser is a spiral cooler cooled by running water. The liquid temperatures in the flasks are measured by mercury thermometers calibrated with water.

The composition of the mixtures is determined on the basis of their refractive indices (Appendix 4). The refractometer is thermostated by a liquid circulating thermostat.

3.1.2. Experimental results

First the mixtures to be separated are presented then the operation of the two distillation systems and finally the results of the experiments are shown.

3.1.2.1. Properties of the charges

The composition of the charge is azeotropic (mole fraction of 1-BuOH is 0.256). It contains 1270 ml of 1-BuOH (component *A*) and 730 ml of water (component *B*).

I. Double-Column System

After mixing of the components the heterogeneous mixture is decanted (*Table 3.1*). The temperature of the charge is T_{ch} = 23 °C.

II. Batch Rectifier

The volumes of the phases (*Table 3.1*) after the decantation slightly differ from those of the previous case. (A possible reason of this difference is that T_{ch} = 27 °C.)
The compositions of the phases are the same as in the case of the DCS.

Configuration		DCS		BR	
Liquid phase	-	*A*-rich phase	*B*-rich phase	*A*-rich phase	*B*-rich phase
Volume	ml	1450	525	1445	550
Mole fraction of *A*	-	0.491	0.018	0.491	0.018

Table 3.1. *Volumes and compositions of the liquid phases to be processed in the DCS (mixture: 1-butanol – water)*
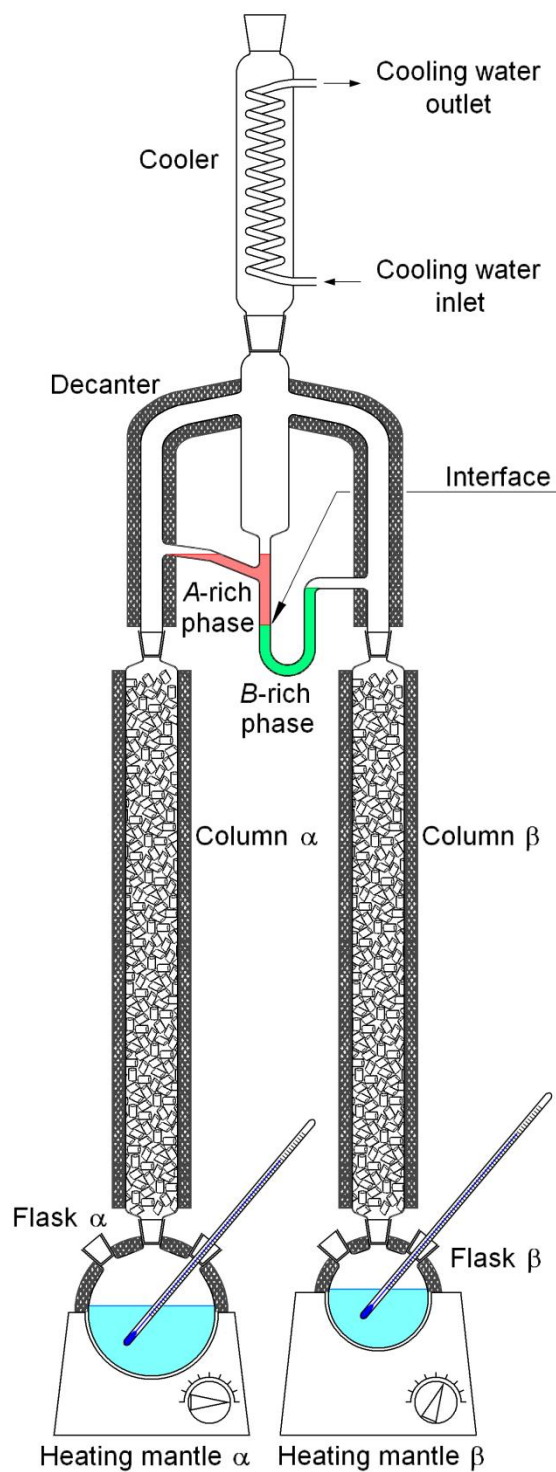
Fig. 3.1. *Laboratory double-column system*

3.1.2.2. Operation of the distillation systems

I. Double-Column System

After the decantation the organic (*A*-rich) phase is fed into Flask α and the aqueous (*B*-rich) one into the Flask β. Initially the decanter is empty and the columns are dry. Both heating mantles are switched on at the same time. Their electric performances are controlled manually so that the two liquids start boiling nearly at the same time. After that the heatings are not modified and the system can be operated without any intervention. When the liquid temperatures in both flasks practically reach the boiling points of the pure components and become constant the heating is switched off. (The ambient pressure is 100.3 kPa.)

II. Batch Rectifier

The binary mixture is processed in the DCS operated as a BR. One of the flasks is empty at the beginning and it is not heated. (Since its holdup is very low, the cold column causes just a negligible material loss.) The two phases of the charge are processed sequentially in two operation steps.

Step 1. Production of the n-BuOH

The *A*-rich phase is fed into Flask α and Flask β is left empty. Initially the decanter is empty and the columns are dry. Only Heating mantle α is switched on. Its electric performance is kept permanently at the maximum during the whole step. The system can be operated without any intervention. When the liquid temperature in Flask α reaches the boiling point of the n-BuOH and becomes constant the heating is switched off. In Flask β the distillate is collected which is the *B*-rich phase of the condensate. The decanter is not emptied because there is need for its liquid holdup in Step 2. (The ambient pressure is 100.1 kPa and the ambient temperature is 27 °C.)

Step 2. Purification of the water

The *B*-rich phase of the charge and the distillate of Step 1 are mixed and they are fed into Flask β. Flask α is emptied. In this step only Heating mantle β is switched on. Its electric performance is kept permanently at the maximum during the whole step. The system can be operated without any intervention. When the liquid temperature in Flask β reaches the boiling point of the water and becomes constant the heating is switched off. In Flask α the distillate is

collected which is the organic phase of the condensate. (The ambient pressure is 100.1 kPa and the ambient temperature is 27 °C.)

3.1.2.3. Results of the experiments

I. Double-Column System

The liquid temperatures in both flasks are registered during the whole process (*Fig. 3.2*). The boiling temperatures of the products are higher than that of the pure components at the ambient pressure. The difference for *A* is 1.2 °C and for *B* is 1.5 - 2 °C. The boiling points elevated can be caused by the pressure drop of the columns and/or by some contaminations in the liquids. (It is possible that the pumice can contain some soluble components which can increase the boiling temperature.)

		Product *A*	Product *B*	Liquid holdup of the decanter	
				A-rich phase	*B*-rich phase
Volume	ml	1230	710	24.5	30.5
Mole fraction of *A*	-	1.000	0.000	0.485	0.018
Recovery	%	96.9	97.3	-	-

Table 3.2. *Properties of the products and the byproducts of the experiment with the DCS (mixture: 1-butanol – water)*

The liquid temperature in Flask β reached much earlier its target value. (Since the setting of the ratio of the heat duties was not optimal.) Until $\tau = 200\,min$ both temperatures reached a constant value. Each component were produced in high purity with good recovery (*Table 3.2*). The overall volume of the byproducts (60 ml) was nearly the same as the volume of the final liquid holdup of the decanter (55 ml). (This means that the holdups of the columns are negligible.)

II. Batch Rectifier

The liquid temperature in the flasks is registered continuously (*Fig. 3.3*). The boiling temperatures of the products are higher than expected also in this case. The total duration $\left(\tau = \tau_1 + \tau_2 = 144 + 53 = 197\,min\right)$ is nearly equal to that of the DCS. Both products are very pure but their recoveries are much lower than in the case of the DCS (*Table 3.3*). By this

configuration not only the final holdup of the decanter is the byproduct but also the distillate of Step 2. Because of the construction of the system a part of the condensate flowing from the cooler gets directly to the cold Column β (and then to the distillate flask) bypassing the decantation space. This phenomenon results in a heterogeneous distillate whose *B*-rich phase is added to the *B*-rich phase of the charge to be processed in Step 2 but the *A*-rich phase is considered as a byproduct. The overall volume of the products and the byproducts is 1922 ml. The reason of the higher loss is that in the case of the BR more fillings and emptying (draining) operations are needed.

		Product *A*	Product *B*	Byproducts from the distillates of Step 1 & 2		Liquid holdup of the decanter	
				A-rich phase	*B*-rich phase	*A*-rich phase	*B*-rich phase
Volume	ml	1110	620	118	20	24	30
Mole fraction of *A*	-	1.000	0.000	0.488	0.019	0.495	0.018
Recovery	%	87.4	84.9	-	-	-	-

Table 3.3. *Properties of the products and the byproducts of the experiment with the BR (mixture: 1-butanol – water)*

3.1.3. Simulation results

The simulation method is the same as in the earlier simulations. First the input data then the results of the simulations are presented.

3.1.3.1. Input data

The height equivalent to a theoretical plate (*HETP*) of the Raschig ring packing is estimated by using Granville's formula (Granville, 1957):

$$HETP\,(m) = 28 \cdot d_p \cdot \overline{m} \cdot \frac{V}{L} \cdot \left(\frac{H}{2.4}\right)^{1/3} \qquad (3.1)$$

where $\overline{m}$ denotes the average slope of the VLE curve weighted by the theoretical plates. V/L is the ratio of the molar flow rates of the vapour and the liquid at the top of the column. By using the reflux ratio:

$$\frac{V}{L} = 1 + \frac{1}{R} \qquad (3.2)$$

On the basis of experimental data completed by calculated ones, for Column α $HETP$ is 0.26 m, that is, $N^\alpha = 3.9 \approx 4$. For the other column $HETP$ is 3.0 m, that is, N^β would be less than 1. Since during the experiments the water product is reached quickly, this value for N^β does not seem to be correct. Therefore another literature source is used for the estimation of N^β. In the book of Kirschbaum (1960) several experiments are evaluated in order to determine the number of theoretical trays among others also for Raschig ring packing. Although these experiments were done under different conditions like our ones (wider columns, another components, larger packing particles, total reflux) but because of the similarities (the same pressure, gas velocity and packing height) their results are useful. Despite their diversities from each other they gave similar results: $1/HETP = 4.5 - 6.5\,m^{-1}$.

Therefore the number of theoretical trays of the 1 m high packed sections of the columns (of holdup of 5 ml) without condenser, decanter and reboiler is considered as 5. In this case the HETP of the Raschig ring packing is 0.2 m. The simulations are done also for $HETP = 0.1m; 0.3m$, that is, for $N^\alpha = N^\beta = 3;10$.

Both reflux and distillate (BR) are homogeneous. The holdup of the decanter is 55 ml and the levels of liquid phases are fixed (after the start-up). The liquid temperature in the decanter is specified as 60 °C. The heat duties of the reboilers are so chosen to give boiling-up periods as long for the DCS as in the experiment ($Q^\alpha = 195W$, $Q^\beta = 145W$). The prescribed purities of both products are 99.5 mol%. The calculations are started with dry trays and decanter except for Step 2 of the BR. At the start of this step the decanter is filled with the liquid remained from Step 1.

3.1.3.2. Results

I. Simulation of the DCS experiment

Similarly to the experiment the purification of *A* demands much more time (147 min) than that of *B* (26 min, *Fig. 3.2a*). Because of the different experimental and calculated durations the reboiler liquid temperature profiles do not coincide but their characters are similar. The reason of the difference of the durations is that the effective heat duties cannot be accurately estimated. Another simulation was done by applying reboiler heat duties resulting the same durations as the measured ones (*Fig. 3.2b*). In both cases the reason of the differences

between the temperatures measured and computed is probably the inaccuracy of the measurement of temperature and/or the increase of boiling points because of the increase of the reboiler pressure. The product quantities are in good agreement with those of the experiment (*Tables 3.2* and 3.*4*). Simulations were also repeated with different numbers of plates ($N^{\alpha} = N^{\beta} = 3;10$). These simulations gave practically identical results (*Table 3.4*). Therefore in the later simulations it is sufficient to apply $N^{\alpha} = N^{\beta} = 5$.

HETP m			Product A	Product B	Liquid holdup of the decanter	
					A-rich phase	B-rich phase
0.1	Volume	ml	1213	678	18	36
	Mole fraction of A	-	0.995	0.000	0.489	0.019
	Recovery	%	97.1	93.1	-	-
0.2	Volume	ml	1218	683	18	36
	Mole fraction of A	-	0.995	0.000	0.489	0.019
	Recovery	%	97.5	93.8	-	-
0.3	Volume	ml	1219	684	18	36
	Mole fraction of A	-	0.995	0.000	0.489	0.019
	Recovery	%	97.6	94.0	-	-

Table 3.4. *Properties of the products and the byproducts of the simulation of the DCS (mixture: 1-butanol – water)*

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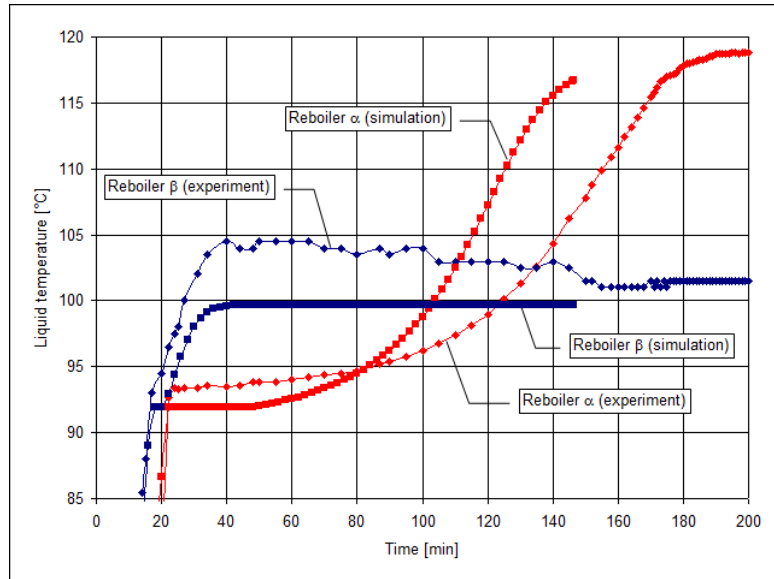
Fig. 3.2a. *Evolution of liquid temperatures in the reboilers of the DCS*

(after the start of boiling, simulation: $N^{\alpha} = N^{\beta} = 5$, mixture: 1-butanol – water)
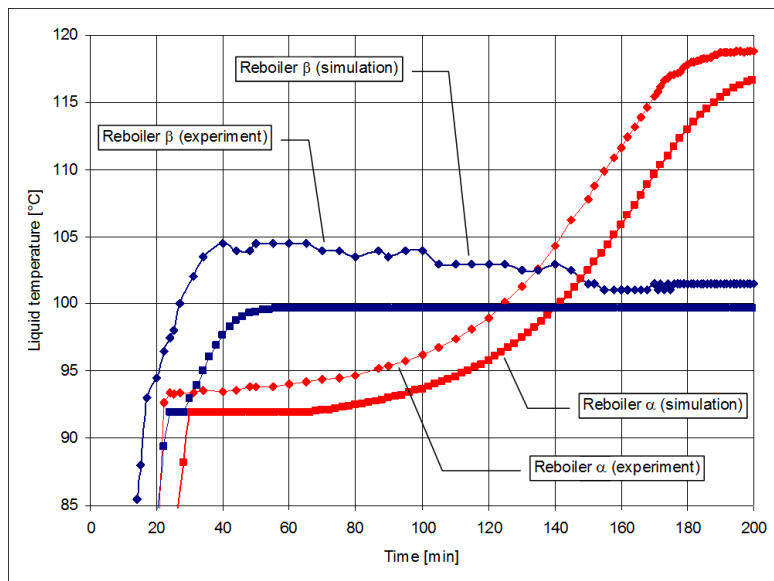
Fig. 3.2b. *Evolution of liquid temperatures in the reboilers of the DCS by applying reboiler heat duties resulting in the same duration for the simulation as the measured one*

(after the start of boiling, simulation: $N^{\alpha} = N^{\beta} = 5$, mixture: 1-butanol – water)

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II. Simulation of the BR experiment

The duration computed of Step 1 (141 min) is in good agreement with the measured one. For Step 2 the duration is prescribed (53 min as in the experiment) instead of the product purity. (For the product *B* it results in much higher purity than 99.5 mol% (*Table 3.5*) similarly to the experiment.) The evolution curves of the reboiler liquid temperatures are almost congruent with the experimental ones (especially for Step 1, *Fig. 3.3*). The reason of the nearly constant difference between the curves is probably the error of the thermometers and/or the increase of boiling points because of the increase of the reboiler pressure. The small difference between the measured and computed quantities of product *A* is caused by the imperfection of the laboratory equipment. The amount of the byproducts also differs for this reason. If the branches of the decanter were closable the vapour could not get to the cold column and condensate there. In the case of product *B* a greater difference can be found.

		Product *A*	Product *B*	Byproducts from the distillates of Step 1 & 2		Liquid holdup of the decanter	
				A-rich phase	*B*-rich phase	*A*-rich phase	*B*-rich phase
Volume	ml	1162	703	52	0	15	38
Mole fraction of *A*	-	0.995	0.000	0.567	-	0.488	0.020
Recovery	%	93.0	93.9	-	-	-	-

Table 3.5. *Properties of the products and the byproducts of the simulation of the BR (mixture: 1-butanol – water)*
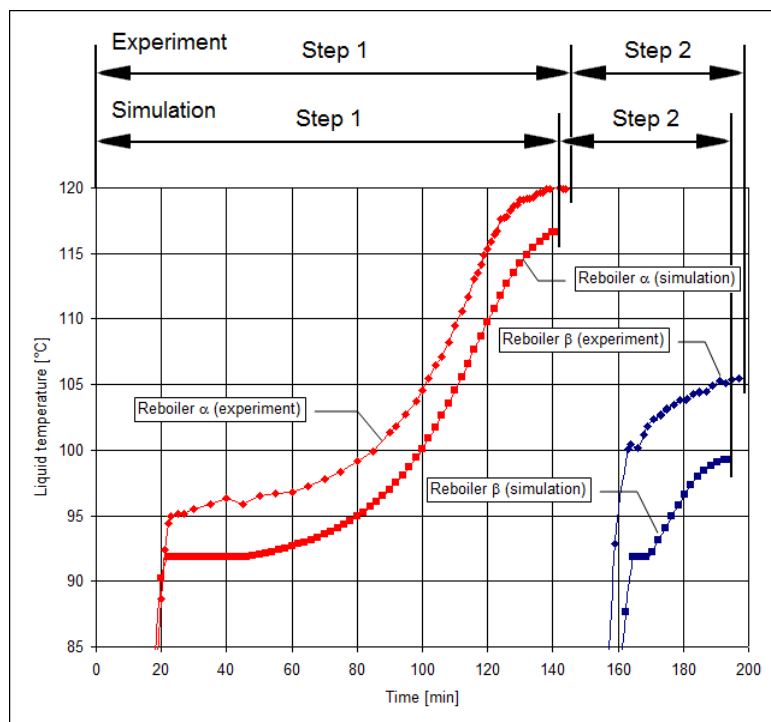
Fig. 3.3. *Evolution of liquid temperatures in the reboiler(s) of the BR*

(after the start of boiling, mixture: 1-butanol – water)

3.1.4. Conclusions

The DCS was studied by laboratory experiments. Our primary aim was to investigate the feasibility of the separation of the heteroazeotropic mixture 1-butanol – water in a DCS, therefore a very simple laboratory equipment was applied. We compared the performance of the DCS with that of the conventional Batch Rectifier. We also performed rigorous simulations by using ChemCAD 6.0 CC-DCOLUMN. On the basis of the results the separation in the DCS proved to be feasible and competitive with that of the BR. By using the DCS higher recovery for 1-butanol was reached during practically the same time and the quantity of the byproducts was also less for the DCS.

3.2. Pilot plant experiments

Because of the simple construction of the previous laboratory equipment the experiments done with it gave less information than desired (no column temperatures, no top temperature, no pressure drop). In addition, the operation of that equipment is less flexible and less convenient (non-variable reflux, heterogeneous wild reflux because of the common condenser and the geometry of the common head of the columns, low decanter holdup). For the successful separation of a binary homoazeotropic mixture by using an entrainer the above imperfections have to be eliminated. Therefore a more sophisticated pilot plant was built for the further experiments.

3.2.1. Description of the laboratory equipment

The Double-Colum System (*Fig. 3.4.*) consists of two distillation columns which have their own reboilers, heater equipments, reflux dividers, condensers and aftercoolers. Their distillates flow into a common decanter from where both columns are fed: Column α by light (organic) phase, Column β by heavy (aqueous) phase. The majority of the measured data are registered by two data loggers.

In this chapter the most important parameters of the system are mentioned. Further details can be found in Appendix 5.
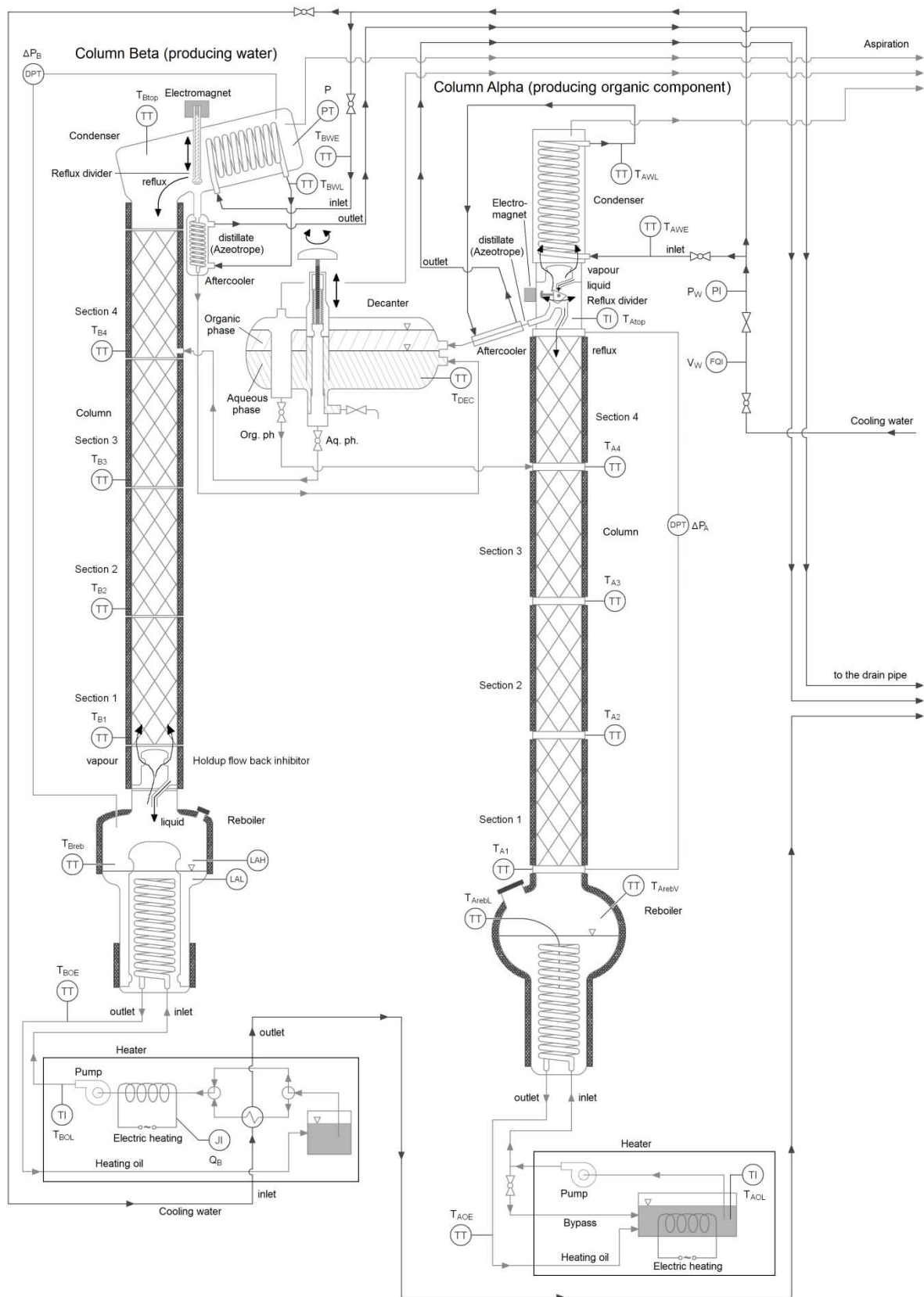
Fig. 3.4. DCS laboratory equipment for the separation of a heteroazeotropic mixture

I. Columns

a. Column α

The column consists of 4 sections made of glass which are filled by structured packing Sulzer CY and are thermally insulated. Its height is 4 x 1 m, its internal diameter is 82 mm. The temperature of the column is measured by resistance thermometers in the joining elements under each section (from down to top: T_{A1}, T_{A2}, T_{A3}, T_{A4}; °C). The pressure drop of the column (ΔP_A, mbar) is also measured.

b. Column β

The column consists of 4 sections made of glass which are filled with structured packing Kühni Rombopak and are thermally insulated. Its height is 4 x 1 m, its internal diameter is 80 mm. The temperature of the column is measured at the bottom of each section (from down to top: T_{B1}, T_{B2}, T_{B3}, T_{B4}; °C). The pressure drop of the column (ΔP_B, mbar) is also measured.

II. Reboilers

a. Reboiler α

The reboiler made of glass can be charged by maximum 10 liters of liquid. The heating of the holdup of the reboiler is realised by heating liquid circulating in a double spiral. The liquid temperature (T_{ArebL}, °C) is measured by a resistance thermometer. The temperature of the vapour space (T_{ArebV}, °C) is measured by an industrial thermocouple. The reboiler has partial thermal insulation.

b. Reboiler β

The reboiler made of glass can be charged by maximum 11 liters of liquid. The heating of the holdup of the reboiler is realised by heating liquid circulating in a quaternary spiral (two upward branches and two returning ones). The temperature (T_{Breb}, °C) is measured by a resistance thermometer. A differential manometer is connected to the reboiler, too. Its other branch is connected to the condenser of Column β. It measures the pressure drop of the column (ΔP_B, mbar). The reboiler has partial thermal insulation.

III. Heaters

a. Heater α

The heating medium is oil which is circulated and heated by electricity. The maximum performance of the electric heater is 6 kW. The flow rate of the oil led into the reboiler spiral can be set by a bypass. The temperature of the oil leaving the heater is displayed on the control panel (T_{AOL}, °C). The temperature of the oil entering (T_{AOE}, °C) is measured by a resistance thermometer. During the operation of the heating equipment the heating is turned on and off depending on the actual value of T_{AOL}. If T_{AOL} is higher than the temperature set ($T_{oil,set}$) then the heating is turned off. Because of the inertia T_{AOL} is still increasing for a while then it begins to decrease. When it reaches $T_{oil,set} - 1$ °C the heating is turned on again. Because of this periodic operation the heat duty is oscillating.

a. Heater β

The heating medium is oil which is circulated and heated by electricity. The temperature of the oil led into the reboiler spiral can be set by a combination of electric heating $(P_{max} = 4\,kW)$ and water cooling. The temperature of the oil leaving the heater is displayed on the control panel (T_{BOL}, °C). The temperature of the oil entering (T_{BOE}, °C) is measured by a resistance thermometer. The actual electric performance or the cooling performance is displayed (Q_B, %).

IV. Condensers

a. Condenser α

The condenser made of glass is open to the atmosphere. The cooling water flows in a triple spiral. The cooling surface is 1 m^2. The temperatures of the entering (T_{AWE}, °C) and leaving cooling water streams (T_{AWL}, °C) are measured by resistance thermometers.

b. Condenser β

The condenser made of glass is open to the atmosphere. The cooling water flows in a quaternary spiral. The top vapour temperature (T_{Btop}, °C) and the temperatures of the entering (T_{BWE}, °C) and leaving cooling water streams (T_{BWL}, °C) are measured by resistance thermometers. A manometer measures the pressure in the condenser which is practically the

ambient pressure (P, mbar). A branch of a differential manometer is connected to the cold end of the condenser. Its other branch is connected to Reboiler α. It measures the pressure drop of the column (ΔP_B, mbar).

V. Aftercoolers

a. Aftercooler α

The distillate leaving the condenser flows through an aftercooler made of steel before arriving in the decanter. The cooling water flows in countercurrent with the distillate.

b. Aftercooler β

The distillate leaving the condenser flows through an aftercooler made of glass before arriving in the decanter. The cooling water flows in countercurrent with the distillate.

VI. Reflux dividers

a. Reflux divider α

The condensate flows back through a pipe into a funnel. The further path of the condensate (back to the column or to the decanter) can be controlled by the variation of the position of the bottom of the funnel by an electromagnet. A thermocouple measures the vapour temperature (T_{Atop}, °C).

b. Reflux divider β

The position of the reflux valve (open or closed) is controlled by an electromagnet.

VII. Decanter

The decanter is made of glass. Its liquid holdup is 3.6 dm^3. There are two outlets: a fixed one for the light liquid phase and a moveable for the heavy phase, whose position can be varied manually. A resistance thermometer measures the temperature of the liquid in the decanter close to the feed location (T_{DEC}, °C).

VIII. Holdup flow back inhibitor of Column β

The holdup flow back inhibitor made of glass is suitable for the storage of 250 cm^3 of liquid flowing back from the column at the end of the experiment.

IX. Registration of the measurement data

a. Registration of the measurement data of Column α

The data logger has an own memory where it stores the measured data which can be copied into a USB drive.

b. Registration of the measurement data of Column β

The control panel of Column β which serves also as a data logger is connected with a computer on which a data registering software runs.

3.2.2. Pilot plant experiments for a binary mixture

3.2.2.1. Charge and initial holdup of the decanter

The components of the mixture are 1-butanol (*A*) and water (*B*).

Because of the geometry of the reboilers the minimum and maximum liquid volumes are

limited: Reboiler α: 6.5 dm^3 < V$_{liquid}$ < 10 dm^3

Reboiler β: 9 dm^3< V$_{liquid}$ < 11 dm^3

These conditions can be satisfied only if the overall composition of the charge is in the heterogeneous composition range. Therefore the initial liquids in the reboilers are saturated phases which were prepared separately. Because of the large quantity of the total charge the decantation could not have been feasible. Into the reboiler of Column α saturated organic phase, into the other one saturated aqueous phase are fed (*Table 3.6*). The decanter is filled with heterogeneous liquid (whose phases are saturated, too).

		V [dm^3]
Reboiler α (organic phase)		8.0
Reboiler β (aqueous phase)		9.0
Decanter	Organic phase	0.9
	Aqueous phase	2.5
Total		**20.4**

Table 3.6. Initial charge of the reboilers and the initial holdup of the decanter
(mixture: 1-butanol – water)

3.2.2.2. Operation of the Double-Column System

The two columns (*Fig. 3.5*) are operated simultaneously.

For both columns there are three operational periods:

 - Boiling up period: until the boiling of the charge in the reboiler
 - Heating up period of the column: until the appearance of the vapour in the top of the column
 - Distillation period: until the complete purification of the product

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During the different operational periods different reflux ratios are applied (*Table 3.7*). In the distillation period theoretically there is no need for direct reflux (from the reflux divider without passing through the decanter) because from the decanter liquid flows into the top of both columns. However, if the reflux ratio of Column α were zero, its vapour flow rate would be much higher which would result in a much shorter residence time in the decanter. In this case the decanter could not work. In an earlier test the operation of the system was studied by applying several different R^{α} and minimum $R^{\alpha} = 3/2$ was found necessary.

	Adjusted reflux ratio	
	Column α (producing 1-butanol)	Column β (producing water)
Boiling up	infinite	infinite
Start up of the column	infinite	infinite
Distillation	3/2	0

Table 3.7. Reflux ratios in each operation periods (mixture: 1-butanol – water)

The distillation periods of both columns must be started at the same time, therefore the start up of both columns must be finished together. Since the effective heat duty of Reboiler α is much higher than that of Reboiler β, Column β needs more time for the boiling up and the start up periods. Therefore the charge in Reboiler α was not boiled up immediately: it was heated up almost until its boiling point ($\sim$ 92 °C) and this temperature was kept without boiling up the liquid. When the other column started being hot, the heat duty of Reboiler α was increased again. (It would have been better to turn on Heater α one and a half hours later.)

During the experiment the timing was not perfect: Compared to Column α I gave a little more time for the start up of Column β than necessary, therefore after that I had to wait 19 minutes for the other column.

Table 3.8 shows the lengths of the different operation periods (the optimal lengths if they are different are in parentheses).
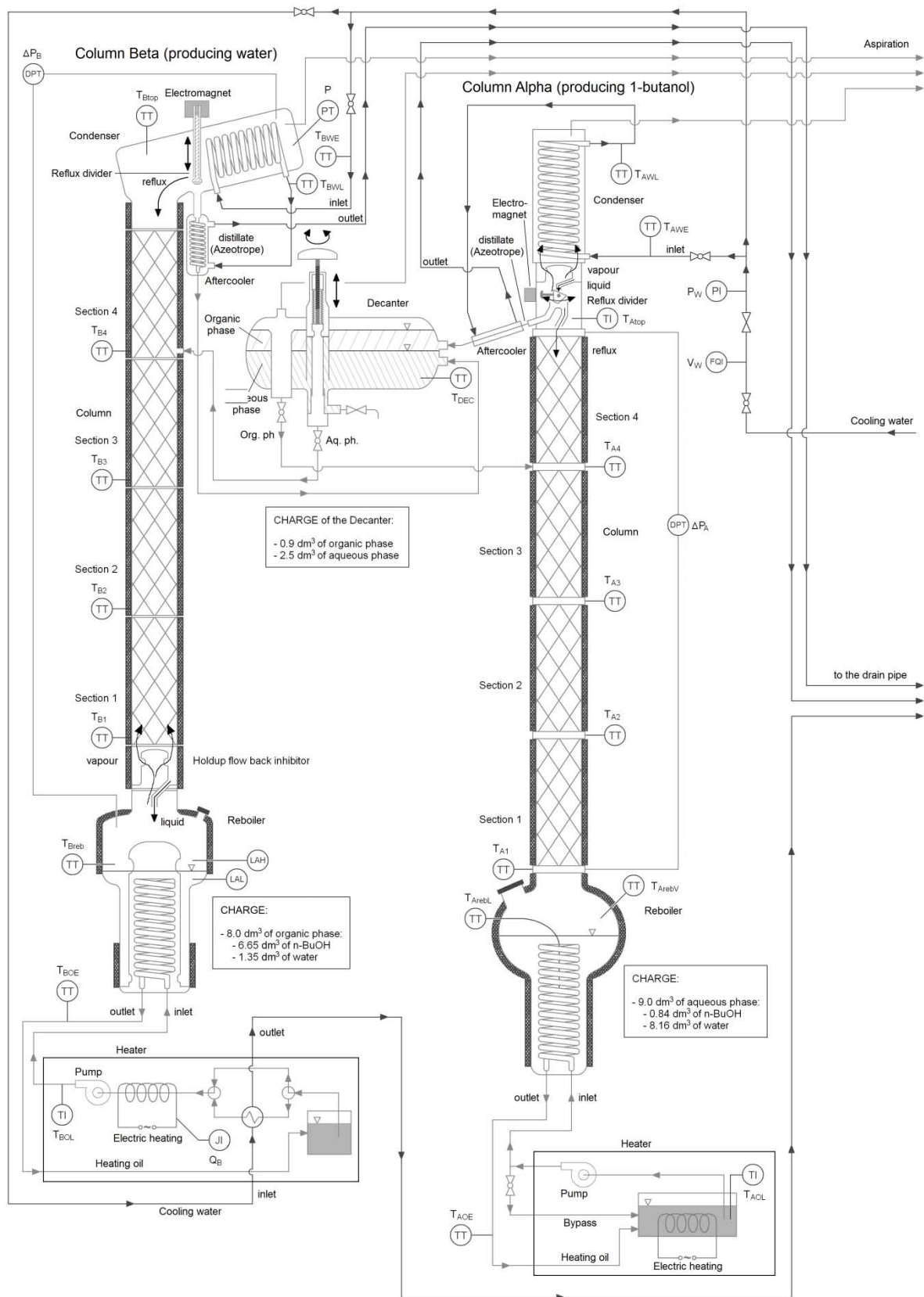
Fig. 3.5. DCS laboratory equipment for the separation of a binary heteroazeotropic mixture

	Column α (producing 1-butanol)		Column β (producing water)	
	Absolute time at the end of the period	Length of the period	Absolute time at the end of the period	Length of the period
Boiling up [min]	148	148 (53)	93	93
Start up of the column [min]	175	27	175	82 (63)
Distillation [min]	357	182	357	182

Table 3.8. Durations of the operation periods (mixture: 1-butanol – water)

3.2.2.3. Results

I. Material balances

At the beginning:

Total quantity = Organic phase of the charge + Aqueous phase of the charge + Organic phase in the decanter + Aqueous phase in the decanter

At the end:

Total quantity = Butanol product + Water product + Organic phase in the decanter + Aqueous phase in the decanter

a. Integral Total Material Balance (Table 3.9):

All data are measured.

		At the beginning		At the end	
		V [dm³]	n_D^{25}	V [dm³]	n_D^{25}
Reboiler α		8.0	1.3889	7.4	1.3968
Reboiler β		9.0	1.3405	9.5	1.3329
Decanter	Organic phase	0.9	-	1.5	-
	Aqueous phase	2.5	-	2.0	-
Total		**20.4**	**-**	**20.4**	**-**

Table 3.9. Volumes and refractive indices of the liquids at the beginning and at the end of the process (mixture: 1-butanol – water)

b. Integral Component Material Balance (of the BuOH, Table 3.10):

All data are calculated data on the basis of the refractive index.

		At the beginning				At the end			
		$x_{BuOH}\%$	$m_{BuOH}\%$	$V_{BuOH}\%$	V_{BuOH} [dm³]	$x_{BuOH}\%$	$m_{BuOH}\%$	$V_{BuOH}\%$	V_{BuOH} [dm³]
Reboiler α		49.1	79.9	83.1	6.65	93.41	98.32	98.63	7.30
Reboiler β		2.0	7.7	9.3	0.84	0.02	0.09	0.11	0.01
Decanter	Org. ph.	49.1	79.9	83.1	0.75	49.1	79.9	83.1	1.25
	Aq. ph.	2.0	7.7	9.3	0.23	2.0	7.7	9.3	0.19
Total		-	-	-	**8.47**	-	-	-	**8.74**

Table 3.10. Composition of the initial and final holdups (mixture: 1-butanol – water)

II. Product purities on the basis of the final boiling temperatures

Since the contact between the columns and the reboiler cannot be cut at the end of the process, the holdup of the columns flows back into the reboilers. Because of that the purities of the products decrease after the shutdown of the heating. Therefore the products are the purest in the moment of the shutdown. Since the mixture is a binary one the purities can be determined on the basis of the boiling points (*Table 3.11*).

	T^{BP}_{final}* [°C]	T^{BP}_{pure} [°C]	x_{BuOH}%	m_{BuOH}%	V_{BuOH}%
BuOH	117.35	117.62	99.87	99.96	99.97
Water	99.3	99.7	0.035	0.14	0.18

Table 3.11. Product purities on the basis of the final boiling temperatures
(mixture: 1-butanol – water)

Ambient pressure: P = 1002.0 mbar

Pressure drop of Column α: ΔP^{α} = 0.1 mbar

Pressure drop of Column β: ΔP^{β} = 0.1 mbar

III. Estimation of the effective heat duty of the reboilers

On the basis of the length of the boiling up period and the calculated initial and final enthalpies of the charges the heat duties can be estimated (*Table 3.12*). The enthalpies are calculated by using the ChemCAD 6.3 flowsheet simulator.

* vapour temperature in the reboiler

	Column α	Column β
Initial volume [dm³]	8.0	9.0
Volumic percent of BuOH [%]	83.1	9.3
Initial temperature [°C]	18.65	18.6
Final temperature [°C]	88.68	91.4
Length of the boiling up [min]	33.5	93
Initial enthalpy [MJ]	-45.49	-132.70
Final enthalpy [MJ]	-44.08	-130.08
Effective heat duty [kW]	**0.70**	**0.47**
Nominal maximal heat duty[kW]	6	4

Table 3.12. Calculation of the effective heat duties of the reboilers during the boiling up (mixture: 1-butanol – water)

The control panel of the Reboiler β displays the actual heat duty percentage. This value was registered during the whole process. On its bases the average heat duty of the reboiler can be estimated (*Table 3.13*). (This is the electric performance, not the effective heat duty!)

Operation period	Electric performance [kW]
Boiling up	1.09
Start up of the column	1.44
Distillation	2.40

Table 3.13. Average electric performance of the Reboiler β (mixture: 1-butanol – water)

IV. Evolution of the temperature in the reboilers

a. Reboiler α (where BuOH is produced)

In this reboiler the liquid and vapour temperatures can be measured separately.

Reboiler α, liquid temperature:

The resistance thermometer is very close to the heating spiral that is why the registered temperature is higher than the real one. Because of the geometrical construction of the reboiler the thermometer cannot be put into a more favourable position, therefore a correction is done by taking into consideration the following conditions:

- In the moment of the turning on of the heating the measured temperature is equal to the liquid temperature.
- After reaching the boiling point the measured liquid temperature should be equal to the vapour temperature.

The evolution of the difference between the measured and the real liquid temperature is estimated by two different functions (*Fig. 3.6*):

- from t = 90 min (1 h before the boiling) until the end of the process: by a linear function $f_2(t)$ fitted to $\Delta T(t) = T_{liq}(t) - T_{vap}(t)$ after reaching the boiling point (t = 150 min).
- from the start until t = 90 min: by a quadratic function $f_1(t)$:
    - which is equal to 0 in t = 0: $f_1(0) = 0$,
    - which is equal to the other function in t = 90 min: $f_1(90) = f_2(90)$,
    - whose slope in t = 90 min is equal to that of the other function: $f_1'(90) = f_2'(90)$.
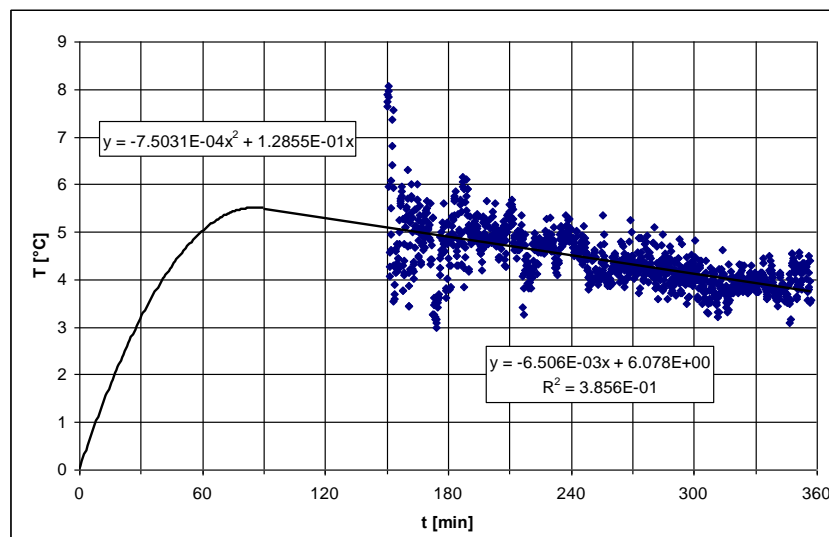
Fig. 3.6. Difference between the measured liquid and vapour temperatures in the reboiler with the fitted curves (Reboiler α, mixture: 1-butanol – water)

The corrected liquid temperature is lower than the measured one and after the boiling up nearly equals to the vapour temperature (*Fig. 3.7*).
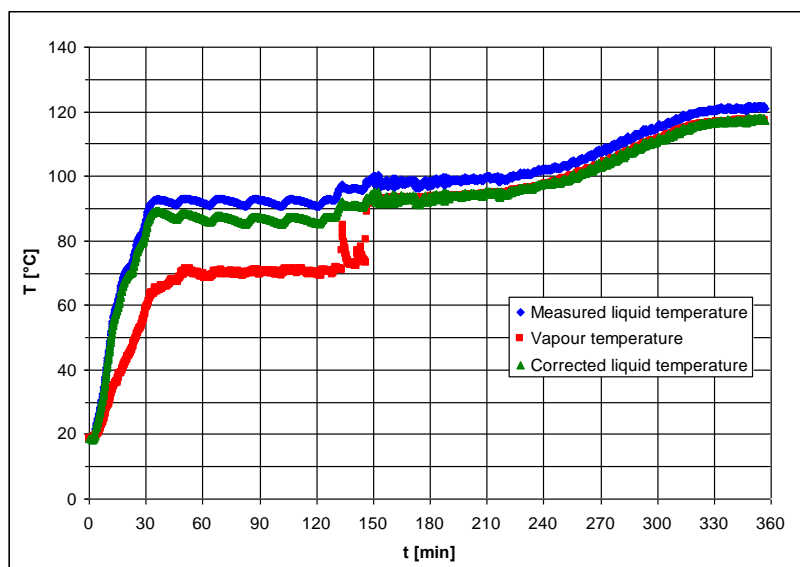
Fig. 3.7. Evolution of the vapour temperature, the measured and the corrected liquid temperatures (Reboiler α, mixture: 1-butanol – water)

In the *Figs. 3.8a-b* can be clearly seen that the temperature increases until the boiling point of the pure BuOH.
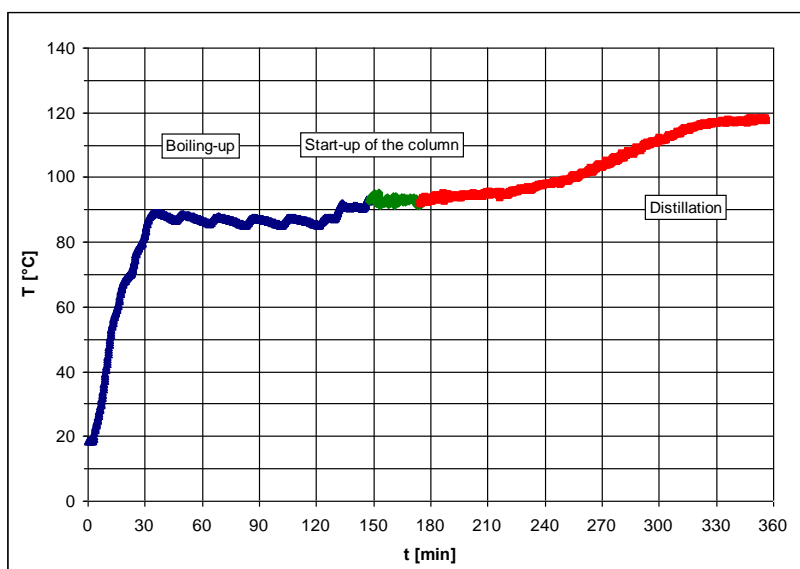
Fig. 3.8a. Evolution of the corrected liquid temperature in Reboiler α: The whole process (mixture: 1-butanol – water)
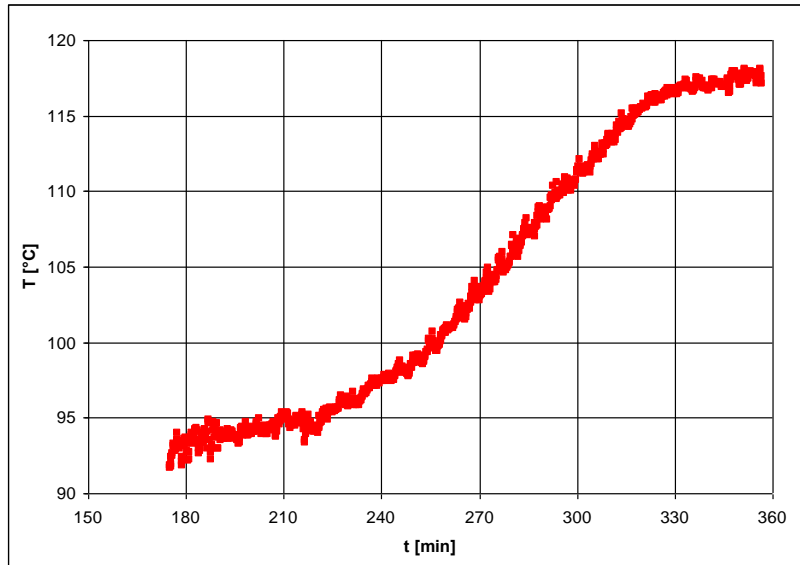
Fig. 3.8b. Evolution of the corrected liquid temperature in Reboiler α:

After reaching the boiling point (mixture: 1-butanol – water)

Reboiler α, vapour temperature (*Fig. 3.9a*):

At the 135th minute I stopped the heating for three minutes. (I heard a sound like crack of glass.) Since I could not find any problem, I turned on the heating again. Just before the shutdown the vapour temperature in Reboiler β leaped up by 13 °C in less than 20 seconds and after slowly decreased (*Fig. 3.9b*). Until reaching the boiling point this phenomenon repeated still two times. In the cases of these leaps the pressure drop did not increase significantly and there was not any boiling instability.

In the *Fig. 3.9c* it can be clearly seen that the temperature increases until the boiling point of the pure BuOH. The curve shows also the periodic operation of the reboiler.
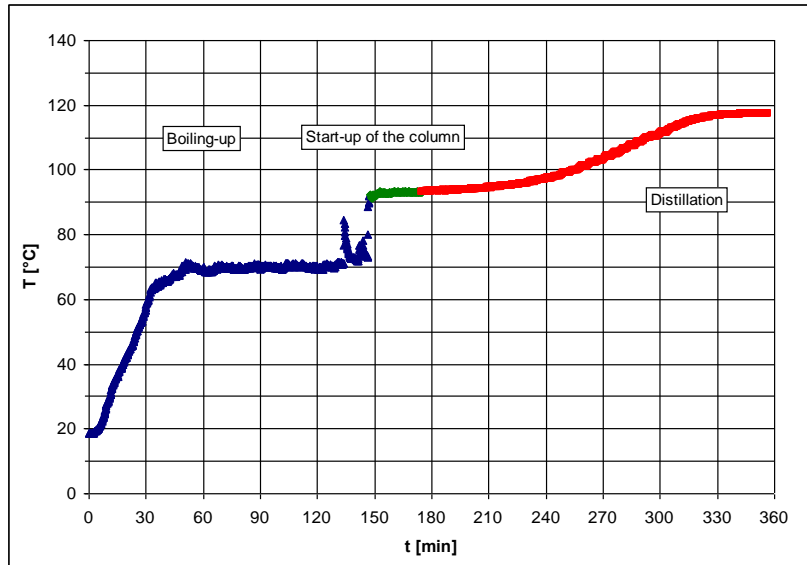
Fig. 3.9a. Evolution of the vapour temperature in Reboiler α: The whole process

(mixture: 1-butanol – water)
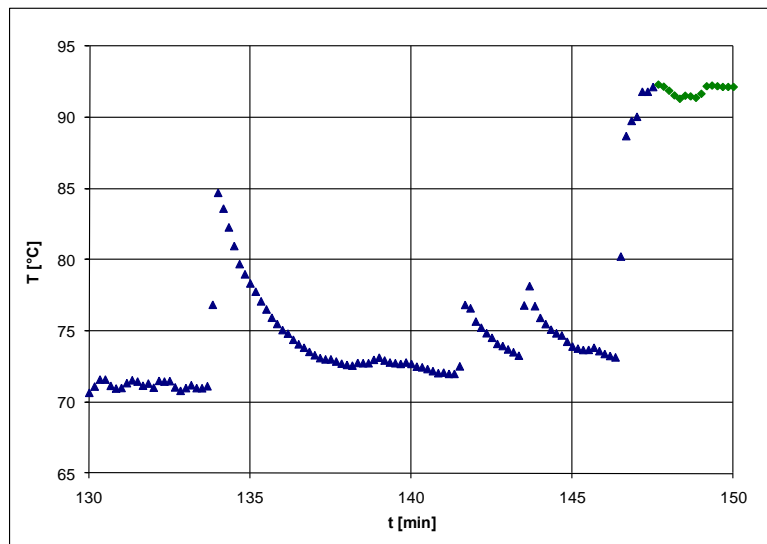
Fig. 3.9b. Evolution of the vapour temperature in Reboiler α: Anomaly of the vapour

temperature just before reaching the boiling point (mixture: 1-butanol – water)

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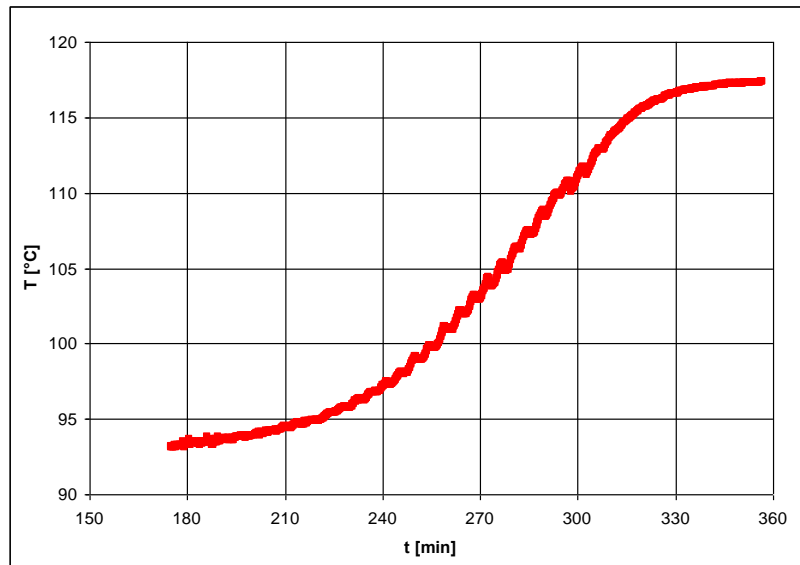
Fig. 3.9c. Evolution of the vapour temperature in Reboiler α: After reaching the boiling point
(mixture: 1-butanol – water)

b. Reboiler β (where water is produced)

Reboiler β, liquid temperature:

The only resistance thermometer in the reboiler is above the liquid level, that is why the liquid temperature cannot be measured. Since the reboiler is thermally well isolated and the heating-up of the liquid is slow, the difference between the vapour and the liquid temperature is negligible.

Reboiler β, vapour temperature (Figs. 3.10a-c):
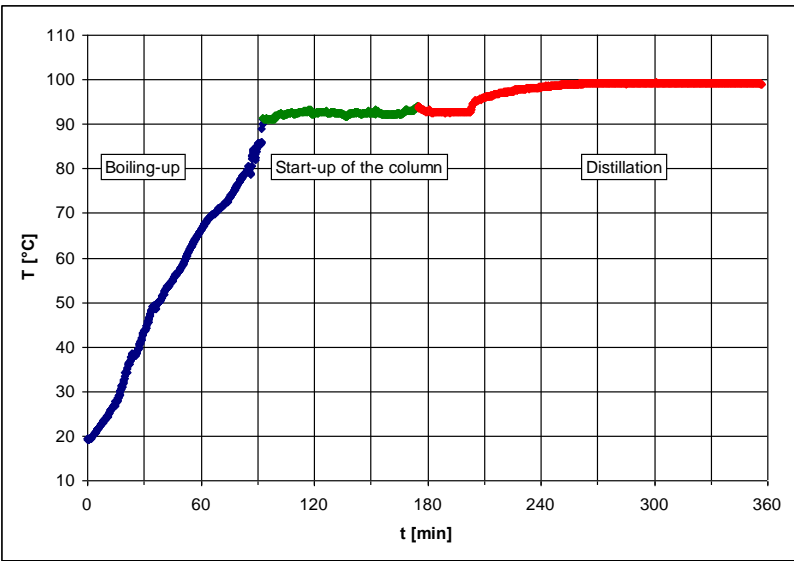
Fig. 3.10a. Evolution of the vapour temperature in Reboiler β: The whole process

(mixture: 1-butanol – water)
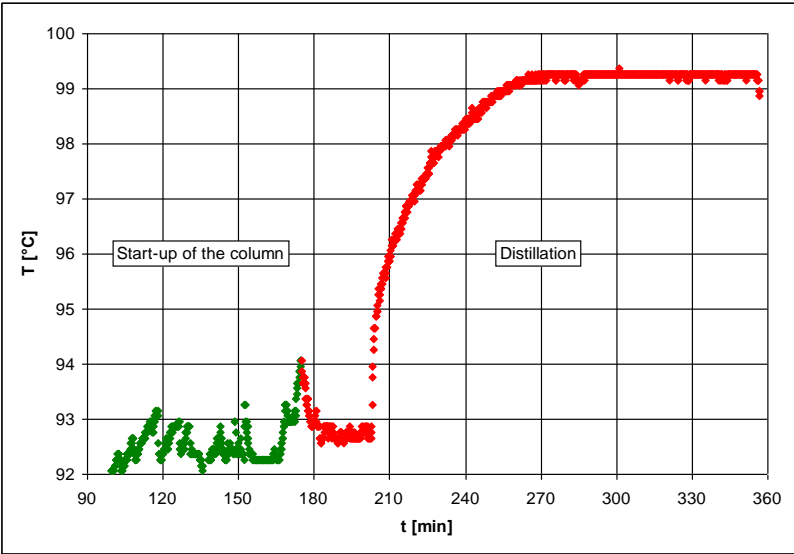
Fig. 3.10b. Evolution of the vapour temperature in Reboiler β:

After reaching the boiling point (mixture: 1-butanol – water)
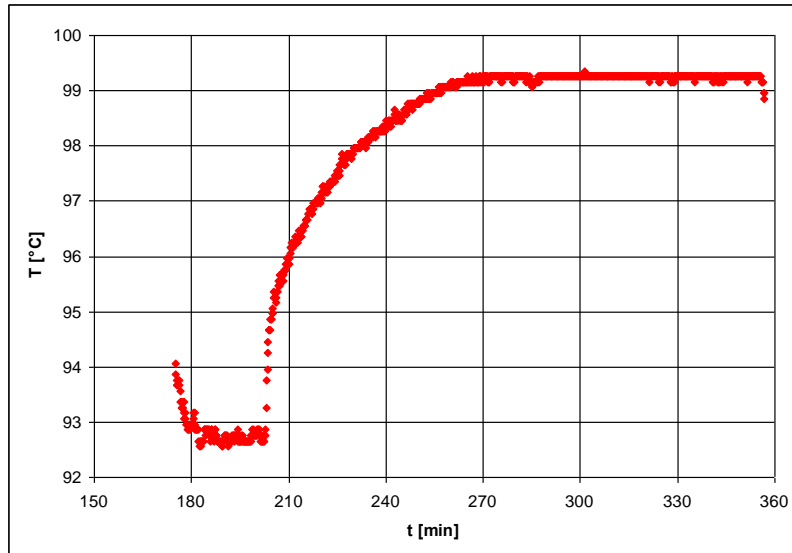
Fig. 3.11c. Evolution of the vapour temperature in Reboiler β: The distillation period

(mixture: 1-butanol – water)

At the beginning of the distillation period the temperature decreases by ~ 1.5 °C.

3.2.2.4. Conclusions

The heteroazeotropic mixture water – 1-butanol was separated in a batch double-column pilot plant. The aqueous and the organic phases of the heterogeneous charge were fed into different reboilers. After the long boiling up and start up periods (49% of the total duration) both components could be produced in high purity in spite of the malfunction of the reflux dividers. The successful experiment proved also the operability of the installation.

3.2.3. Pilot plant experiments for a ternary mixture

3.2.3.1. Processing of the mixture isopropanol – water in the Batch Rectifier by using n-hexane as entrainer

In this experiment only Column α is used. The reboiler of Column β serves as a distillate tank. The equipment is used in the same structure as during the experiment with the binary mixture (*Fig. 3.5*).

3.2.3.1.1. The charge and the initial holdup of the decanter

The components of the mixture are isopropanol, water and n-hexane.

Since an isopropanol-lean isopropanol (*A*) – water (*B*) mixture can be concentrated until the binary azeotropic composition also by applying traditional distillation, the composition of the charge chosen is the binary azeotropic one ($x\%_{BAZ,A} = 66.2\,mol\%$). To this mixture some n-hexane (entrainer, *E*) is added.

The decanter is filled with ternary heterogeneous liquid (*Table 3.14*) whose phases are of the same compositions as those of a mixture of ternary azeotropic composition (organic phase: $\vec{x}\%_{TAZ}^{Er} = [20.2, 5.6, 74.2]\,mol\%$, aqueous phase: $\vec{x}\%_{TAZ}^{Br} = [12.6, 86.9, 0.5]\,mol\%$). The volumetric ratio of the phases $\left(\dfrac{V_{DEC}^{org}}{V_{DEC}^{aq}} = \dfrac{1.9\,dm^3}{1.6\,dm^3} = 1.19\right)$ chosen strongly differs from that of the ternary azeotrope $\left(\dfrac{V_{TAZ}^{org}}{V_{TAZ}^{aq}} = 27.7\right)$. This phase ratio more balanced give higher stability for the decantation.

	Volume [dm³]			
	A	*B*	*E*	Total (after mixing)
Reboiler	7.2	0.9	0.45	8.5
Decanter	0.93	1.14	1.63	3.5

Table 3.14. Initial charge and the initial holdup of the decanter

(mixture: isopropanol – water + n-hexane)

3.2.3.1.2. Operation of the Batch Rectifier

Because of the slow purification of the isopropanol the pure product could not be obtained at the end of the first working day. Therefore the installation must be stopped before reaching the pure product. The decanter holdup was kept for the next day when the experiment was restarted (*Table 3.15*) but the production must be stopped again before reaching pure isopropanol. The product could be obtained on the third day, only. It means that during the 3-day experiment the cold installation was restarted two times.

Each day there were three operational periods (*Table 3.15*):
 - Boiling up period: until the boiling of the charge in the reboiler,
 - Heating up period of the column: until the appearance of the vapour at the top of the column,
 - Distillation period: until the end of the day (1st and 2nd days) or until the reaching of the product (3rd day).

During the operation of the column the outlet of the aqueous phase of the decanter was usually closed. Therefore only the organic phase could flow out and the quantity of the aqueous phase increased. The total volume of the phases was constant because of the fixed upper outlet. The growth of the quantity of the aqueous phase indicated well the purification process of the reboiler liquid. During the operation the outlet of the aqueous phase was open several times to let flow out the growth of the aqueous phase. Near to the end of the production (the 3rd day) the volume of the aqueous phase was decreased below its original one in order to ensure enough space for the entrainer which had to be removed from the column. At the beginning of the 3rd day the volume of the reboiler liquid was 7.3 dm^3. In order to keep the heating surface wet the liquid volume must be at least 6.5 dm^3. For the total removal of the entrainer a space of about 0.7 dm^3 was necessary in the decanter. Therefore the entrainer removal process must be started after less than 1 hour of distillation. (During this time about 0.1-0.2 dm^3 of aqueous phase could leave.)

Table 3.15 shows the lengths of the different operation periods.

Day	Operational period	Absolute time at the end of the period [min]	Length of the period [min]	Adjusted reflux ratio of the reflux divider
1st day	Boiling up	54	54	infinite
	Start up of the column	96	42	infinite
	Distillation	461	365	3/2
2nd day	Boiling up	501	40	infinite
	Start up of the column	528	27	infinite
	Distillation	945	417	1/2 (until t = 567 min) 0 (until the shut down)
3rd day	Boiling up	1001	56	infinite
	Start up of the column	1044	43	infinite
	Distillation	1090	46	0

Table 3.15. Durations of the operation periods and the adjusted reflux ratios
(mixture: isopropanol – water + n-hexane)

During the different operational periods different reflux ratios were applied in the reflux divider of the column (*Table 3.15*). Since only the distillate is led into the decanter, this reflux is heterogeneous. In the first distillation period $R^\alpha = 3/2$ was applied in order to decrease the vapour flow rate. In this case it is sure that the residence time in the decanter is enough for the phase separation. Since the purification process was slow, the second day a lower reflux ratio was adjusted ($R^\alpha = 1/2$). After almost 40 min of operation by this way it was clear that the decanter operated well despite the higher vapour flow rate. Therefore R^α was modified to 0 and until the end of the whole process this value was applied in the distillation periods.

It must be noted that because of the imperfect operation of the reflux divider about 10-30 % of the condensate flowed back to the column even if $R^\alpha = 0$. It means that R^α was practically $0.1 - 0.4$.

3.2.3.1.3. Results

First the product purity is determined by different methods than the material balances are calculated. The effective heat duty of the heater is estimated and the evolution of the temperatures in the reboiler and the column are shown and explained.

I. Product purity

a. By the boiling temperature

The mixture loaded into the reboiler was ternary but after the start up of the column the majority of the entrainer was found in the column holdup. Therefore at the beginning of the production period the composition of the liquid in the reboiler was near to the binary azeotropic one. Its boiling point displayed was 80.3 °C (vapour temperature in the reboiler), that of the binary azeotrope is 80.1 °C. The boiling point of the pure isopropanol is 82.5 °C that is the total temperature variation of the liquid in the reboiler can be about 2 °C during the production cycle (*Fig. 3.12*). Since the temperature measured by the thermocouple can differ from the real temperature by a few tenth of degree, the actual liquid composition can be only estimated with a significant uncertainty on the basis of the temperature.
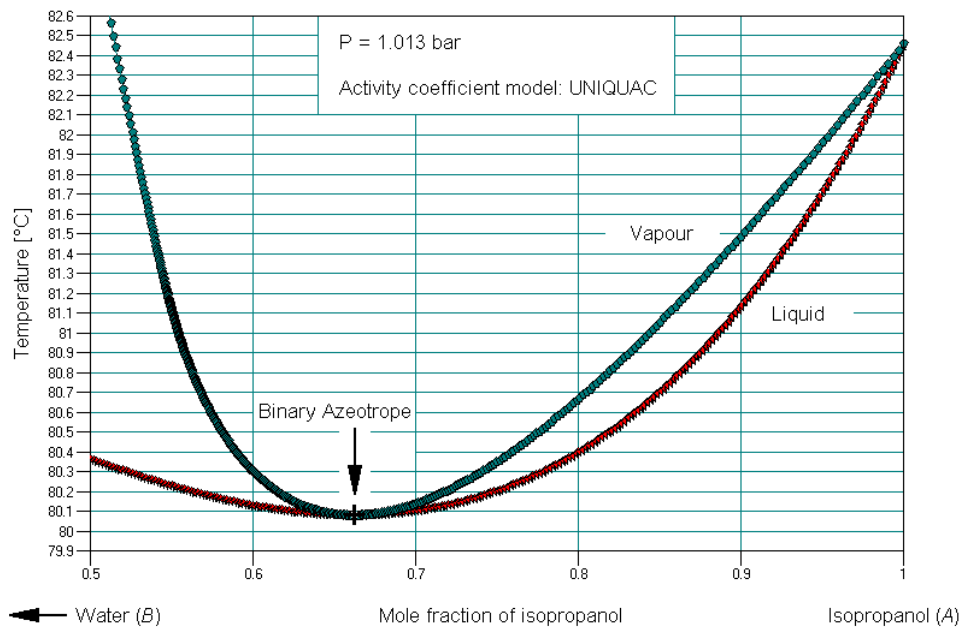
Fig. 3.12. Boiling and dew point curves of the mixture isopropanol – water
(in the isopropanol-rich composition range)

b. By the volume of the aqueous phase removed

In the course of the operation of the column the condensate arriving at the decanter resulted in 1.4 dm^3 of aqueous phase (which was released gradually to the distillate tank). Since the water content of the aqueous phase is 60 V/V%, the volume of the water removed from the reboiler liquid is about 0.8 dm^3. Supposing that the entrainer is completely removed from the reboiler the product contains 6.0 dm^3 of *A* and 0.1 dm^3 of *B*. In this case the purity of Product *A* is 98 V% (97.9 w%, 93.2 mol%).

c. By gas chromatography and the Karl-Fischer analysis

The *B* content of the product (5.9 w%) determined by the Karl-Fischer method is accepted without any modification. The concentrations of *A* and *E* (*A*: 814.47 g/dm^3, *B*: 0.53 g/dm^3) determined by gas chromatography (with flame ionisation detector) are normalised for being in accordance with the concentration of *B*. The composition of the product determined by these methods is shown in *Tables 3.17a-b*.

On the basis of the volumes and the compositions of the liquids the integral total and component material balances are calculated. In these balances the initial and the final quantities are compared.

At the beginning:

Total quantity = Charge + Entrainer + Organic phase in the decanter + Aqueous phase in the decanter

At the end:

Total quantity = Isopropanol product + Distillate + Organic phase in the decanter + Aqueous phase in the decanter

a. Integral Total Material Balance

All data in *Table 3.16* are measured, nearly at the same temperatures (23-24 °C). The difference between the initial and final total volumes is about -0.7 dm^3 (-6 %). The reasons of this difference can be the loss of evaporation and the holdup of the column.

The total packed volume (packing + empty space) is

$$V_{packed} = 4 \cdot 100\,cm \cdot \frac{(8\,cm)^2 \cdot \pi}{4} = 20106\,cm^3 \approx 20.1\,dm^3 \,.$$

The liquid volume missing is 3.5 % of the packed volume.

		Volume at the beginning [dm^3]	Volume at the end [dm^3]
Reboiler		8.5	6.1
Distillate tank		0	1.88
Decanter	Total	3.5	3.3
	Org. ph.	*1.9*	*2.0*
	Aq. ph.	*1.6*	*1.3*
Total		**12.0**	**11.28**

Table 3.16. Volumes of the liquids at the beginning and at the end of the process

(mixture: isopropanol – water + n-hexane)

b. Integral Component Material Balance of the isopropanol and the water (Tables 3.17a-b)

The volumes of the initial holdups and those of their components are measured. The component concentrations of the initial holdups are calculated. The volumes of the final holdups are measured. The product composition is calculated on the basis of the results of the quantitative analyses, the other final compositions are determined by LLE calculation. The volumes of the components are calculated.

		At the beginning				At the end			
		$x\%_A$	$w\%_A$	$V\%_A$	V_A [dm^3]	$x\%_A$	$w\%_A$	$V\%_A$	V_A [dm^3]
	Reboiler	64.0	82.7	84.2	7.20	82.7	94.0	95.2	5.81
	Distillate tank	-	-	-	0	12.6	31.9	36.8	0.69
Decanter	Total	13.9	24.9	25.1	0.93	14.6	23.3	22.8	0.75
	Org. ph.	*20.1*	*15.7*	*13.5*	*0.26*	*20.2*	*15.7*	*13.6*	*0.27*
	Aq. ph.	*12.5*	*31.8*	*36.7*	*0.59*	*12.6*	*31.9*	*36.8*	*0.48*
	Total	**-**	**-**	**-**	**8.13**	**-**	**-**	**-**	**7.25**

Table 3.17a. Isopropanol content of the initial and final holdups

(mixture: isopropanol – water + n-hexane)

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	At the beginning				At the end			
	$x_B\%$	$w_B\%$	$V_B\%$	V_B [dm³]	$x_B\%$	$w_B\%$	$V_B\%$	V_B [dm³]
Reboiler	33.6	13.0	10.5	0.90	17.3	5.9	4.7	0.29
Distillate tank	-	-	-	0	86.9	66.2	60.5	1.14
Decanter — Total	71.9	38.6	30.8	1.14	65.7	31.5	24.4	0.81
Decanter — Org. ph.	5.6	1.3	0.9	0.02	5.6	1.3	0.9	0.02
Decanter — Aq. ph.	87.0	66.3	60.7	0.97	86.9	66.2	60.5	0.79
Total	-	-	-	**2.04**	-	-	-	**2.24**

Table 3.17b. Water content of the initial and final holdups

(mixture: isopropanol – water + n-hexane)

	At the beginning				At the end			
	$x\%_E$	$w\%_E$	$V\%_E$	V_E [dm³]	$x\%_E$	$w\%_E$	$V\%_E$	V_E [dm³]
Reboiler	2.4	4.3	5.3	0.45	0.0	0.1	0.1	0.01
Distillate tank	-	-	-	0	0.5	1.9	2.6	0.05
Decanter — Total	14.2	36.5	44.1	1.63	19.7	45.2	52.8	1.74
Decanter — Org. ph.	74.3	83.0	85.6	1.63	74.2	83.0	85.5	1.71
Decanter — Aq. ph.	0.5	1.9	2.6	0.04	0.5	1.9	2.6	0.03
Total	-	-	-	**2.08**	-	-	-	**1.80**

Table 3.17c. N-hexane content of the initial and final holdups

(mixture: isopropanol – water + n-hexane)

The difference between the initial and final isopropanol volumes is -0.88 dm³ (-11 %). Since at the end of the production the holdup of the reboiler contains mainly isopropanol, the vapour coming from there has high isopropanol content. Therefore the holdup of the hot column contains mainly isopropanol, too. Another possible reason of the lower final isopropanol quantity is that the aqueous phase of the decanter flowed into the distillate tank (reboiler of the other column) through the cold Column β. Before this experiment this column was used for water production from water – 1-butanol mixture, therefore some water was stuck there,

which was washed out by the aqueous phase. It results in the growth of the water quantity and the loss of isopropanol because a part of the isopropanol in the form of aqueous phase is stuck there. It can be also the reason of the difference between the initial and final water volumes which is 0.20 dm^3 (10 %). The main reason of the error of the material balance of the n-hexane (-0.28 dm^3, -14 %) is the loss of evaporation.

III. Estimation of the effective heat duty of the heater

The heater tries to ensure the stability of the inlet oil temperature by consecutive heating and non-heating periods. In the heating period maximum heating is applied ($P_{max} = 6\ kW$), in the other one the heating is turned off. On the basis of the duration ratio of heating (p) and the maximum heat duty of the reboiler the average heat duty (P_{av}) can be determined. During the distillation these periods were measured several times (*Table 3.18*). It can be stated that the average heat duty is about 15% of the maximum one (less than 1 kW).

$T_{oil,in}$ [°C]	Period with heating [s]	Period without heating [s]	p [%]	P_{av} [kW]
88	76	415	15.5	0.93
88	72	486	12.9	0.77
89	75	441	14.5	0.87
90	73	439	14.3	0.86

Table 3.18. Determination of the average heat duty of the heater

(mixture: isopropanol – water + n-hexane)

IV. Evolution of the temperature in the reboiler and in the column

Figs. 3.13-14 show the evolution of the liquid and vapour temperatures in the reboiler. The start up and the distillation periods are plotted without the shut down periods. The liquid temperature displayed is higher than the real one because the end of the resistance thermometer is very close to the heating spiral. In spite of the difference between the displayed values, after the boiling up the temperature of the liquid equals that of the vapour. *Figs. 3.13-14* show that the boiling point hardly changed in the distillation period of the 1st day. On the 2nd day (after 630 min of total time) the vapour temperature started decreasing slowly and its oscillation became heavier. The reason of the decrease was the continuous

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increase of hexane content of the reboiler. (The aqueous phase continuously pushed out the organic phase from the decanter.) On the basis of my earlier experiences the stability of the boiling is sensitive for the composition of the reboiler liquid. Probably that is why the oscillation of the vapour temperature was heavier. At t = 775 min the heating was turned off for 9 minutes (because of an unexpected alarm in the building), therefore reboiler temperatures decreased by about 5-8 °C. After the restart the original temperatures were reached in 5 minutes, the unexpected drop out of the heating did not result in further problems.
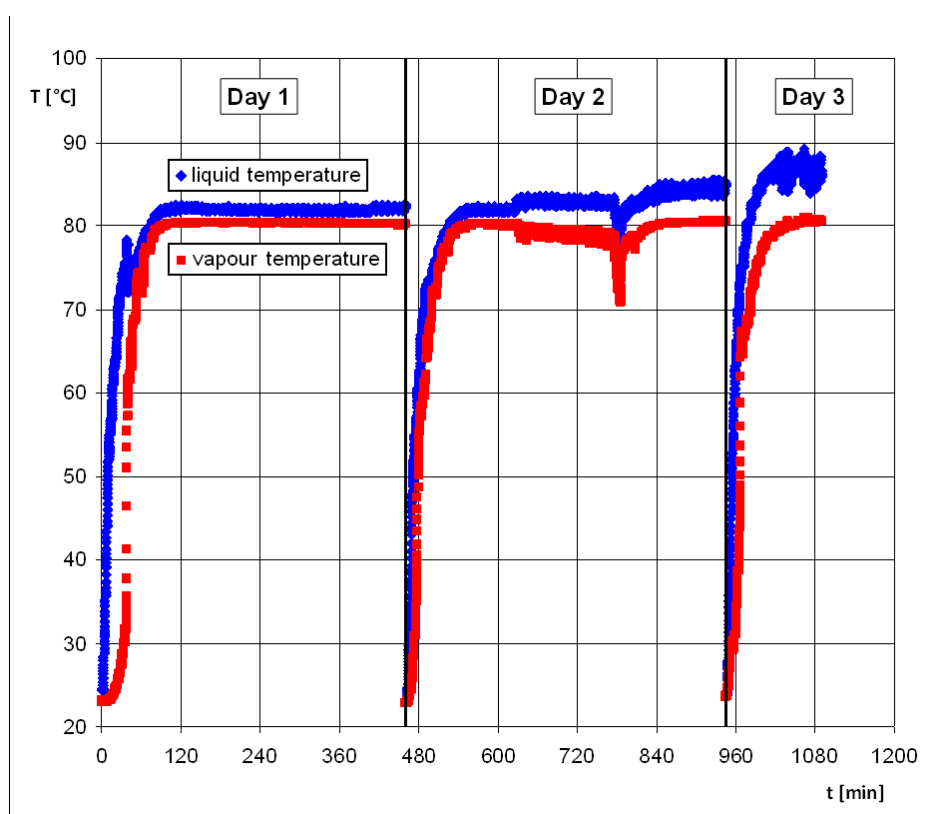
Fig. 3.13. Liquid and vapour temperatures in the reboiler
(mixture: isopropanol – water + n-hexane)
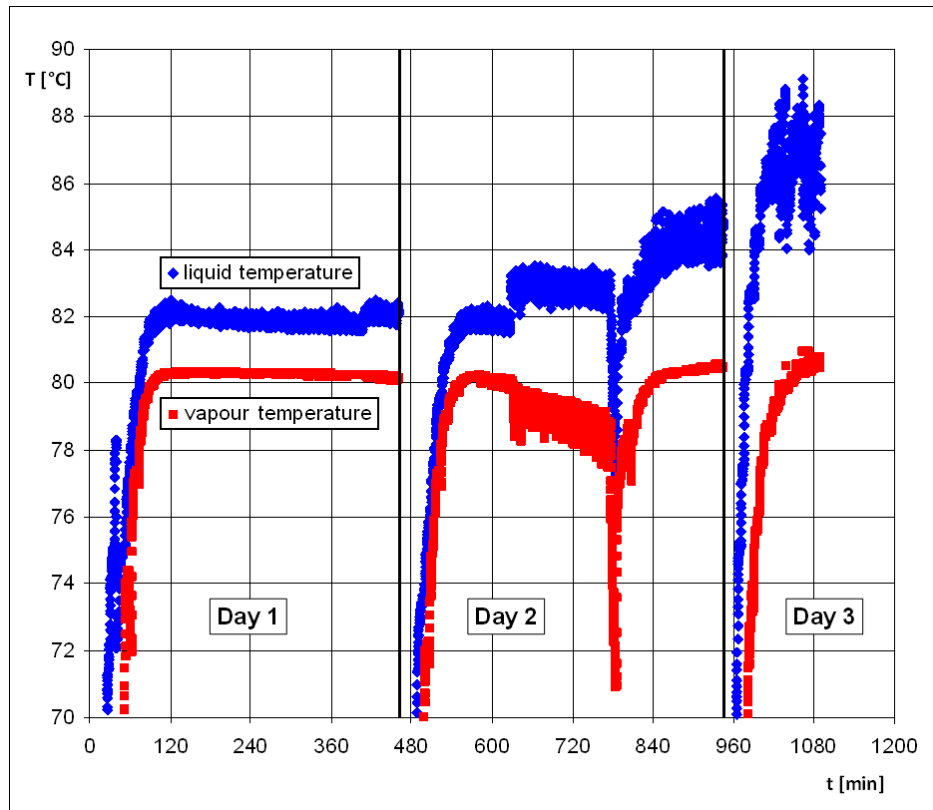
Fig. 3.14. Liquid and vapour temperatures in the reboiler (zoomed on the distillation periods, mixture: isopropanol – water + n-hexane)

Fig. 3.15 shows the evolution of the temperatures below each column section.

The temperature in Section 1 (the lowest) was always near to the binary azeotropic temperature (T_{BAZ}^{BP}). Its value was near to that of the reboiler temperature, obviously.

The temperature in Section 2 (T_2) on the 1st day was near to T_{BAZ}^{BP}. When the entrainer started accumulating in the reboiler, it started oscillating between T_{BAZ}^{BP} and T_{TAZ}^{BP} according to the oscillation of the heating. On the 2nd day when the reflux ratio was decreased from ½ to 0 (*t = 567 min*), the oscillation stopped and T was stabilised near to T_{TAZ}^{BP}. When aqueous phase was released the first time to the distillate tank (*t = 820 min*), T_2 increased quickly to T_{BAZ}^{BP} and it started oscillating again between T_{BAZ}^{BP} and T_{TAZ}^{BP}. When aqueous phase was released the second time to the distillate tank (t = 905 min), T_2 became stable at T_{BAZ}^{BP} and it remained there also on the 3rd day.

The temperature in Section 3 was above T_{TAZ}^{BP} by about 5 °C until t = 905 min (2nd day, 2nd release of the aqueous phase from the decanter), then it increased until reaching T_{BAZ}^{BP} and remained there.

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The temperature in Section 4 (T_4) was stable and near to T_{TAZ}^{BP} on the 1st and 2nd days. On the 3rd day after a while it increased until T_{BAZ}^{BP}.

The behaviour of the top vapour temperature is similar to that of T_4 (*Fig. 3.16*).

The column was able to produce top vapour of ternary azeotropic composition until the end of the process. The vapour temperatures of the two upper sections and the top of the column increased near to the end of the production, during the removal of the entrainer from the product.
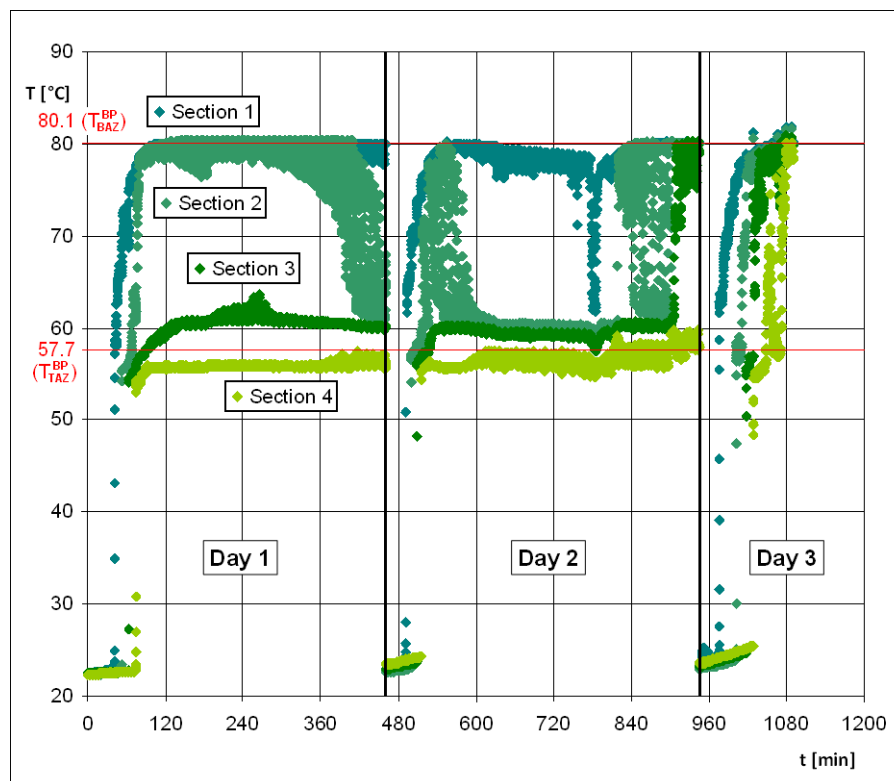
Fig. 3.15. Evolution of the temperatures below each column section
(lowest: Section 1, upper: Section 4; mixture: isopropanol – water + n-hexane)
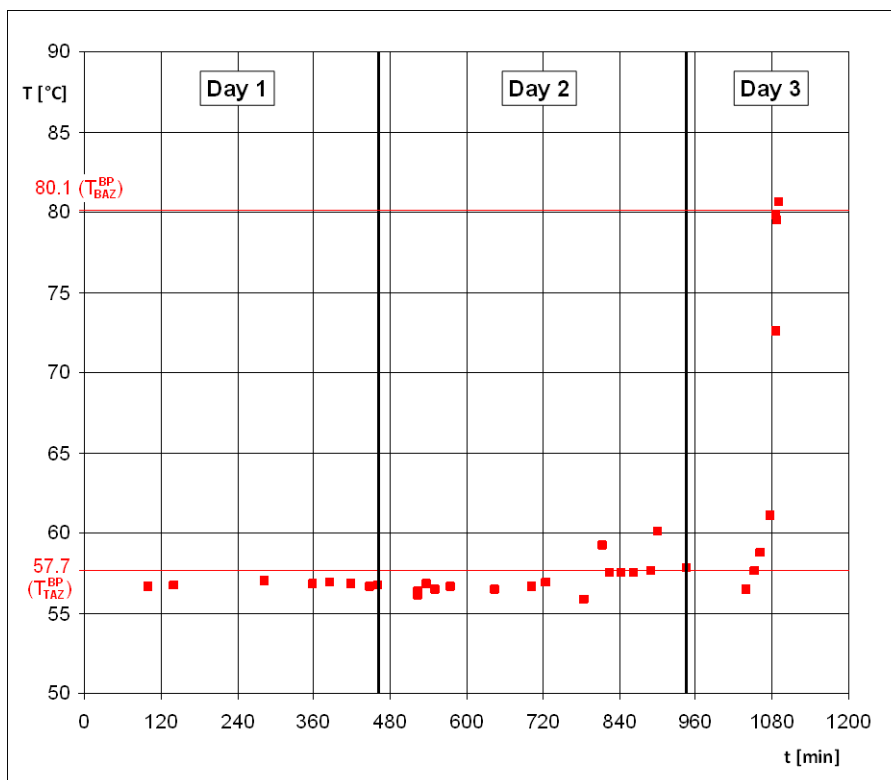
Fig. 3.16. Evolution of the top vapour temperature (mixture: isopropanol – water + n-hexane)

3.2.3.1.4. Conclusions

From the homoazeotropic mixture isopropanol – water isopropanol was produced in a batch rectifier pilot plant equipped with a decanter. To the charge of azeotropic composition n-hexane was added as entrainer. In spite of the stability problems of the boiling, the malfunction of the reflux divider and the volumetric limit of the reboiler, the purification of the isopropanol was feasible. The final product contained less than 5 V% of contamination (mainly water). The column could have produced isopropanol also in higher purity but because of the low liquid level in the reboiler, the experiment had to be finished.

3.2.3.2. Processing of the mixture isopropanol – water in the Generalised Double-Column System by using n-hexane as entrainer

3.2.3.2.1. The charge and the initial holdup of the decanter:

The components of the mixture are isopropanol (*A*), water (*B*) and n-hexane (*E*).

The total volumes of isopropanol and water in the reboilers must be nearly the same to insure that the heating spirals of the reboilers are always under liquid. If the charge compositions in both reboilers were identical they would be very far from those of the pure components and the experiment would last very long time (several days). Therefore in Reboiler α – where Product *A* is accumulated – the charge had isopropanol – water binary azeotropic composition which can be reached also by applying traditional distillation (*Table 3.19*). Entrainer is also added to the charge. In Reboiler β – where Product *B* is accumulated – the volumetric charge composition is the inverse of that of the other charge.

The decanter is filled with ternary heterogeneous liquid (*Table 3.19*) whose phases are of the same compositions as those of a mixture of ternary azeotropic composition (organic phase: $\vec{x}\%_{TAZ}^{Er} = [20.2, 5.6, 74.2]\,mol\%$, aqueous phase: $\vec{x}\%_{TAZ}^{Br} = [12.6, 86.9, 0.5]\,mol\%$).

		Volume [dm³]			
		A	*B*	*E*	Total
		isopropanol	*water*	*n-hexane*	(after mixing)
Reboiler α		8.0	1.0	0.5	9.5
Reboiler β		1.0	8.0	0.0	9.0
Decanter	Total	0.92	1.37	0.91	3.2
	Organic	-	-	-	1.0
	Aqueous	-	-	-	2.2

Table 3.19. Initial charge and the initial holdup of the decanter
(mixture: isopropanol – water + n-hexane)

3.2.3.2.2. Operation of the Generalised Double-Column System

The two columns (*Fig. 3.17*) are operated simultaneously. The condensate of Column α is led into the decanter. The organic phase of the decanter is led into Column α between Sections 3 and 4. The aqueous phase arrives in Column β, at the bottom of Section 2. The condensate of Column β is partially refluxed. The distillate is led into the other column, between Sections 3 and 4.

Because of the slow purification of the isopropanol and water the pure products could not be obtained at the end of the first day. Therefore the equipment must be stopped before reaching the prescribed product purities. The next day the experiment was restarted and finished.

Each day there were three operational periods for each column (*Table 3.20*):
 - Boiling up period: it lasts until the boiling of the charges in both reboilers,
 - Heating up period of the column: until the appearance of the vapour at the top of the column,
 - Distillation period: until the end of the day (1st day) or theoretically until reaching the prescribed product purities (2nd day).

During the operation of the columns the outlet of the aqueous phase of the decanter was usually closed. Therefore only the organic phase could flow out and the quantity of the aqueous phase increased. The total volume of the phases was constant because of the fixed upper outlet. The process of the purification of the isopropanol cannot be indicated by the accumulation of the aqueous phase in the decanter so clearly like in the case of the BR because the distillate of the Column β is led into the Column α. (During the operation of the BR only the organic phase of the decanter is led into the column.) The growth of the level of the aqueous phase indicates only the right operation of the column. The outlet of the aqueous phase was opened several times to let flow out the excess of the aqueous phase.
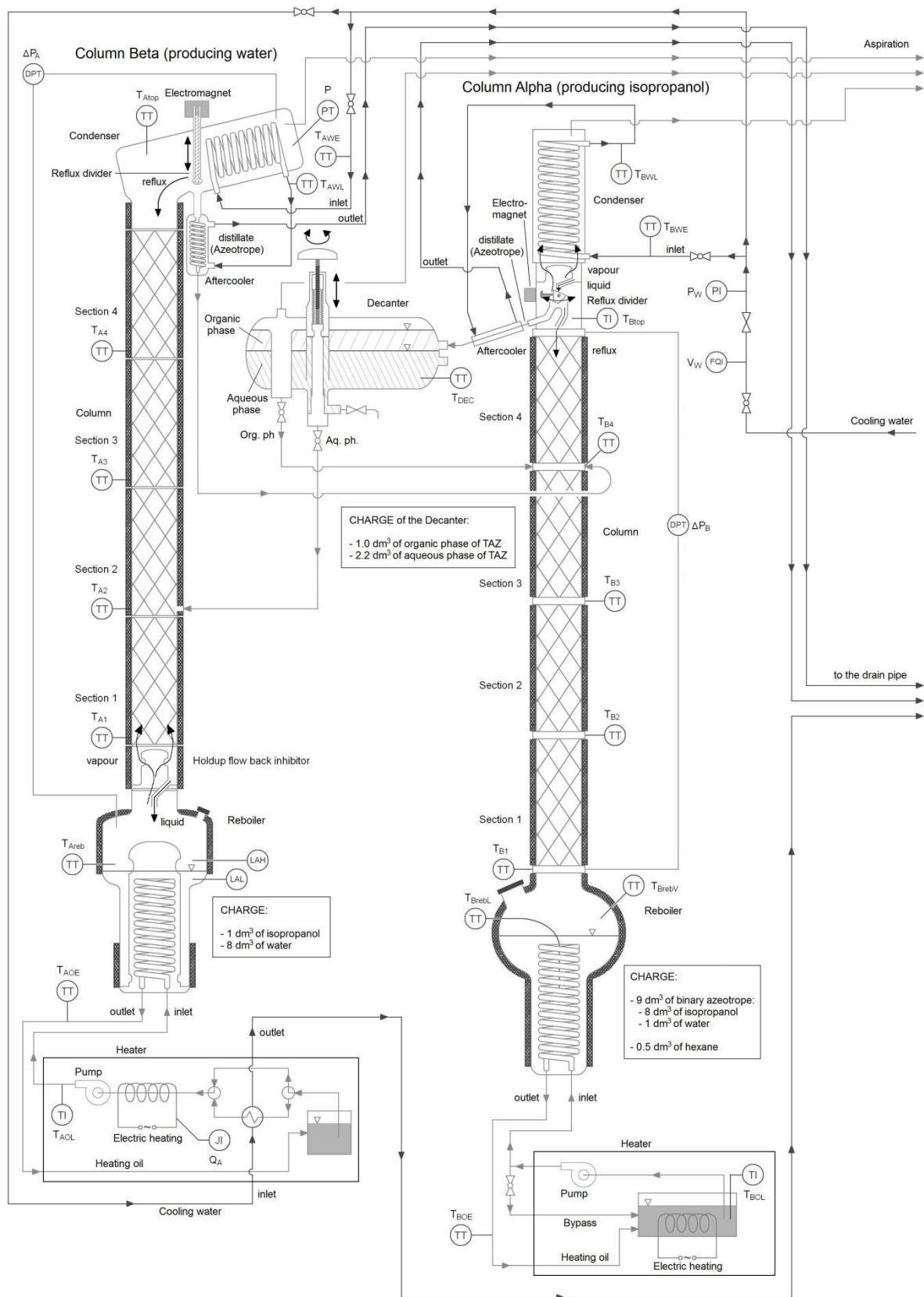
*Fig. 3.17. GDCS laboratory equipment for the separation of
a ternary heteroazeotropic mixture*

During the different operational periods different reflux ratios were applied (*Table 3.20*). In the first distillation period $R^\beta = 1/2$ was applied in order to decrease the flow rate of the distillate led to Column α. This reflux ratio was later increased to $R^\beta = 1$ because the liquid volume in Reboiler α increased nearly by 0.5 dm^3 since the start of the distillation period and therefore the boiling became more unstable. During the experiment the malfunction of the reflux divider of Column β was detected: the reflux valve could not be totally closed. Therefore almost the whole quantity of the condensate, except for the wild reflux, was removed as distillate independently from the reflux ratio adjusted. On the second day, almost right after the start up of Column β the temperature of the heating oil was decreased from 113 to 109 °C in order to avoid the too high distillate flow rate, which could have disturbed the operation of Column α. In consequence of this modification the top of the column cooled down to nearly 40 °C, the top vapour production of Column β was stopped. The heating was operated in order to keep warm the column for a possible reuse. Finally, the vapour production of Column β was not restarted. It means that on the 2nd day the system was operated as a BR.

It must be also noted that, because of the imperfect operation of the reflux divider of Column β nearly 10-30 % of the condensate flowed back to the column even if R^α was set zero. It means that R^α was practically 0.1 – 0.4.

Day	Operational period	Absolute time at the end of the period [min]		Length of the period [min]		Adjusted reflux ratio of the reflux divider	
	Column	α	β	α	β	α	β
1st day	Boiling up	37	96	37	96	infinite	infinite
	Start up of the column	109	169	72	73	infinite	infinite
	Distillation	619	619	510	450	0	1/2 (until t = 220 min) 1 (until the shut down)
2nd day	Boiling up	643	774	24	155	infinite	infinite
	Start up of the column	680	864	37	90	infinite	infinite
	Distillation	993	873	113	9	0	0

Table 3.20. Durations of the operation periods and the adjusted reflux ratios
(mixture: isopropanol – water + n-hexane)

3.2.3.2.3. Results

First the product purities are determined by different methods then the material balances are calculated. The applied heat duties of the heaters are estimated and the evolution of the temperatures in the reboilers and in the columns are shown and explained.

I. Product purities

a. By boiling temperatures

The composition of the reboiler liquid of Column α cannot be determined on the basis of the reboiler vapour temperature because of the small difference of the boiling points of the isopropanol – water azeotrope ($T_{BAZ}^{BP} = 80.1°C$) and the pure isopropanol ($T_A^{BP} = 82.5°C$), as it was detailed in the chapter about the BR pilot plant experiment (Chapter 3.2.3.I.).

Since the charge of Column β does not contain entrainer and the entrainer content of the aqueous phase of the decanter led into Column β is low (2.9 V%), the holdup of Reboiler β (including also the product) is practically binary mixture isopropanol – water. On the basis of the final vapour temperature (99.2 °C) and pressure in the reboiler (1002.4 mbar absolute pressure + 6.0 mbar pressure drop) the purity of the water product is 99.5 V% (99.6 w%, 99.9 mol%).

b. By gas chromatography and Karl-Fischer analysis

The *B* contents of the products (in weight percent) determined by the Karl-Fischer method are accepted without any modification. The concentrations of *A* and *E* (in g/dm³) determined by gas chromatography (with flame ionisation detector) are normalised. The compositions of the products are shown in *Tables 3.22a-c*. We can state that the water was produced in acceptable purity. The isopropanol content of the other product increased significantly but it remained below the purity expected. (The experiment had to be stopped earlier than necessary because of boiling instability in Reboiler α. It caused a large deviation of the top vapour composition from the ternary azeotropic one. It resulted in the disappearance of the interface in the decanter, therefore there was no liquid-liquid separation.)

The parameters of the gas chromatography analysis are detailed in Appendix 6.

II. Material balances

On the basis of the volumes and the compositions of the liquids the integral total and component material balances are calculated. In these balances the initial and the final quantities are compared.

At the beginning:
Total quantity = Charge of Reboiler α + Entrainer + Charge of Reboiler β + Organic phase in the decanter + Aqueous phase in the decanter

At the end:
Total quantity = Isopropanol product + Water product + Organic phase in the decanter + Aqueous phase in the decanter

a. Integral Total Material Balance

All data in *Table 3.21* are measured, nearly at the same temperatures (22-26 °C). The difference between the initial and final total volumes is nearly -0.8 dm^3 (-3.7 %). The reason of this difference can be primarily the evaporative loss and partially the holdup of the column. (The total volume of the packing is 20.1 dm^3. The missing liquid volume is 4.0 % of the packing volume.)

		Volume at the beginning [dm^3]	Volume at the end [dm^3]
Reboiler β		9.0	8.3
Reboiler α		9.5	9.0
Decanter	Total	3.2	3.6
	Org. ph.	*1.0*	*1.2*
	Aq. ph.	*2.2*	*2.4*
Total		**21.7**	**20.9**

Table 3.21.Volumes of the liquids at the beginning and at the end of the process
(mixture: isopropanol – water + n-hexane)

b. Integral Component Material Balance of the components (Tables 3.22a-c)

The volumes of the initial holdups and those of their components are measured. The compositions of the initial holdups are calculated. The volumes of the final holdups are measured. The product compositions are calculated on the basis of the results of the gas chromatography and Karl-Fischer analysis. The final decanter liquid compositions are calculated from the ternary azeotropic composition and liquid-liquid equilibrium. The volumes of the components are also calculated.

	At the beginning				At the end			
	$x\%_A$	$w\%_A$	$V\%_A$	V_A [dm^3]	$x\%_A$	$w\%_A$	$V\%_A$	V_A [dm^3]
Reboiler α	64.0	82.7	84.2	8.00	**71.4**	**89.3**	**91.3**	8.22
Reboiler β	2.9	9.0	11.1	1.00	**0.7**	**2.2**	**2.8**	0.23
Decanter Total	13.3	27.9	29.6	0.95	13.4	27.6	29.1	1.05
Decanter *Org. ph.*	*20.2*	*15.7*	*13.6*	*0.14*	*20.2*	*15.7*	*13.6*	*0.16*
Decanter *Aq. ph.*	*12.6*	*32.0*	*36.9*	*0.78*	*12.6*	*32.0*	*36.9*	*0.89*
Total	-	-	-	**9.95**	-	-	-	**9.50**

Table 3.22a. Isopropanol content of the initial and final holdups

(mixture: isopropanol – water + n-hexane)

	At the beginning				At the end			
	$x_B\%$	$w_B\%$	$V_B\%$	V_B [dm^3]	$x_B\%$	$w_B\%$	$V_B\%$	V_B [dm^3]
Reboiler α	33.7	13.0	10.5	1.00	**28.6**	**10.7**	**8.7**	0.78
Reboiler β	97.1	91.0	88.9	8.00	**99.3**	**97.8**	**97.2**	8.07
Decanter Total	79.3	49.8	42.0	1.34	78.5	48.5	40.7	1.46
Decanter *Org. ph.*	*5.6*	*1.3*	*0.9*	*0.01*	*5.6*	*1.3*	*0.9*	*0.01*
Decanter *Aq. ph.*	*86.9*	*66.2*	*60.6*	*1.33*	*86.9*	*66.2*	*60.6*	*1.45*
Total	-	-	-	**10.34**	-	-	-	**10.31**

Table 3.22b. Water content of the initial and final holdups

(mixture: isopropanol – water + n-hexane)

		At the beginning			At the end			
		$x_B\%$	$w_B\%$	$V_B\%$	V_B [dm^3]	$x_B\%$	$w_B\%$	$V_B\%$	V_B [dm^3]
	Reboiler α	2.3	4.3	5.3	0.50	0.0	0.0	0.0	0.00
	Reboiler β	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.00
Decanter	Total	7.4	22.3	28.4	0.91	8.1	23.9	30.2	1.09
	Org. ph.	*74.2*	*83.0*	*85.5*	*0.85*	*74.2*	*83.0*	*85.5*	*1.03*
	Aq. ph.	*0.5*	*1.8*	*2.5*	*0.06*	*0.5*	*1.8*	*2.5*	*0.06*
	Total	-	-	-	**1.41**	-	-	-	**1.09**

Table 3.22c. N-hexane content of the initial and final holdups

(mixture: isopropanol – water + n-hexane)

The difference between the initial and final isopropanol volumes is -0.45 dm^3 (-4.5 %). Since at the end of the production the holdup of Reboiler α contains mainly isopropanol, the vapour coming from there has high isopropanol content. Therefore the holdup of the hot Column α contains mainly isopropanol, too. This is a possible reason of the error of the material balance. The error of the material balance of water is practically zero (-0.3 %), the same for n-hexane is more considerable (- 0.32 dm^3, -22.7 %). The material balance errors can be caused by the loss of evaporation and also by the inaccuracy of the measurement of the initial component quantities, the final liquid volumes and the final concentrations.

III. Estimation of the applied heat duties of the heaters

a. Heater α

The heater tries to ensure the stability of the inlet oil temperature by consecutive heating and non-heating periods. In the heating period maximum heating is applied ($P_{max}^{\alpha} = 6\,kW$), in the other period the heating is turned off. On the basis of the time ratio of heating and the maximum heat duty of the reboiler the average applied heat duty can be determined. During the distillation these periods were measured several times (*Table 3.23*). It can be stated that the applied heat duty was between 16-26 % of the maximum one (1.0-1.6 kW).

T$_{oil,set}$ [°C]	Period with heating [s]	Period without heating [s]	p [%]	P$_{app}$ [kW]
89	79	400	16.5	0.99
93	83	280	22.9	1.37
93	90	252	26.3	1.58
93	92	256	26.4	1.59
94	86	279	23.6	1.41
95	91	253	26.4	1.59

Table 3.23. Average applied heat duty of Heater α (mixture: isopropanol – water + n-hexane)

b. Heater β

The heat duty of Heater β is shown in percentage (*p*) continuously on a display on the control panel of the heater. Since the maximum heat duty of the heater is known ($P_{max}^{\beta} = 4\,kW$) the applied heat duty (P_{app}) can be calculated easily for each set oil temperature ($T_{oil,set}$, *Table 3.24*). It was between 21-36 % of the maximum one (0.8-1.5 kW).

T$_{oil,set}$ [°C]	p [%]	P$_{app}$ [kW]
108	27	1.08
108	24	0.96
108	21	0.84
110	25	1.00
110	25	1.00
110	25	1.00
115	35	1.40
115	36	1.44

Table 3.24. Applied heat duty of Heater β (mixture: isopropanol – water + n-hexane)

 a. Column α

Figs. 3.18a-b show the evolution of the liquid and vapour temperatures in the reboiler of Column α (T_{ArebL} , T_{ArebV}). The start-up and the distillation periods are plotted without the shut down periods. The liquid temperature displayed is higher than that of the vapour because the resistance thermometer immersing into the liquid is close to the heating spiral. After the entrainer had left Reboiler α the vapour temperature was stable until the shut down. It did not vary because the boiling point of the mixture is not sensitive to the composition, and the variation of the composition was neither significant. The reason of the oscillation of the liquid temperature is the periodic operation of the heater.
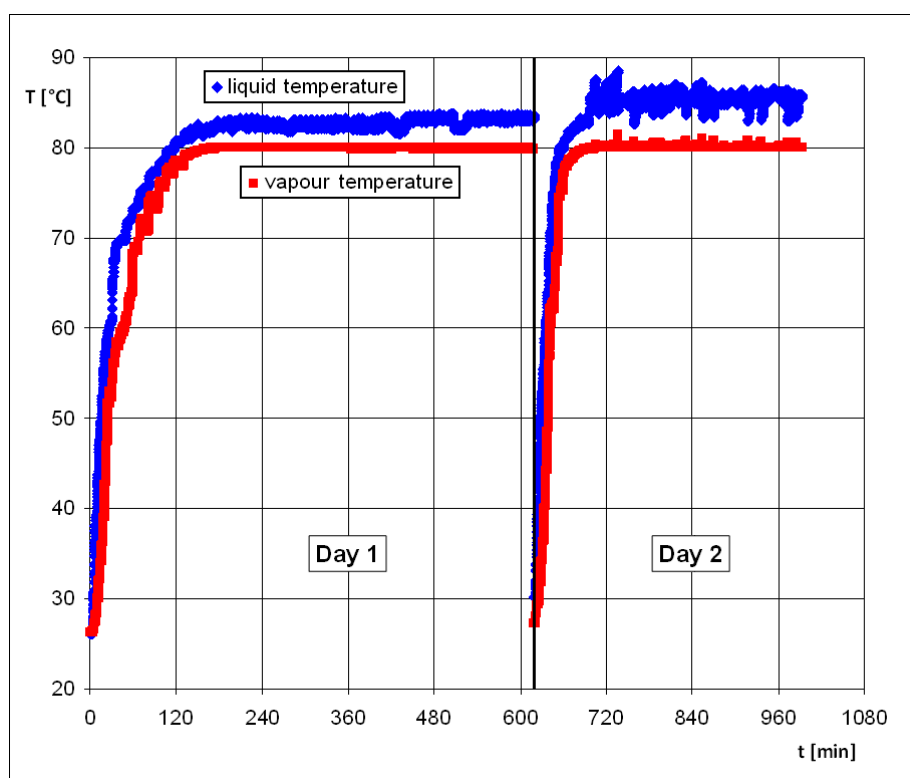
Fig. 3.18a. Liquid and vapour temperatures in Reboiler α

(mixture: isopropanol – water + n-hexane)

Fig. 3.18b. Liquid and vapour temperatures in Reboiler α (zoomed on the distillation periods, mixture: isopropanol – water + n-hexane)

Fig. 3.19 shows the evolution of the temperatures below each section of Column α ($T_{A1}, T_{A2}, T_{A3}, T_{A4}$). The temperature in the lowest section (T_{A1}) exceeded that of the ternary azeotrope (T_{TAZ}^{BP}) already at the beginning (also on the 2nd day). It reached T_{BAZ}^{BP} gradually, and remained there until the end of the operation. When the vapour reached Sections 2 and 3, T_{A2} and T_{A3} were close to T_{TAZ}^{BP}. The entrainer ran out quickly from the reboiler, therefore these temperatures jumped up to T_{BAZ}^{BP}. Then because of the boiling instability in Reboiler α, T_{A2} oscillated for a while (between 280 min and 360 min) between T_{BAZ}^{BP} and T_{TAZ}^{BP}. Just after reaching T_{BAZ}^{BP}, T_{A3} fell down to T_{TAZ}^{BP} because a part of the *E*-rich phase flowed back to Column α, due to the growth of the volume of the *B*-rich phase in the decanter. T_{A2} and T_{A3} jumped up to T_{BAZ}^{BP} at $t = 347min$ min when 0.6 dm^3 of *B*-rich (aqueous) phase was released to Column β. Then both temperatures remained there. On the 2nd day after the start-up, they remained more or less at T_{BAZ}^{BP}. T_{A4} was generally close to T_{TAZ}^{BP} during the process but sometimes when the operation was disturbed (release of *B*-rich phase from the decanter, hydraulic shock caused by the wrong operation of Reboiler α) it jumped up even until T_{BAZ}^{BP}. The same

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phenomenon was observed for the top vapour temperature (*Fig. 3.20*). On the 2nd day this frequent change of top vapour composition resulted in the upset of the equilibrium in the decanter, and the liquid became homogeneous. For the formation of the two-phase liquid nearly two hours was necessary. When the decanter holdup became homogeneous for the second time, the experiment was stopped after 30 minutes.

Fig. 3.19. Evolution of the temperatures below each section of Column α
(lowest: Section 1, upper: Section 4; mixture: isopropanol – water + n-hexane)
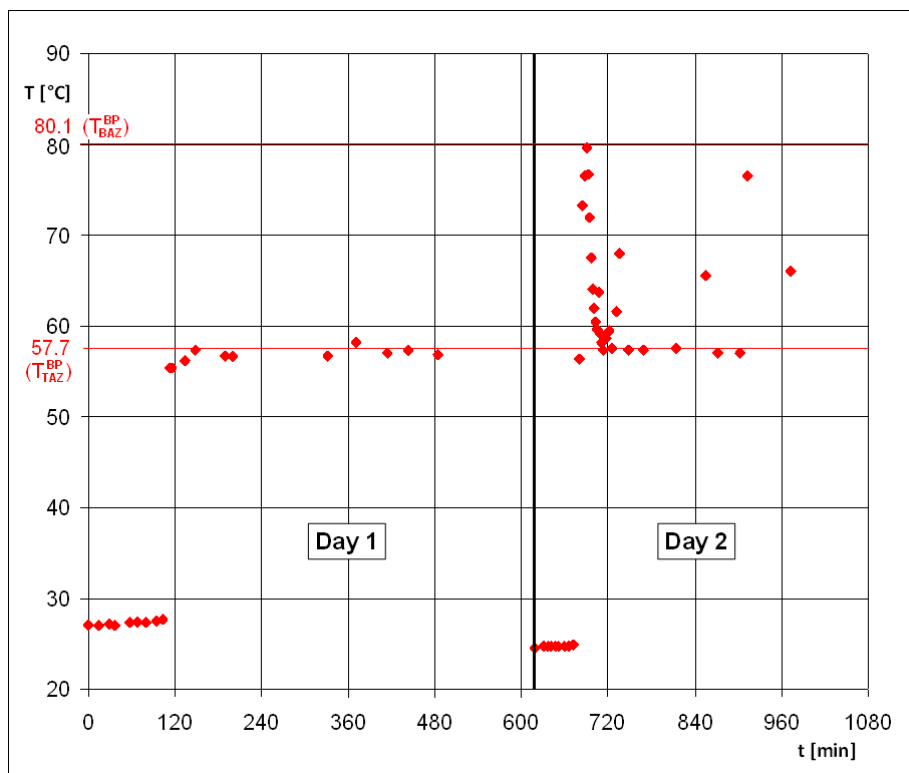
Fig. 3.20. Evolution of the top vapour temperature of Column α

(mixture: isopropanol – water + n-hexane)

b. Column β

Figs. 3.21a-b show the evolution of the reboiler temperature (T_{Breb}). The start up and the distillation periods are plotted again without the cooling down periods. At $t = 252min$ the heating of Reboiler β was decreased (oil temperature: from 110 °C to 100 °C) therefore the reboiler temperature stopped increasing and started to decrease. This intervention was done in order to avoid a too high distillate flow rate, which resulted in the increase of the volume of the holdup of Reboiler α. The higher liquid level resulted in boiling instabilities in Reboiler α. Our aim was the abolishment of this harmful phenomenon. Then the heating was increased again in order to continue the purification of the water. During the experiment the outlet of the aqueous phase of the decanter was opened several times in order to decrease the quantity of the aqueous phase. Whenever this cold liquid flowed into Column β, the reboiler temperature decreased by a few degrees. At the end of the experiment the boiling temperature of the holdup of Reboiler β approached closely that of the pure water (99.2 °C).

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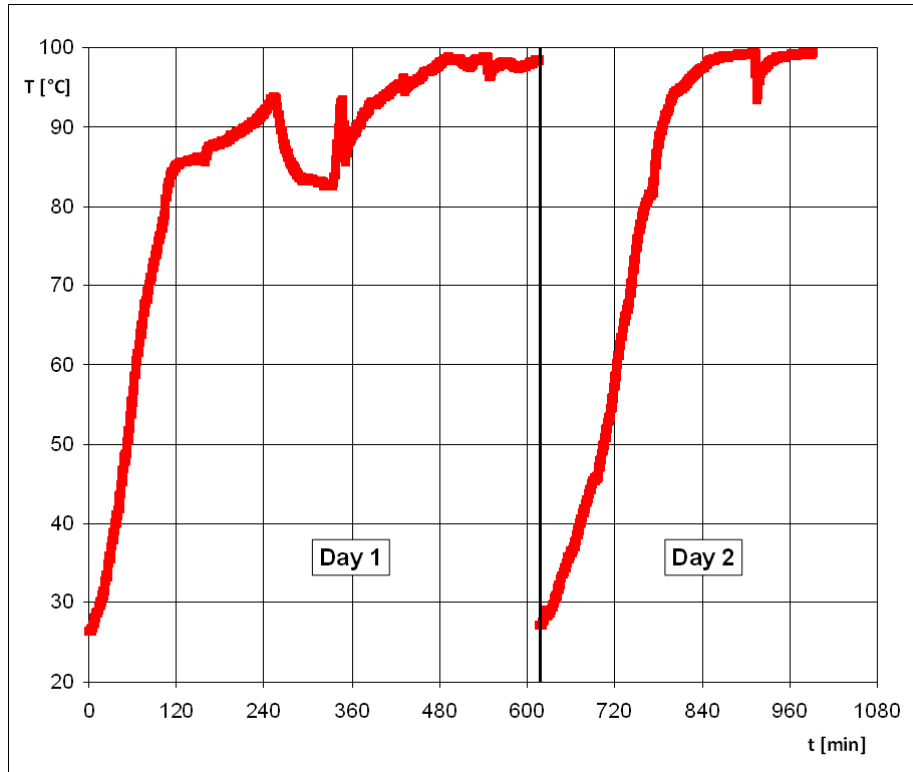
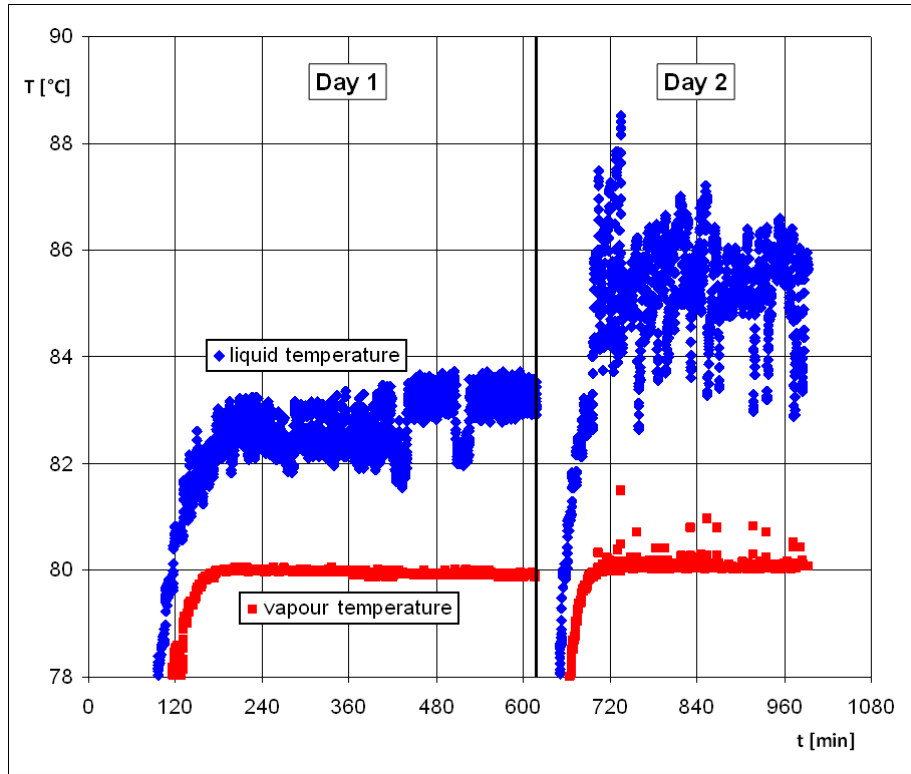*Fig. 3.21a. Vapour temperature in Reboiler β (mixture: isopropanol – water + n-hexane)*
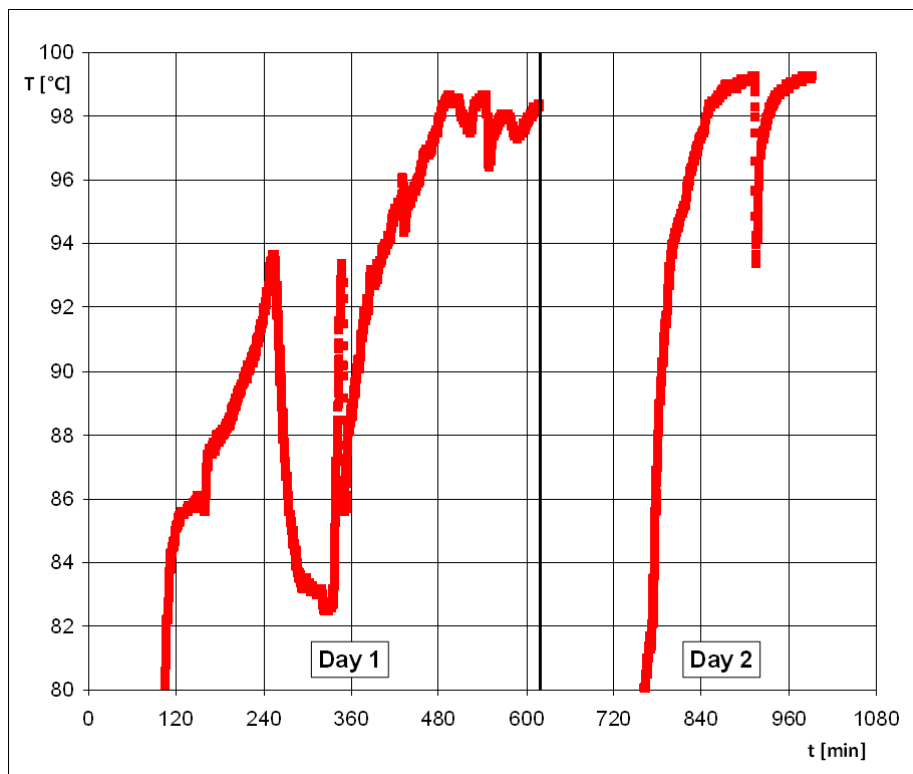
Fig. 3.21b. Vapour temperature in Reboiler β (zoomed on the distillation periods,

mixture: isopropanol – water + n-hexane)

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Fig. 3.22 shows the evolution of the temperatures below each section of Column β ($T_{B1}, T_{B2}, T_{B3}, T_{B4}$). At the beginning each temperature is equal to T_{BAZ}^{BP}, even below the lowest column section. Then these temperatures started increasing one after the other because of the decrease of the isopropanol content of the reboiler liquid. At $t = 252min$ min the heating of Reboiler β was decreased (oil temperature: from 110 °C to 100 °C). Therefore all column temperatures decreased deeply under the boiling point of the reboiler liquid, Column β was practically stopped. At $t = 332min$ the heating of Reboiler β was increased to 105 °C then to 110 °C because aqueous phase from the decanter was earlier released to the column, therefore the liquid in Reboiler β needed further purification. At $t = 505min$ when all column section temperatures exceeded 99 °C, the oil temperature of Heater α was decreased from 115 to 105 °C in order to prevent the disturbance of the operation of the other column. Later the oil temperature was set to 110 then 108 °C, which provided stable operation for Column α until the end of the 1st day. It was disturbed just by the aqueous phase sometimes coming from the decanter. On the 2nd day the operation of Column β was also stable.
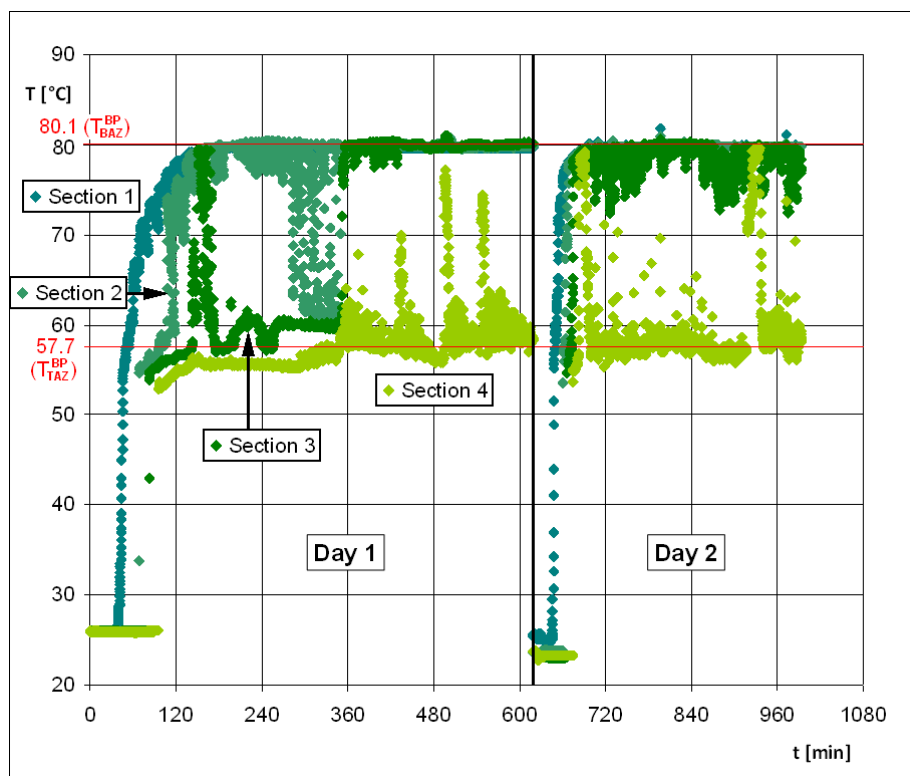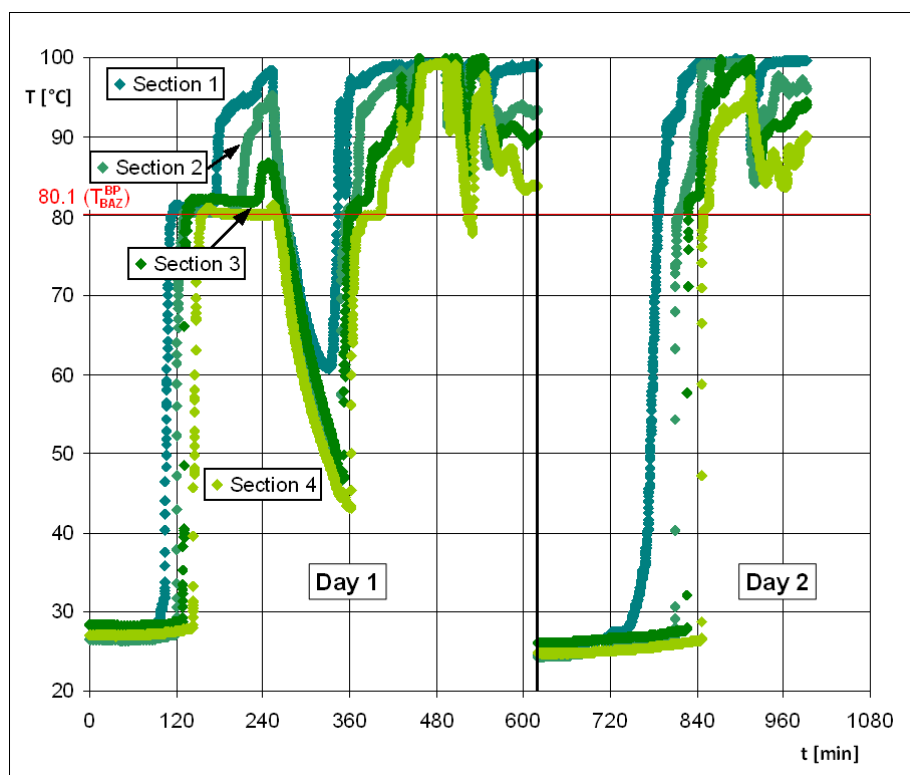

Fig. 3.22. Evolution of the temperatures below each section of Column β
*(lowest: Section 1, upper: Section 4; mixture: isopropanol – water + n-hexane)*

Since the reflux divider could not operate correctly, almost the whole condensate was withdrawn except for the wild reflux. The aqueous phase is led below Section 4. Therefore in this upper column section practically there is practically no separation. T_{B4} can be considered as the top vapour temperature (*Fig. 3.23*). (The resistance thermometer above Section 4 measures much lower vapour temperature (T_{Btop}) because of the heat loss, e.g. 92 °C instead of 100 °C.)
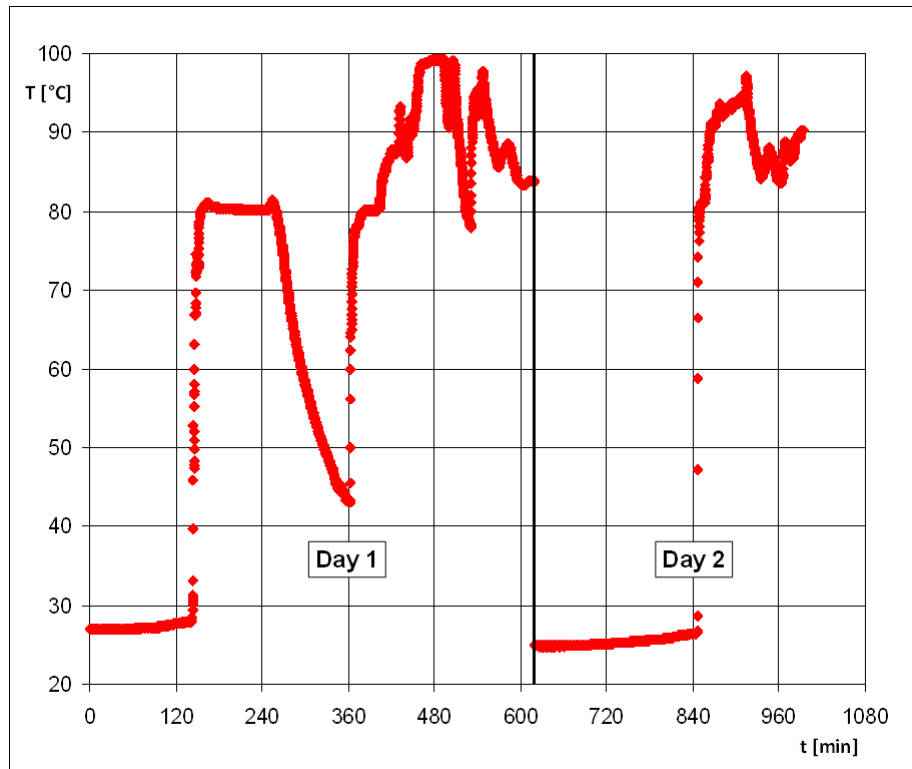
Fig. 3.23. Evolution of the top vapour temperature of Column β (identical with the temperature below Section 4)

3.2.3.2.4. Conclusions

Our aim was to validate the Generalised Double-Column System (GDCS) for heteroazeotropic batch distillation. For this purpose we intended to produce both components purely and simultaneously from the homoazeotropic mixture isopropanol – water in a pilot plant equipped with a decanter. N-hexane was added as entrainer to the charge.

During the experiment several malfunctions occurred: the boiling was not stable in Reboiler α, the composition of the top vapour of Column α did not remained continuously close to the

ternary azeotropic one, the reflux divider of Column α did not operate well because of manufacturing defect, and the reflux divider of Column β did not work satisfactory.

The water could be produced in acceptable purity (99.3 mol%). The isopropanol content of the other product increased significantly but it remained below the purity expected (from 64.0 mol% to 71.4 mol%).

After the sources of the malfunctions are removed, the isopropanol will can be also produced in much higher purity. Unfortunately, due to lack of time, these malfunctions could not be eliminated during thesis period. The experiment has shown that the simultaneous production of isopropanol and water in the GDCS is feasible.

CONCLUSIONS AND FURTHER TASKS

Conclusions

The separation of the azeotropic mixtures needs special distillation methods like heteroazeotropic distillation. In the pharmaceutical and fine chemical industries it is often applied in batch mode.

We suggested a new Double-Column System (DCS) for heteroazeotropic batch distillation (BHD). The system is operated in closed mode without continuous product withdrawal. This configuration was investigated by feasibility studies based on a simplified model (assumption of maximal separation, neglect of hold-up) and by dynamic simulation (based on a detailed model) by using a professional simulator (ChemCAD CC-DCOLUMN). The performance of this new DCS was compared with the traditional Batch Rectifier (BR). For the new configuration we determined the minimal operational time. The calculations and the simulations were performed for the heteroazeotropic mixture 1-butanol – water and for the ternary heteroazeotropes isopropanol – water + benzene or cyclohexane (entrainer). For both configurations we determined the optimal quantity of entrainer to be applied and for the new double-column system (DCS) the optimal divison of the entrainer, the charge and the total heat duty providing the minimal operational time for the different configurations. The new configuration proved to be feasible and competitive with the conventional BR. For the binary mixture DCS gave similar and for the ternary one better performance than the BR. Its main benefit is that it produces less byproducts to be separated later.

Then we generalised the DCS (Generalised Double-Column System, GDCS) and studied the separation of the minimum homoazeotropic mixture isopropanol – water by applying cyclohexane and n-hexane as entrainer in this configuration. The GDCS has three supplementary operational parameters comparing with the original DCS: the feed tray location (f^{α}) of the distillate of Column β (producing water) in Column α (producing isopropanol), the feed tray location of the aqueous phase of the decanter in Column β (f^{β}) and the reflux ratio in Column β (R^{β}). These parameters provide the possibility of a more flexible and more efficient operation like that of the original DCS.

First the feasibility of the GDCS was studied by a simplified method by using only the integral material balances. The separation by the GDCS proved to be feasible.

Then the influence of the supplementary operational parameters of the GDCS was studied by rigorous simulation. This study made clear the choice of the values of the operational parameters: the distillate of Column β must be fed into one of the upper plates of Column α, the aqueous phase from the decanter must be fed into one of the lower plates of Column β, and the reflux ratio of Column β must be low ($R^\beta < 1$).

After that the minimum duration of the process was determined for the GDCS and for the original DCS and their performances were compared (duration, specific energy demands of the products). By the downhill simplex method the optimum values of the operational parameters were also determined. The above investigations were done for three different charge compositions and for both entrainers. In every case shorter duration was obtained for the GDCS. The specific energy demands of the products were also lower in almost all cases. Finally the performances of the entrainers were compared. On the basis of the VLLE conditions the n-hexane is more advantageous than the cyclohexane. This is also confirmed by the simulation results, as well: for n-hexane the duration is always shorter, the amounts of the products are in the majority of the cases higher and the total amount of the byproducts is always lower for both configurations.

After the feasibility studies and simulations the configurations were validated by laboratory and pilot plant experiments.

First a laboratory experiment was performed for the DCS. Our primary aim was to investigate the feasibility of the separation of the heteroazeotropic mixture 1-butanol – water in the new configuration, therefore a very simple laboratory equipment was applied. We compared the performance of the DCS with that of the conventional Batch Rectifier. We also performed rigorous simulations by using ChemCAD CC-DCOLUMN. On the basis of the results the separation in the DCS proved to be feasible and competitive with that of the BR. By using the DCS higher recovery for 1-butanol was reached during practically the same time and the quantity of the byproducts was also less for the DCS.

Because of the simple construction of the laboratory equipment the experiments done with it gave less information than desired and its operation is less flexible and less convenient. For the successful separation of a binary homoazeotropic mixture by using an entrainer a more sophisticated pilot plant was built for the further experiments.

First the heteroazeotropic mixture water – 1-butanol was separated in a batch double-column pilot plant. The aqueous and the organic phases of the heterogeneous charge were fed into different reboilers. After the long boiling up and start up periods (almost half of the total duration) both components could be produced in high purity in spite of the malfunction of the reflux dividers.

After the successful experiment the processing of ternary heteroazeotropic mixtures followed. First from the homoazeotropic mixture isopropanol – water isopropanol was produced in the equipment operated as a batch rectifier equipped with a decanter. To the charge of azeotropic composition n-hexane was added as entrainer. In spite of the stability problems of the boiling, the malfunction of the reflux divider and the volumetric limit of the reboiler, the purification of the isopropanol was feasible. The final product contained less than 5 V% of contamination (mainly water). The column could have produced isopropanol also in higher purity but because of the low liquid level in the reboiler, the experiment had to be finished.

Then we intended to produce simultaneously both components of the homoazeotropic mixture isopropanol – water in the equipment operated as GDCS. N-hexane was added as entrainer to the charge.
During the experiment several malfunctions occurred: the boiling was not stable in Reboiler α, the composition of the top vapour of Column α did not remained continuously close to the ternary azeotropic one, the reflux divider of Column α did not operate well because of manufacturing defect, and the reflux divider of Column β did not work satisfactory.
The water could be produced in acceptable purity. The isopropanol content of the other product increased significantly but it remained below the purity expected.
After the sources of the malfunctions are removed, the isopropanol will can be also produced in much higher purity. Unfortunately, due to lack of time, these malfunctions could not be eliminated during thesis period. The experiment has shown that the simultaneous production of isopropanol and water in the GDCS is feasible.

Further tasks

The pilot plant experiments showed that the operations of the double-column systems are more complicated than that of the Batch Rectifier, especially in the case of the processing of a ternary mixture. For the sake of the knowledge of the stable operation (e.g. heterogeneous holdup in the decanter continuously, reaching of the prescribed purity in both reboilers at the same time, stable boiling in the reboilers) further experiments are needed.

For these pilot plant experiments first both reflux dividers should be repaired. The heating spirals of the reboilers must be changed to other heat transfer elements, whose total immersions need lower liquid levels in the reboilers. In this manner during the process greater variations of liquid volumes could be permitted in the reboilers, which would make possible the processing of charges from wider composition range.

A very important task is the control of the heating of the reboilers. The stability of the heterogeneous holdup in the decanter depends on the ratio of the vapour flow rates of the two columns, which depend on the ratio of the heat duties applied in the reboilers. The vapour flow rates can be controlled also by the reflux dividers much more quickly therefore the control of the system should be extended to them, too.

In addition, for the determination of the heat duties the actual liquid temperatures in the reboilers also must be taken into consideration because of two reasons:

- The increase of the boiling temperatures must be followed by the heat duties for the sake of the sustainment of the boiling.

- The increase of the reboiler temperature shows the increase of the purity. The heat duties must be controlled so that the products reach their prescribed purities at the same time.

After the abolishment of the defects and the elaboration of the control of the pilot plant equipment it is worthy to do further experiments for the binary homoazeotropic mixture.

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Appendix 1

Properties of pure components and azeotropes

1. Pure components

The main properties of the components used in this work are involved into *Table A.1*. The data sources are the books of Riddick and Bunger (1970), Perry and Green (1984), Ohe (1976) and Raznjevic (1964).

Component		water	1-butanol	isopropanol	benzene	cyclohexane	n-hexane
Formula		H_2O	$C_4H_{10}O$	C_3H_8O	C_6H_6	C_6H_{12}	C_6H_{14}
Molar weight [g/mol]		18.02	74.12	60.10	78.11	84.16	86.18
Boiling point[1] [°C]		100	117.66	82.5	80.1	80.74	68.74
Antoine coefficients	A	7.95864	7.37903	7.7361	6.89326	6.85532	6.89122
	B	1663.125	1313.878	1357.427	1203.828	1209.299	1178.802
	C	227.528	174.361	197.336	219.921	223.527	225.200
Liquid density[2] [g/cm³]		0.997	0.806	0.781	0.873	0.773	0.656
Molar heat of vaporisation[3] [kJ/mol]		40.66	43.13	39.92	30.80	29.91	28.79

Table A.1. Properties of pure components

2. Mixture 1-butanol (*A*) – water (*B*)

The VLE and LLE of this mixture were described by the NRTL model, whose binary interaction parameters (BIPs) are from the ChemCAD Component Database:

$$B_{AB} = 215.427\,K^{-1}, \ B_{BA} = 1468.34\,K^{-1}, \ \alpha = 0.3634$$

The computed compositions of the azeotrope and equilibrium phases and the boiling points are shown in *Table A.2*.

[1] at *P = 1 atm = 101 325 Pa*

[2] at *T = 25 °C*

[3] at the boiling point at *P = 1 atm*

Component or mixture	Mole fraction		Boiling point [°C]
	1-butanol	water	
1-butanol	1	0	117.92
water	0	1	99.99
azeotrope	0.2562	0.7438	92.14
organic phase[4]	0.568	0.432	92.14
aqueous phase[4]	0.012	0.988	92.14

Table A.2. Computed compositions and boiling points of the system 1-butanol – water

3. Mixture isopropanol (*A*) – water (*B*) + entrainer (*E*)

In this work three entrainers were used for the mixture isopropanol – water: benzene, cyclohexane and n-hexane. All BIPs are taken from Gmehling et al. (1991-2010) and Sorensen et al. (1979-1987).

3.1. Benzene as entrainer

For the description of VLE and LLE of this ternary system the same set of BIPs were used (*Table A.3*).

Components		A_{ij}	A_{ji}
i	j	cal/mol	cal/mol
Isopropanol	Water	300.19	109.55
Isopropanol	Benzene	54.8831	319.618
Water	Benzene	746.0207	1710.29

Table A.3. UNIQUAC binary interaction parameters for mixture

isopropanol – water – benzene

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[4] at $T = T_{AZ}$

3.2. Cyclohexane as entrainer

First the same set of BIPs was used for the description of VLE and LLE (*Table A.4*) then different sets of parameters were used for the sake of the more accurate modelling (*Table A.5*).

Components		A_{ij}	A_{ji}
i	j	cal/mol	cal/mol
Isopropanol	Water	300.19	109.55
Isopropanol	Cyclohexane	-192.936	848.376
Water	Cyclohexane	687.9576	2499.682

Table A.4. UNIQUAC binary interaction parameters for the mixture

isopropanol – water – cyclohexane

Equilibrium type	Components		BIP type	A_{ij}	A_{ji}
	i	j		cal/mol	
VLE	Isopropanol	Water	binary VLE	231.6935	194.1258
	Isopropanol	Cyclohexane	binary VLE	-210.864	903.8054
	Water	Cyclohexane	binary LLE	1073.8088	2478.647
LLE	Isopropanol	Water	ternary LLE	-486.469	-1444.483
	Isopropanol	Cyclohexane	ternary LLE	-426.7732	-858.7728
	Water	Cyclohexane	ternary LLE	1842.2629	2005.4923

Table A.5. UNIQUAC binary interaction parameters for the separate description of VLE and

LLE of the mixture isopropanol – water – cyclohexane

3.3. N-hexane as entrainer

For the description of VLE and LLE different set of BIPs were applied (*Table A.6*).

| Equilibrium type | Components | | BIP type | A_{ij} | A_{ji} |
	i	j		cal/mol	
VLE	Isopropanol	Water	binary VLE	231.6935	194.1258
	Isopropanol	N-hexane	binary VLE	-194.4253	863.5296
	Water	N-hexane	binary LLE	1189.7228	2308.5419
LLE	Isopropanol	Water	ternary LLE	11.375982	194.02721
	Isopropanol	N-hexane	ternary LLE	-175.0315	565.30163
	Water	N-hexane	ternary LLE	328.0685	2033.512

Table A.6. UNIQUAC binary interaction parameters for the separate description of VLE and LLE of the mixture isopropanol – water – n-hexane

3.4. Computed azeotropic compositions and boiling points of the ternary systems

The azeotropic compositions and boiling temperatures were calculated on the basis of the UNIQUAC model, used common and separate BIPs for the description of VLE and LLE (*Table A.7*).

Entrainer	Component or azeotrope		Mole fraction			Type of azeotrope	Boiling point [°C]
			A	*B*	*E*		
-	*A - B*	common BIPs	0.674	0.326	0	homoTmin	80.20
		separate BIPs	0.662	0.338			80.09
	A		1	0	0	-	82.26
	B		0	1	0	-	100.00
benzene	common BIPs	*A - B - E*	0.238	0.239	0.523	heteroTmin	65.57
		B - E	0.298	0	0.702	homoTmin	69.22
		A - E	0.416	0	0.584	homoTmin	71.56
	E		0	0	1	-	80.09
cyclohexane	common BIPs	*A - B - E*	0.236	0.222	0.542	heteroTmin	63.88
		A - E	0.389	0	0.611	homoTmin	69.09
		B - E	0	0.300	0.700	homoTmin	69.35
	separate BIPs	*A - B - E*	0.216	0.248	0.536	heteroTmin	63.45
		A - E	0.382	0	0.618	homoTmin	68.88
		B - E	0	0.300	0.700	homoTmin	69.35
	E		0	0	1	-	80.72
n-hexane	separate BIPs	*A - B - E*	0.191	0.169	0.640	heteroTmin	57.72
		A - E	0	0.211	0.789	homoTmin	61.52
		B - E	0.294	0	0.706	homoTmin	61.81
	E		0	0	1	-	68.73

Table A.7. Computed compositions and boiling points of the systems
isopropanol – water + entrainer

Appendix 2

Better processing sequence in the BR for a binary heterogeneous charge

(Derivation of Inequality 2.1)

One production cycle consists of two distillation steps. We select the sequence of the processing of the phases so that the overall quantity of the two products in the first cycle be maximal. (In this case the quantity of the byproduct is minimal.) After Step 1 the distillate is added to the other phase, and they are processed together, since their compositions are the same. (They are both saturated.)

1. Sequence *AB*

The heterogeneous charge is separated into *A*-rich and *B*-rich phases by decantation (*Fig. A.1*). First the *A*-rich phase is distilled: the reboiler residue is Product *A*, the distillate is *B*-rich phase. After that the two *B*-rich phases are mixed together. (Their compositions are the same.) The three operations done until now can be replaced by a single fictive one (Task 1) whose input is the charge and outputs are Product *A* and the united *B*-rich phase (*Fig. A.2*). Then this mixture is distilled (Task 2): the reboiler residue is Product *B*, the distillate is the final *A*-rich phase, which is the only byproduct.
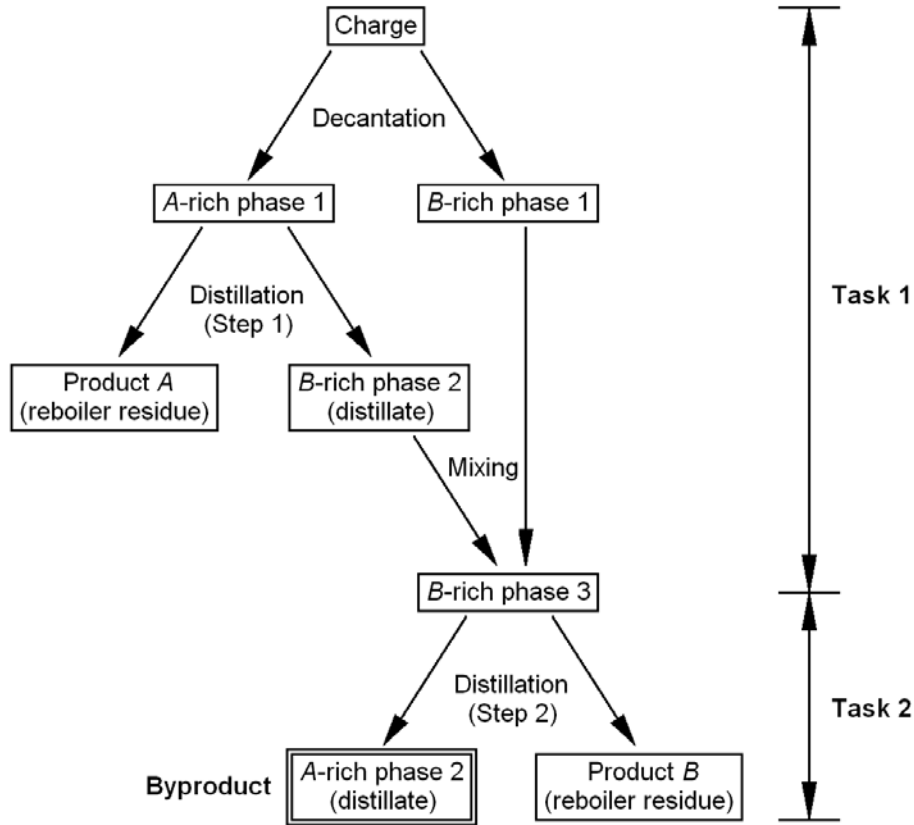
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Fig. A.1. Scheme of sequence AB

Fig. A.2. Simplified scheme of sequence AB with molar quantities and compositions

1.1. Task 1

Total Material Balance:

$$U_{ch} = U^{ProdA} + U^{Br} \tag{A.1}$$

Component Material Balance (CMB) for component A:

$$U_{ch} \cdot x_{ch,A} = U^{Br} \cdot x_A^{Br} + U^{ProdA} \cdot x_A^{ProdA} \tag{A.2}$$

If (A.1) and (A.2) are united, we get the following equation:

$$U_{ch} \cdot x_{ch,A} = U^{Br} \cdot x_A^{Br} + \left(U_{ch} - U^{Br}\right) \cdot x_A^{ProdA} \tag{A.3}$$
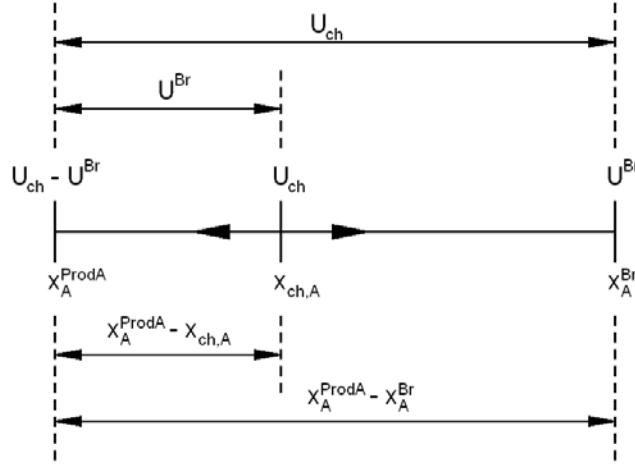
Fig. A.3. Separation scheme (Sequence AB, Task 1)

By rearranging (A.3) the relative quantity of the *B*-rich phase by the "lever rule" (*Fig. A.3*):

$$\frac{U^{Br}}{U_{ch}} = \frac{x_A^{ProdA} - x_{ch,A}}{x_A^{ProdA} - x_A^{Br}} \tag{A.4}$$

1.2. Task 2

CMB for *A*:

$$\left(U^{Br} - U^{Ar}\right) \cdot \left(x_A^{Br} + x_B^{ProdB} - 1\right) = \cdot U^{Ar} \cdot \left(x_A^{Ar} - x_A^{Br}\right) \tag{A.5}$$

Fig. A.4. Separation scheme (Sequence AB, Task 2)

Relative quantity of the *A*-rich phase (*Fig. A.4*):
$$\frac{U^{Ar}}{U^{Br}} = \frac{x_A^{Br} + x_B^{ProdB} - 1}{x_A^{Ar} + x_B^{ProdB} - 1} \tag{A.6}$$

Expressing it by using the total charge quantity only (from Eqs. A.4 and A.6):

$$\frac{U^{Ar}}{U_{ch}} = \frac{x_A^{Br} + x_B^{ProdB} - 1}{x_A^{Ar} + x_B^{ProdB} - 1} \cdot \frac{x_A^{ProdA} - x_{ch,A}}{x_A^{ProdA} - x_A^{Br}} = u_{SeqAB}^{bp} \tag{A.7}$$

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2. Sequence *BA*

The heterogeneous charge is separated into *A*-rich and *B*-rich phases by decantation (*Fig. A.5*). First the *B*-rich phase is distilled: the reboiler residue is Product *B*, the distillate is *A*-rich phase. This latter one is mixed with the other *A*-rich phase obtained by the decantation. (Their compositions are the same.) The operations done until now can be replaced by a fictive one (Task 1) whose input is the charge and outputs are Product *B* and *A*-rich phase (*Fig. A.6*). Then this mixture is distilled (Task 2): the reboiler residue is Product *A*, the distillate is *B*-rich phase, which is the only byproduct.
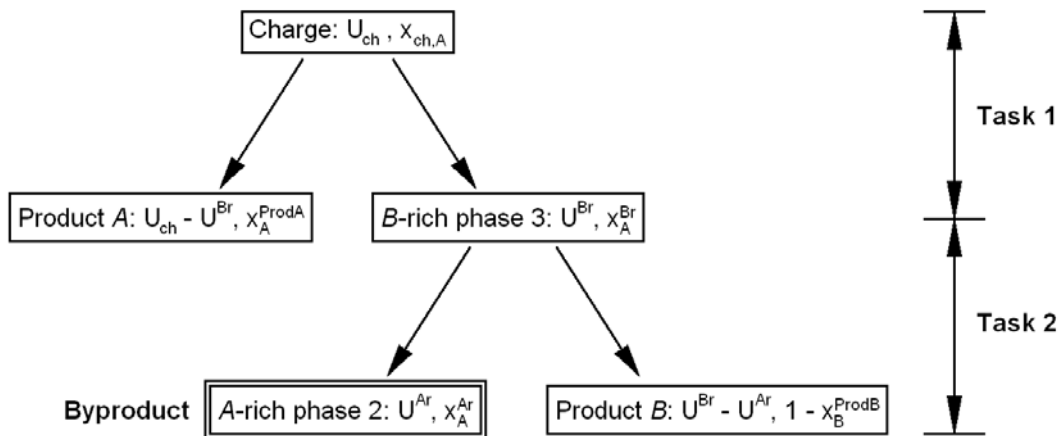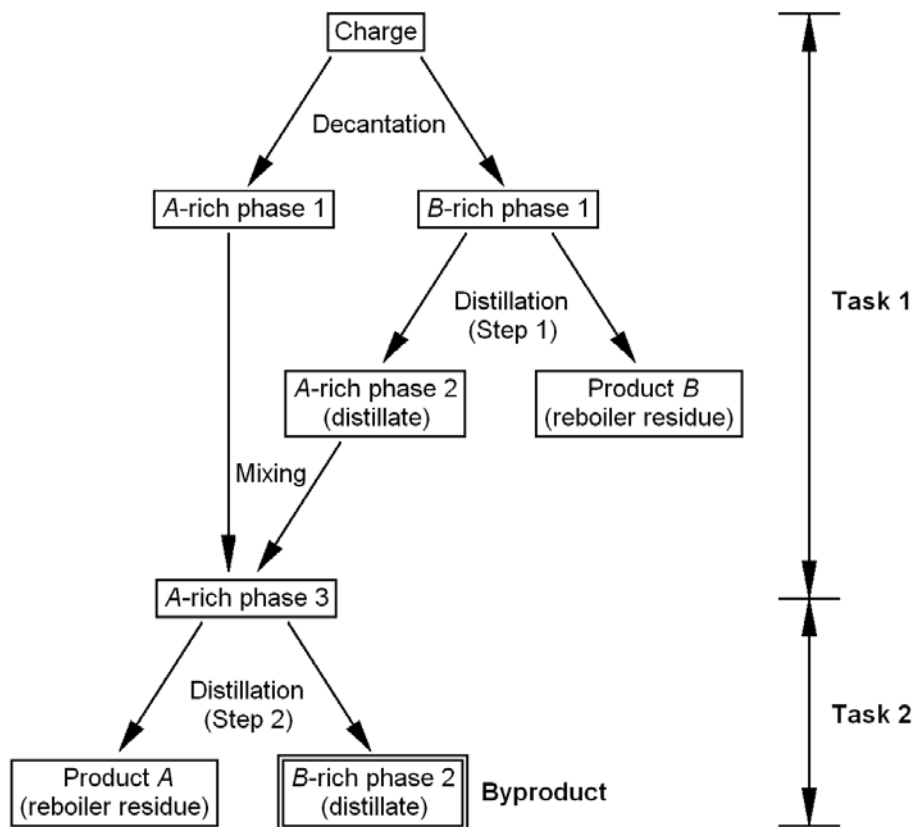

Fig. A.5. Scheme of sequence BA
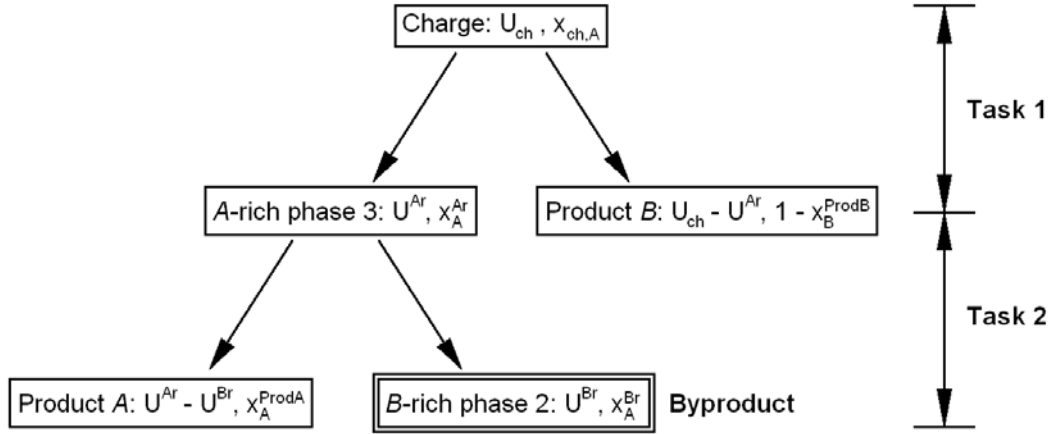
Fig. A.6. Simplified scheme of sequence BA with molar quantities and compositions

2.1. Task 1

CMB for *A*:

$$\left(U_{ch} - U^{Ar}\right) \cdot \left(x_{ch,A} + x_B^{ProdB} - 1\right) = U^{Ar} \cdot \left(x_A^{Ar} - x_{ch,A}\right) \tag{A.8}$$
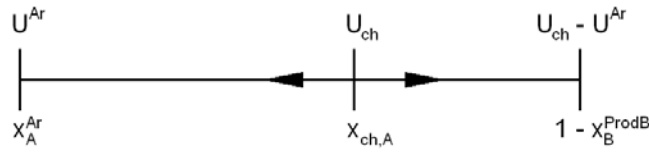
Fig. A.7. Separation scheme (Sequence BA, Task 1)

Relative quantity of the *A*-rich phase (*Fig. A.7*):

$$\frac{U^{Ar}}{U_{ch}} = \frac{x_{ch,A} + x_B^{ProdB} - 1}{x_A^{Ar} + x_B^{ProdB} - 1} \tag{A.9}$$

2.2. Task 2

CMB for *A*:

$$U^{Br} \cdot \left(x_A^{Ar} - x_A^{Br}\right) = \left(U^{Ar} - U^{Br}\right) \cdot \left(x_A^{ProdA} - x_A^{Ar}\right) \tag{A.10}$$

Fig. A.8. Separation scheme (Sequence BA, Task 2)

Relative quantity of the B-rich phase (*Fig. A.8*):
$$\frac{U^{Br}}{U^{Ar}} = \frac{x_A^{ProdA} - x_A^{Ar}}{x_A^{ProdA} - x_A^{Br}} \tag{A.11}$$

Expressing it by using the total charge quantity only (from Eqs. A.9 and A.11):

$$\frac{U^{Br}}{U_{ch}} = \frac{x_A^{ProdA} - x_A^{Ar}}{x_A^{ProdA} - x_A^{Br}} \cdot \frac{x_{ch,A} + x_B^{ProdB} - 1}{x_A^{Ar} + x_B^{ProdB} - 1} = u_{SeqBA}^{bp} \tag{A.12}$$

3. Comparison of the byproduct quantities for the two cases

The *A*-rich phase must be distilled first if:
$$u_{SeqAB}^{bp} \le u_{SeqBA}^{bp} \tag{A.13}$$

In details (from Eqs. A.7 and A.12):

$$\frac{x_A^{Br} + x_B^{ProdB} - 1}{x_A^{Ar} + x_B^{ProdB} - 1} \cdot \frac{x_A^{ProdA} - x_{ch,A}}{x_A^{ProdA} - x_A^{Br}} \le \frac{x_A^{ProdA} - x_A^{Ar}}{x_A^{ProdA} - x_A^{Br}} \cdot \frac{x_{ch,A} + x_B^{ProdB} - 1}{x_A^{Ar} + x_B^{ProdB} - 1} \tag{A.14}$$

After rearranging Inequality A.14 we get the following formula for the limit charge composition:

$$x_{ch,A} \ge \frac{\dfrac{x_A^{ProdA}}{x_A^{Ar}} - \dfrac{1 - x_B^{ProdB}}{x_A^{Br}}}{\left(x_A^{ProdA} - x_A^{Ar}\right) - \left(1 - x_B^{ProdB} - x_A^{Br}\right)} \cdot x_A^{Ar} \cdot x_A^{Br} = x_{ch,A}^{min} \tag{A.15}$$

If the inequality is satisfied then the *A*-rich phase must be processed first otherwise the *B*-rich phase. It must be noted that the above rule is independent from the composition of the top vapour. (The composition does not have to be azeotropic.)

4. Effect of the mutual solubilities and prescribed product purities on the processing sequence

The partial derivatives of the right hand side of Inequality A.15 shows the dependence of the limit charge composition on the mutual solubility of the components and the prescribed product purities.

4.1. Solubility of A in B

The derivative of $x_{ch,A}^{min}$ by x_A^{Br} is considered:

$$\frac{\partial x_{ch,A}^{min}}{\partial x_A^{Br}} = \frac{\left(x_A^{ProdA} + x_B^{ProdB} - 1\right) \cdot \left(x_A^{ProdA} - x_A^{Ar}\right)}{\left[\left(x_A^{Br} + x_B^{ProdB} - 1\right) + \left(x_A^{ProdA} - x_A^{Ar}\right)\right]^2} > 0 \tag{A.16}$$

Fig. A.9 shows that both factors of the numerator are positive. Since the denominator is also positive, the value of the fraction is positive.

We can state that the higher the solubility of *A* in *B*, the higher the limit concentration of *A*.
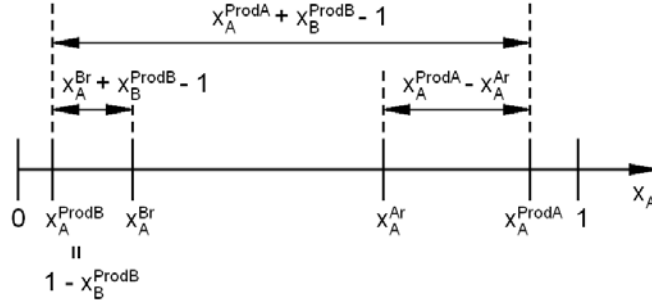
Fig. A.9. Relations of the product and phase compositions

4.2. Solubility of B in A

The derivative of $x_{ch,A}^{min}$ by $\left(1-x_A^{Ar}\right)$ is considered:

$$\frac{\partial x_{ch,A}^{min}}{\partial\left(1-x_A^{Ar}\right)}=-\frac{\left(x_A^{ProdA}+x_B^{ProdB}-1\right)\cdot\left(x_A^{Br}+x_B^{ProdB}-1\right)}{\left[\left(x_A^{Br}+x_B^{ProdB}-1\right)+\left(x_A^{ProdA}-x_A^{Ar}\right)\right]^2}<0 \qquad (A.17)$$

Fig. A.9 shows that both factors of the numerator are positive. Since the denominator is also positive, the value of the fraction after the minus sign is positive.

We can state that the higher the solubility of *B* in *A*, the lower the limit concentration of *A*.

4.3. Prescribed purity of Product A

The derivative of $x_{ch,A}^{min}$ by x_A^{ProdA} is considered:

$$\frac{\partial x_{ch,A}^{min}}{\partial x_A^{ProdA}}=-\frac{\left(x_A^{Ar}-x_A^{Br}\right)\cdot\left(x_A^{Br}+x_B^{ProdB}-1\right)}{\left[\left(x_A^{Br}+x_B^{ProdB}-1\right)+\left(x_A^{ProdA}-x_A^{Ar}\right)\right]^2}<0 \qquad (A.18)$$

Since both factors of the numerator and also the denominator are positive, the value of the fraction after the minus sign is positive.

We can state that the higher the prescribed purity of *A*, the lower the limit concentration of *A*.

4.4. Prescribed purity of Product B

The derivative of $x_{ch,A}^{min}$ by x_B^{ProdB} is considered:

$$\frac{\partial x_{ch,A}^{min}}{\partial x_B^{ProdB}} = \frac{\left(x_A^{Ar} - x_A^{Br}\right) \cdot \left(x_A^{ProdA} - x_A^{Ar}\right)}{\left[\left(x_A^{Br} + x_B^{ProdB} - 1\right) + \left(x_A^{ProdA} - x_A^{Ar}\right)\right]^2} > 0 \qquad \text{(A.19)}$$

Since both factors of the numerator and also the denominator are positive, the value of the fraction is positive.

We can state that the higher the prescribed purity of B, the higher the limit concentration of A.

5. Product sequence for pure products, effect of the mutual solubilities

If the products are supposed to be pure components ($x_A^{ProdA} = x_B^{ProdB} = 1$), Inequality A.15 can be simplified:

$$x_{ch,A} \geq \frac{1}{1 + \dfrac{1 - x_A^{Ar}}{x_A^{Br}}} = x_{ch,A}^{min} \qquad \text{(A.20)}$$

Since $\left(\dfrac{\partial x_{ch,A}^{min}}{\partial x_A^{Br}} = \dfrac{1 - x_A^{Ar}}{\left(x_A^{Br} + 1 - x_A^{Ar}\right)^2} > 0\right)$ and $\left(\dfrac{\partial x_{ch,A}^{min}}{\partial\left(1 - x_A^{Ar}\right)} = -\dfrac{x_A^{Br}}{\left(x_A^{Br} + 1 - x_A^{Ar}\right)^2} < 0\right)$, the effects of

the mutual solubilities on the product sequence are the same as when the more general Inequality A.15 is the starting point of the derivation.

Appendix 3

The downhill simplex method

The **downhill simplex method** or **Nelder-Mead method** is a commonly used nonlinear optimization technique, which is a well-defined numerical method for twice differentiable and unimodal problems. This heuristic search algorithm was proposed by Nelder and Mead (1965). This technique is for minimising an objective function in a multi-dimensional space. An N-dimensional polytope which is the convex hull of its N+1 vertices is called as N-dimensional simplex.

Examples: - N = 1: a line segment on a line,

- N =2: a triangle on a plane,

- N = 3: a tetrahedron in the 3D space.

In the case of the minimisation of a function of N variables, first N+1 points must be considered ($P_0, P_1, ... P_N$). The value of the function at P_i is denoted by y_i.

H is defined as the subscript such that $y_H = \max_i(y_i)$ and L as the subscript such that $y_L = \min_i(y_i)$, respectively. $\overline{P}$ is defined as the centroid of the set of points with $i \neq H$. The distance of two points P_i and P_j is denoted as $[P_i P_j]$.

In each step of the algorithm a new point P^* is determined by the reflection of P_H to $\overline{P}$:

$$P^* = (1 - \alpha) \cdot \overline{P} - \alpha \cdot P_H \qquad (A.21)$$

α is a positive constant: the *reflection coefficient*. Thus P^* is on the line joining P_H and $\overline{P}$, on the opposite side of $\overline{P}$ than P_H. The distance of P^* from $\overline{P}$ is $\alpha \cdot [P_H \overline{P}]$.

If $y_L \leq y^* < y_H$ then P_H is replaced by P^* and the above step is repeated.

If $y^* < y_L$, that is, a new minimum has been found then P^* can be expanded to P^{**} by the following way:

$$P^{**} = \gamma \cdot P^* + (1 - \gamma) \cdot \overline{P} \qquad (A.22)$$

where γ is the *expansion coefficient* and $\gamma > 1$.

If $y^{**} < y_L$ then P_H is replaced by P^{**} and the algorithm returns at its starting point.

If $y^{**} \geq y_L$ then the expansion has failed and P_H is replaced by P^*. Then the algorithm starts again.

If $y^* \geq y_H$ then instead of P_H a new point is generated:

$$P^{**} = \beta \cdot P_H + (1 - \beta) \cdot \overline{P} \qquad (A.23)$$

where β is the *contraction coefficient* and $0 < \beta < 1$.

If $y^{**} < y_H$ then P_H is replaced by P^* and the algorithm returns at its starting point.

If $y^{**} \geq y_H$ then each P_i is replaced by $(P_i + P_L)/2$ and the algorithm starts again.

Appendix 4

Refractive index – composition calibration for the mixture
1-butanol – water

Phase	Mass % of 1-BuOH	Mole % of 1-BuOH	Vol. % of 1-BuOH	Refractive index at 25 °C (measured)
Rich in water	0.00	0.00	0.00	1.3325
	4.76	1.20	5.82	1.3405
Rich in 1-BuOH	79.77	48.94	82.99	1.3889
	80.89	50.71	83.96	1.3894
	82.03	52.59	84.95	1.3898
	84.37	56.75	86.97	1.3909
	85.57	59.04	88.00	1.3914
	90.29	69.33	92.00	1.3935
	95.10	82.51	96.00	1.3955
	100.00	100.00	100.00	1.3973

Table A.8. Compositions and refractive indices of the mixtures used for the calibration

$$y = -1.941 \times 10^{-6} \times x^2 + 4.529 \times 10^{-4} \times x + 1.3714$$

$$R^2 = 0.9998$$
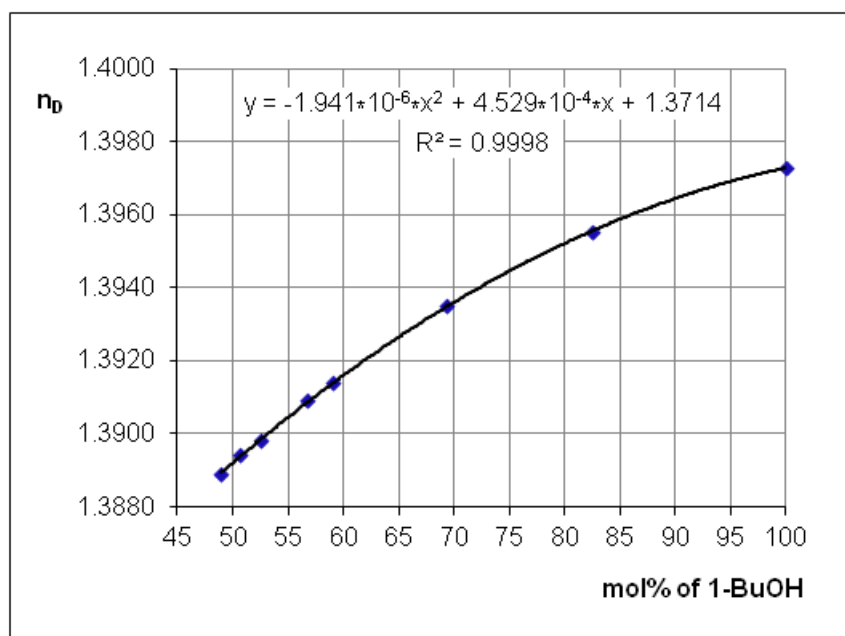
Fig. A.10. Refractive index of the mixture 1-butanol – water in the function of the 1-butanol content (at 25 °C)

Appendix 5

Description of the laboratory equipment

I. Columns

a. Column α

- Column sections:

    - Type: CS80/1000

    - No. of pieces: 4

    - Material: glass

    - *H = 4 x 1 m*

    - *D = 82 mm* (Because of the error of the manufacturer the internal diameter is larger than 80 mm.)

- Structured packing:

    - Type: Sulzer CY

    - *D = 80 mm*

    - *H = 4 x 1 m*

-Joining elements between the column sections:

    - No. of pieces: 4

    - Material: PTFE

    - *D = 80 mm*

    - 3 radial bores in the same distance from each other: one for the resistance thermometer, one for the sampling, one for the feed if it exists.

-Thermal insulation:

    - No. of pieces: 4

    - Material: NBR foam

- Instrumentation:

    - 4 resistance thermometers Pt100 measure the temperature in the joining elements (from down to top: T_{A1}, T_{A2}, T_{A3}, T_{A4}; °C).

    - A branch of a differential manometer is connected to the lowest joining element. Its other branch is connected to the joining element between the upper column section and Reflux divider α. It measures the pressure drop of the column (ΔP_A, mbar).

b. Column β

- Column sections:

    - Type: unknown

    - No. of pieces: 4

    - Material: glass

    - *H = 4 x 1 m*

    - *D = 80 mm*

    - Two radial outlets at the bottom: one for the resistance thermometer, one for the sampling or the feed.

- Structured packing:

    - Type: Kühni Rombopak

    - *H = 4 x 1 m*

    - *D = 80 mm*

-Thermal insulation:

    - No. of pieces: 4

    - Mantles attached around the column sections

    - Electric heating is possible.

- Instrumentation:

    - 4 resistance thermometers Pt100 measure the temperature of the bottoms of the column sections (from down to top: T_{B1}, T_{B2}, T_{B3}, T_{B4}; °C).

Remark for both columns:

The aftercoolers and under them the decanter are next to the upper column sections, at the same height and the liquids flow just by the gravity. Therefore the inlet of the reflux is over the 3rd column section at both columns. (The lower 3 sections are operating.) Since the reflux dividers do not operate well (neither *R=0* nor *R=infinite* is possible), the 4th sections have reflux, too.

II. Reboilers

a. Reboiler α

- Manufacturer: De Dietrich Process Systems Gmbh

- Type: VSH10

- Material: glass

- Charging: There is an orifice at the top of the reboiler which can be closed by a cap fixed by a screw.

- Discharging: There is an outlet at the bottom which can be open/closed by a ball valve.

- Heating:

  - by heating liquid circulating in a double spiral (one upward and one returning one, inlet and outlet at the bottom)

  - Type of the spiral: HEM150/6

  - Heat transfer surface: 0.6 m^2

- Maximum liquid volume: 10 dm^3

- Minimum liquid volume: 6.5 dm^3 (The spiral must be under liquid.)

- Instrumentation:

  - An industrial thermocouple measures the temperature of the vapour space (T_{ArebV}, °C).

  - A resistance thermometer Pt100 measures the temperature of the liquid (T_{ArebL}, °C).

- Thermal insulation:

  - Material: NBR foam

  - Position: The whole reboiler is insulated except for its top which is uncovered in order to see the the boiling and the level of the liquid during the operation.

b. Reboiler β

- Type: unknown

- Manufacturer: Günter DIEHM Process Systems

- Material: glass

- Charging: There is an orifice at the top of the reboiler which can be closed by a screw-tonned cap.

- Discharging: There is an outlet at the bottom which can be open/closed by a ball valve.

- Heating: by heating liquid circulating in a quaternary spiral (two upward branches and two returning ones, inlet and outlet at the bottom)

  The spiral is surrounded by a glass tube which has 4 radial holes at the top and bottom for the sake of the circulation of the heated liquid on the basis of the principle of thermosyphon. To intensify cooling-down a thin spiral glass tube is attached to the inner surface of the reboiler. In this tube cooling water can be circulated.

- Maximum liquid volume: 11 dm^3

- Minimum liquid volume: 9 dm^3 (The spiral must be under liquid.)

- Instrumentation:
    - A resistance thermometer Pt100 measures the vapour or liquid temperature, depending on the liquid level (T_{Breb}, °C).
    - A branch of a differential manometer is connected to the reboiler, too. Its other branch is connected to the condenser of Column β. It measures the pressure drop of the column (ΔP_B, mbar).
    - A level sensor is built in to <u>a</u>larm if the liquid <u>l</u>evel is too <u>h</u>igh (*LAH*).
    - A level sensor <u>a</u>larms if the liquid <u>l</u>evel is too <u>l</u>ow (*LAL*).
- Thermal insulation:
    - Material: NBR foam
    - Position: The top of the reboiler (the vapour space) and its bottom are covered by the insulant material. (In the middle part of the reboiler the liquid has to be let cool down for the sake of the natural convection.)

III. Heaters

a. Heater α

- Manufacturer: ABiX Technologie
- Type: unknown
- Heating medium: oil, type: Therminol SP
- Heating of the heating medium:
    - by electricity
    - P_{max} = 6 kW
- Cooling of the heating medium: -
- Flow rate of the heating medium: A bypass branch can be opened by a ball valve in order to decrease the oil flow rate.
- Operation: The heater shuts down the electric heating if the temperature reaches the set temperature and turns it on when the temperature is less by 1.0 °C than the set one.
- Instrumentation:
    - The temperature of the <u>oil</u> <u>l</u>eaving the heater is displayed on the control panel (T_{AOL}, °C).
    - A resistance thermometer Pt100 measures the temperature of the <u>oil</u> <u>e</u>ntering (T_{AOE}, °C).

b. Heater β

- Manufacturer: Juchheim Laborgeräte Gmbh

- Type: JUVO-4-kW-Thermostat 55040.11

- with microprocessor based programmable controller, type: 55105.00

- Heating medium: oil, type: Marlotherm SH 51016.00

- Heating of the heating medium:

    - by electricity

    - $P_{max} = 4\ kW$

- Cooling of the heating medium: with cooling water

- Flow rate of the heating medium: cannot be varied

- Operation: The heater regulates the electric heat performance in order to provide the desired oil temperature set previously. If the temperature set point is decreased the heater shuts down automatically the electric heating and turns on the water cooling.

- Instrumentation:

    - The temperature of the oil leaving the heater is displayed on the control panel (T_{BOL}, °C).

    - A resistance thermometer Pt100 measures the temperature of the oil entering (T_{BOE}, °C).

    - The actual electric performance or the cooling performance is displayed (Q_B, %).

IV. Condensers

a. Condenser α

The vertical condenser is connected to the reflux divider and to the aspiration tube of the laboratory by a flexible plastic pipe, that is, it is open to the atmosphere.

- Type: unknown

- Material: glass

- Cooling:

    - with cooling water circulating in a triple spiral (The water flows in the same direction in all the three branches.)

    - Heat transfer surface: 1 m^2

- Instrumentation:

    - A resistance thermometer Pt100 measures the temperature of the entering cooling water (T_{AWE}, °C).

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- A resistance thermometer Pt100 measures the temperature of the leaving cooling water (T_{AWL}, °C).
- Thermal insulation: -

The pressure (P_W, bar) and the total volume of the cooling water (of Condenser α, Condenser β and Heater β; V_W, m^3) is indicated but not registered automatically.

b. Condenser β

The condenser is connected to the upper column section and to the aspiration tube of the laboratory by a flexible plastic pipe, that is, the condenser is open to the atmosphere. It is slightly inclined to the horizontal direction. Before the cooling spiral a reflux divider is built in.
- Manufacturer: ILUDEST Destillationsanlagen GmbH
- Type: unknown
- Material: glass
- Cooling:
    - by cooling water circulating in a quaternary spiral (The water flows in the same direction in all the four branches.)
    - Heat transfer surface: unknown
- Instrumentation:
    - One resistance thermometer Pt100 measures the temperature of the top vapour arriving (T_{Btop}, °C).
    - A manometer measures the pressure in the condenser which is practically the ambient pressure (P, mbar).
    - A branch of a differential manometer is connected to the cold end of the condenser. Its other branch is connected to Reboiler α. It measures the pressure drop of the column (ΔP_B, mbar).
    - A resistance thermometer Pt100 measures the temperature of the entering cooling water (T_{BWE}, °C).
    - A resistance thermometer Pt100 measures the temperature of the leaving cooling water (T_{BWL}, °C).
- Thermal insulation:
    - Material: glass wool covered by a metal foil

- Position: Just the neck of the condenser connected to the upper column section is insulated.

- Reflux divider: see ***Subsection VI.a***

V. Aftercoolers

a. Aftercooler α

The distillate leaving the condenser flows through an aftercooler slightly inclined to the horizontal direction before arriving in the decanter.

- Type: unknown

- Material: steel

- Cooling:

    - with cooling water circulating in the jacket. (The water flows in countercurrent with the distillate.)

    - Heat transfer surface: unknown

- Instrumentation: -

- Thermal insulation: -

b. Aftercooler β

The distillate leaving the condenser flows through a vertical aftercooler before arriving in the decanter.

- Type: unknown

- Material: glass

- Cooling:

    - by cooling water circulating in the jacket. (The water flows in countercurrent with the distillate.)

    - Heat transfer surface: unknown

- Instrumentation: -

- Thermal insulation: -

VI. Reflux dividers

a. Reflux divider α

- Type: RSM QVFB015e

- Operation: The condensate flows back through a pipe into a funnel. Under the funnel there are inlets of two tubes. One of them is vertical and lets flow the liquid back to the column. The other one goes out from the column, this is for the distillate. The funnel can be moved around a horizontal axis therefore the condensate can flow into any direction. The position of the funnel is controlled by an electromagnet whose active and passive periods can be adjusted at the control panel of Reflux divider α (lengths of the reflux and withdrawal periods).

- Range of the length of the reflux and withdrawal periods:
    - reflux: 0.2 – 12 s
    - withdrawal: 0.2 – 12 s

    Since none of them is zero neither total reflux nor total withdrawal is possible.

- Instrumentation:
    - A thermocouple measures the vapour temperature which is displayed on the control panel but cannot be registered automatically (T_{Atop}, °C).

b. Reflux divider β

- Manufacturer: ILUDEST Destillationsanlagen GmbH

- Type: unknown

- Operation: Between the orifice where the vapour enters and the spiral there is another orifice where the distillate can flow out. This outlet can be closed by a glass stick whose end is made of ground glass like the outlet. At the upper end of the stick there is a magnetic material thus the stick is moved by an electromagnet. When the electromagnet is activated the stick is taken up and the outlet is open (total withdrawal). When it is not active the stick is down and it closes the outlet (total reflux). Arbitrary reflux can be adjusted at the control panel of Column β: the lengths of the reflux and the withdrawal periods can be set and their proportion is the reflux ratio.

VII. Decanter

- Type: KCE8520

- Manufacturer: De Dietrich Process Systems Gmbh (QVF)

- Material: glass

- Charging: The is an orifice for the aspiration. Before the operation the decanter can be filled
through that.

- Operation: There is an inlet at the end of the decanter where the condensate enters. Near to
the other end there are two outlets: a fixed one for the light liquid phase and a
moveable for the heavy phase. Since the upper outlet is fixed, the decanter can
separate only if the liquid level is not lower than the height of this outlet. The
other outlet is a tube with two orifices at its side. This tube is surrounded by a
fixed tube which hangs from the top of the decanter and lets flow the heavy phase
around the inner tube. The liquid level of the heavy phase between the two tubes
is the same as the position of the orifices of the inner tube. Since this tube can be
moved vertically by a manual controller, the quantity of the heavy phase can be
varied. (Since the total volume is fixed, the quantity of the light phase varies, too.)

- Discharging: At the mobile outlet there is another outlet which can be opened/closed by a
valve. It is connected to the bottom of the decanter therefore the decanter can be
emptied through that.

- V = 3.6 dm^3

- Instrumentation:

  - A resistance thermometer Pt100 measures the temperature of the liquid in the decanter
  close to the feed location (T_{DEC}, °C).

VIII. Holdup flow back inhibitor of Column β

This element is built in under the lowest section of Column α. In its center there is cylinder on
the side of which near to the top there are orifices. The vapour coming from the reboiler
ascends through these holes. Around this cylinder the bottom of this element is closed, there is
only a small outlet for the liquid flowing back from the column. This orifice can be closed by
a PTFE valve. Thus at the end of the experiment if the valve is closed the holdup of the
column do not flow back to the reboiler.

- Material: glass

- Liquid volume capacity: 250 cm^3

Remark: The capacity of 250 cm^3 is not enough for the total holdup. The valve cannot close perfectly the orifice, the liquid leaks.

IX. Registration of the measurement data

a. Registration of the measurement data of Column α

The data logger has an own memory where it stores the measured data which can be copied into a USB drive.

- Manufacturer: Honeywell International Inc.

- Type: Minitrend QX

- Software: Trend Server Pro 6.1.33

- Registered parameters: T_{AWE} , T_{BOE} , T_{AOE} , T_{ArebV} , T_{A1} , T_{A2} , T_{A3} , T_{A4} , T_{AWL} , T_{BWE} , T_{BWL} , ΔP_A , T_{ArebL} , T_{DEC}

b. Registration of the measurement data of Column β

The control panel of Column β which serves also as a data logger is connected with a computer on which a data registering software runs.

- Manufacturer: ILUDEST Destillationsanlagen GmbH

- Type: [DC/MIC]^2

- Software: MIC-TOP II (ACW) Version 1.44 (2000)

- Registered parameters: T_{Breb} , T_{Btop} , T_{B1} , T_{B2} , T_{B3} , T_{B4} , P , ΔP_B

Appendix 6

Parameters of the gas chromatography analysis

The analysis was performed by using a column Rt-Qplot (30 m x 0.32 mm x 10 μm) installed into a gas chromatograph (TRACE GC of Thermo Fisher) equipped with a flame ionisation detector (FID) and an autosampler. The method of the dosage and quantitative analysis of the isopropanol and hexane is shown in *Tables A.9-10*.

Solvent	Internal standard	Oven program	Injector	Vector gas
water	ethyl acetate	130 °C for 0.5 min then 20 °C/min until 180 °C then 3 °C/min until 240 °C then 240 °C until 5 min	T = 240 °C Injected volume = 1 μl Split Ratio = 20 Split Flow = 34 ml/min	1.7 ml/min

Table A.9. Method for the dosage and quantitative analysis of the isopropanol

Solvent	Internal standard	Oven program	Injector	Vector gas
iso-propanol	ethyl acetate	50 °C for 0.5 min then 20 °C/min until 180 °C then 3 °C/min until 240 °C then 240 °C until 5min	T = 240 °C Injected volume = 1 μl Split Ratio = 20 Split Flow = 34 ml/min	1.7 ml/min

Table A.10. Method for the dosage and quantitative analysis of the hexane

Sommaire de la thèse doctorale de Ferenc Dénes intitulée
« Nouveaux systèmes de double-colonne pour distillation hétéroazéotropique discontinue »

La distillation est la méthode la plus souvante pour la séparation des mélanges liquides (par exemple la récuperation des composants des mélanges de solvants déchets). A cause du besoin d'énergie très élevé, la conception et l'opération optimale sont très importantes des points de vue économique et environnementale. Pour la séparation des mélanges azéotropiques, il y a besoin des méthodes de distillation spéciales, comme la distillation hétéroazéotropique. Dans l'industrie pharmaceutique et chimie fine, elle est appliquée souvant en mode discontinu.

Les objectifs de la thèse sont les suivants :
- l'étude de la faisabilité d'un nouveau système de double-colonne (SCD) pour distillation hétéroazéotropique discontinue, et sa comparaison avec le réctificateur discontinu (RD) traditionnel équippé d'un décanteur,
- l'étude des configurations ci-dessus par modélisation rigoureuse,
- l'extension du SDC (système de double colonne généralisé, SDCG), et l'étude de cette nouvelle configuration par les méthodes ci-dessus,
- l'étude expérimentale des deux configurations pour prouver la faisabilité de la séparation, et pour valider les résultats de calcul.

J'ai étudié deux nouveaux configurations de double-colonne pour distillation hétéroazéotropique. Ces configurations sont appropriées à la récuperation simultanée des composants des mélanges binaires hétéroazéotropiques et homoazéotropiques (en utilisant un tiers corps (entraîneur)). Elle sont opérées en système fermé, c'est-à-dire, il n'y a pas de soutirage de produit continu.

D'abord, en appliquant un modèle simplifié, j'ai étudié la faisabilité de la séparation d'un mélange hétéroazéotropique (1-butanol - eau), puis celle d'un mélange homoazéotropique (2-propanol - eau) aidé par entraîneur benzène ou cyclohexane, en utilisant le SDC. Puis, j'ai étudié cette configuration par modélisation rigoureuse, en appliquant le simulateur dinamique du logiciel professionnel ChemCAD (CC-DColumn). J'ai comparé la nouvelle configuration avec le RD, sur la base des résultats obtenus par toutes les deux méthodes d'étude. Le SDC s'est avéré faisable et compétitif avec le RD : pendant la même durée ou plus courte, les rendements des composants ont été plus élevés.

Puis, on a étendu le SDC à un système plus flexible (système de double-colonne généralisé, SDCG) qui est approprié à la séparation des mélanges binaires homoazéotropiques aidé par entraîneur (en le cas présent : cyclohexane ou n-hexane). J'ai étendu la méthode de faisabilité aussi à l'étude de cette configuration. Le SDCG s'est avéré aussi faisable. En appliquant modélisation rigoureuse, j'ai étudié les effets des nouveaux paramètres opératoires sur la durée, et j'ai comparé le SDCG avec le SDC. Le SDCG s'est avéré encore plus avantageux que le SDC : la durée a été plus courte, et les besoins spécifiques d'énergie des produits ont été plus bas.

J'ai étudié le SDC et le SDCG aussi par des manipulations exécutées sur installations de taille laboratoire et pilote.

D'abord, j'ai fait des manipulations laboratoires pour la séparation du mélange binaire hétéroazéotropique, en utilisant une installation en verre qui a été opérée aussi comme RD et SDC. Le SDC s'est avéré faisable et compétitif avec le RD aussi sur la base des résultats de ces manipulations : pendant la même durée, les rendements des tous les deux composants ont été plus élevés.

Puis, en utilisant l'installation pilote comme SDC, j'ai étudié la séparation ci-dessus. Après cette manipulation, j'ai étudié la séparation du mélange binaire homoazéotropique en appliquant n-hexane comme entraîneur, en opérant le système comme RD et SDCG. La manipulation faite avec le SDCG a montré que la production simultanée de deux composants est faisable avec cette configuration.