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Enhanced separation of maximum boiling azeotropic mixtures with extractive heterogeneous-azeotropic distillation

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Highlights

- Separation of quaternary mixtures with maximum boiling azeotropes are investigated.
- Separation of two mixtures are modelled in flowsheet simulator environment.
- Extractive heterogeneous-azeotropic distillation is experimentally verified.
- The heat integrated EHAD method is investigated with optimized total annual cost.

- Chloroform can be utilized as lower, organic rich phase of phase separator.

Abstract

In the separation industry the extractive heterogeneous-azeotropic distillation (EHAD) is a new and powerful innovation, that is capable of making the separation of highly non-ideal mixtures feasible and economical. In the last years there has been much attention paid to the separation of the minimum boiling homogeneous azeotropes. Although maximum boiling azeotropes are fewer in numbers than the minimum boiling ones but their separation is more complicated but it could be solved with the EHAD, too. Since EHAD is not limited to the separation of minimum boiling azeotropes, the separation of the maximum boiling azeotropes is studied in this work. Our work is motivated by industrial problems because there are such maximum boiling azeotropes in the liquid wastes of the fine chemical industry. The separation of highly non-ideal Water-Acetone-Chloroform-Methanol and Water-Ethyl Acetate-Chloroform-Ethanol quaternary mixtures are investigated and optimized in professional flowsheet simulator environment. Total Annual Costs are also determined. The purity requirement is 99.5 m/m% for Chloroform and the bottom product should be as clear as possible in water so that less liquid organic waste has to be incinerated. It is also an important merit of the EHAD that the chemicals in the distillate can be usually reused supporting sustainability. Different solutions for the separations supplemented with heat integration are examined. On the basis of the computer simulations and the experimental verification it can be concluded, the first time on the literature, that the separation efficiency of EHAD is superior also for the separation of the maximum boiling azeotrope mixtures.

Abbreviations

D-LP   Lower, organic phase

DMSO   Dimethyl sulfoxide

EHAD   Extractive Heterogeneous-azeotropic Distillation

HI   Heat integration

LLVF   Liquid-Liquid-Vapour Flash

M&S   Marshall & Swift index

RD   Reboiler duty

RR   Reflux ratio

TAC   Total Annual Cost $[1000\$/year]$

VLE   Vapour-Liquid Equilibrium

VLLE   Vapour-Liquid-Liquid Equilibrium

Keywords

extractive heterogeneous-azeotropic distillation; cost estimation; modelling; highly non-ideal mixtures; maximum boiling azeotropes; heat integration

Nomenclature

D   Distillate

F   Feed

m/m%   Weight percent

N_{Feed} Number of mixture feed stage

N_{Total} Number of total stages

p $[bar]$

Q_{RD} Heat of duty
        $[MJ/h]$

T   Temperature   [°C]

U   UNIQUAC parameter

W   Bottom product

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y   Year

1. Introduction

If such non-ideal mixtures are to be separated where both heterogeneous and homogeneous azeotropes are also present, a new hybrid tool devoted to the separation of such quaternary mixtures, the so-called extractive heterogeneous-azeotropic distillation (EHAD) can be used (Toth et al., 2017; Toth et al., 2016a; Toth et al., 2016b). This new hybrid separation tool combines the advantages of the extractive and the heterogeneous azeotropic distillations (Szanyi et al., 2004a; Toth et al., 2016a). The extractive agent or entrainer, which is water, is removed in the bottom product together with those components of the original mixture that it extracts (Skiborowski et al., 2013, 2014). EHAD differs from the heteroextractive distillation (Rodriguez-Donis et al., 2007) since no new azeotrope is formed and the extractive and relative volatility changing the effect of the autoentrainer, which is fully utilized (Mizsey et al., 2002; Zhao et al., 2017). On the other hand, rectification is also taking place while EHAD is applied (Szanyi et al., 2004b). The extractive process works along one mass balance line in the complex diagram and EHAD crosses the distillation boundaries with the liquid-liquid phase splitting in the limited solubility region (Szanyi et al., 2004b, 2005).

In the recent years the extractive heterogeneous-azeotropic distillation (EHAD) method gave great results in this field of separation (Szanyi, 2005). It combined two of the best separation methods for non-ideal mixtures, extraction and distillation (Toth et al., 2016a). Also combined in a way that it remained a continuous technology (Luyben, 2015; Toth et al., 2017). Although there are fewer in numbers in some parts of the industry, but it can be used efficiently (Toth et al., 2016a). In the case of minimum boiling azeotropes EHAD has been already examined in more research works (Toth et al., 2017; Toth et al., 2016a; Toth et al., 2016b). The aim of this paper is to investigate EHAD separation of two quaternary mixtures from fine chemical industry, which contain maximum boiling azeotrope. **Fig. 1** shows the EHAD column in the case of separation of maximum boiling azeotrope.

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Usually the maximum boiling azeotropic mixtures contain Chloroform, which is used as a solvent in many industries. It can be stated, separation alternatives of quaternary mixtures contained Chloroform have not been studied comprehensively. Pressure swing and extractive distillation can be used as viable method for separation of Acetone-Chloroform binary mixture (Gorak and Sorensen, 2014; Luyben, 2013).

Luyben (2008) investigated the application of continuous extractive distillation to separate the mentioned system. Several solvents were explored applying Aspen Plus flowsheet simulations, but only dimethyl sulfoxide (DMSO) was found to achieve the desired separation (Luyben, 2013). Hostrup et al. (1999) recommended extractive solvent was methyl-n-pentyl ether and Dimian (2003) used toluene as an extractive agent for the separation of Chloroform and Acetone mixture. It should be mentioned that foreign material addition to the system is necessary in these methods, which contradicts the green chemical principles. Continuous pressure swing distillation was also studied by (Luyben, 2013). It was found that pressure-swing azeotropic distillation is much more expensive for the separation of Acetone-Chloroform system than extractive distillation in terms of both capital and energy (Luyben, 2013). Van Kaam et al. (2008) introduced that heterogeneous extractive batch distillation is capable of separating of Chloroform-Methanol-Water ternary mixture. It can be determined that the separation of mixtures that contain Chloroform is a complex and expensive method.

2. Material and methods

Two quaternary mixtures are selected for evaluation of EHAD technique which are used solvents from pharmaceutical industry. The feed composition of mixtures is selected according to the industrial separation problem.

- Mixture I: 10 m/m% Water, 40 m/m% Acetone, 30% Chloroform and 20 m/m% Methanol

- Mixture II: 4.6 m/m% Water, 33.2 m/m% Ethyl Acetate, 44.9 m/m% Chloroform and 17.3 m/m% Ethanol

The aim is to remove Chloroform content as the organic rich phase of phase separator (see **Fig. 1**). The purity requirement is 99.5 m/m%. Comprehensive evaluation is investigated in the case of Mixture I, which is subsequent separation of bottom product of EHAD column. The separation of Water-Acetone-Methanol ternary mixture is also optimized with purity prescription of 99.5 m/m%.

The components of the examined quaternary mixtures form binary and ternary azeotropes as well. Supplementary part summarizes all cases with boiling temperatures (Gmehling et al., 1994; Gmehling and Onken, 1977; Marsden, 1954). The residue curve maps of ternary Chloroform-Acetone-Water and Chloroform-Methanol-Water mixtures can be seen in Supplementary part too.

The Acetone-Chloroform-Methanol-Water quaternary mixture forms five azeotropes: one maximum boiling homogeneous azeotrope (Acetone-Chloroform), two minimum boiling homogeneous azeotropes (Methanol-Acetone, Methanol-Chloroform), one minimum boiling heterogeneous azeotrope (Chloroform-Water), one ternary azeotrope (Acetone-Methanol-Chloroform). The mixture has 2 stable nodes (pure Water component and Acetone-Chloroform maximum boiling azeotrope), 2 unstable nodes (Methanol-Acetone, Methanol-Chloroform), 4 saddle points (pure Chloroform, Methanol and Acetone, Chloroform-Water heterogeneous azeotrope). Four nodes change its nature: stable node become saddle point (pure Chloroform and pure Methanol), unstable node become saddle point (pure Acetone and Chloroform-Water).

The Water-Ethyl Acetate-Chloroform-Ethanol mixture contains eight azeotropes: one maximum boiling homogeneous azeotrope (Ethyl Acetate-Chloroform), three minimum boiling homogeneous azeotropes (Ethanol-Chloroform, Ethyl Acetate-Ethanol, Ethyl Acetate-Chloroform) and two ternary azeotropes (Water-Ethyl Acetate-Ethanol, Water-Chloroform-Ethanol) and two minimum boiling heterogeneous azeotropes (Ethyl Acetate-Water, Chloroform-Water). The mixture has 12 stable node points. It contains 3 stable nodes (pure Ethanol component, pure Water component and Ethyl Acetate-Chloroform maximum boiling azeotrope), The two ternary azeotropes are the unstable nodes (Water-Chloroform-Ethanol and Ethyl Acetate-Ethanol-Water). Saddle points are pure Ethyl Acetate, pure Chloroform, Ethyl Acetate-Water,

Chloroform-Water, Ethanol-Ethyl Acetate, Ethanol-Chloroform and Ethanol-Water azeotropes. The pure Chloroform and pure Ethyl Acetate components changes their nature: stable node become saddle point. Ethanol-Chloroform and Chloroform-Water azeotropes become also saddle point from unstable node.

As it can be seen the separation of quaternary mixtures complex distillation method is needed. Professional flowsheet simulator (ChemCAD) are carried out before the investigation of laboratory experiment (Abrams and Prausnitz, 1975; Egner et al., 1999; Gmehling et al., 1994; Sabri et al., 2017; Toth et al., 2017; Wiśniewska-Goclowska and Malanowski, 2001). Rodriguez-Donis et al. (2007) analysed the feasibility conditions for seven configurations of continuous processes combining extractive distillation and decanter for the separation of mixtures with heterogeneous azeotropes. It included the two configurations displayed in **Fig. 2**. The Configuration (1) is used to evaluate the effect of the addition of water. The Configuration (2) is identical to the real EHAD constructions (Rodriguez-Donis et al., 2007). Continuous operations are investigated (Yimin et al., 2017).

The difference between the two configurations is the place of feed of the extractive water. In the case of Configuration (1) the water addition is achieved into mixer between column and phase separator. The maximum flooding of the top of column and the effect of water addition can be investigated with Configuration (1). The water feeding before the decanter can give more flexibility in the composition of the vapour exiting the top of the column. After that, the real EHAD column can be investigated with Configuration (2). **Fig. 3** shows the complete flowsheet of separation Mixture I and Mixture II with heat integration (HI) (An et al., 2015). It can be seen only Configuration (2) is investigated in the case of comprehensives evaluation. The heat duty of each column reboiler can be utilized for preheat feed flows in order to reduce the energy consumption of separation. First column represents the EHAD technique. In the second column, the Acetone-Methanol-Water mixture is separated. Acetone can be enriched in distillate product using extractive distillation with water feed as entrainer and Methanol-Water can be separated simply in third column.

Fig. 3 shows the separation of Mixture II too. The separation of bottom product (Water-Ethyl Acetate-Ethanol mixture) of EHAD column in the case of Mixture II is really complex, possible solutions are described by Toth et al. (2017). This ternary mixture can also be separated with EHAD, so that split it into two azeotropic pairs: Ethyl Acetate-Water as lower phase of decanter and Ethanol-Water as bottom product. The following parameters are optimized during the simulations in the case of first (EHAD) column:

- number of theoretical trays of the distillation column (N_{Total}),

- feed tray location (N_{Feed}),

- reflux ratio (RR),

- water mass flow (F_{Water}),

- temperature of phase separator (T_{LLVF}),

- temperature of heat integration (T_{HI}),

- pressure of phase separator (p_{LLVF}).

Five parameters (N_{Total}, N_{Feed}, RR, F_{Water}, T_{HI}) of second column and four parameters (N_{Total}, N_{Feed}, RR, T_{HI}) of third column are optimized in the case of Mixture I. The feed parameters are the following: mass flow: 1000 kg/h; feed temperature 20 °C; pressure 1 bar. K-values model is UNIQUAC, the Global Phase Option is V/L/L/S and SCDS columns with valve trays are applied. The binary azeotropes of the mixtures with UNIQUAC parameters (U_{ij}-U_{jj} and U_{ji}-U_{ii}) are available in Supplementary part. The target of the simulation is to find the lowest energy requirements and in parallel the smallest apparatus sizes.

The EHAD column is examined experimentally in laboratory apparatus. The column sizes and structure are the same as in the previous examination with minimum boiling azeotropic mixtures (Toth et al., 2017; Toth et al., 2016a; Toth et al., 2016b). The main parameters of the column are the following: structured packing, internal diameters of 0.04 m. The column has 10 theoretical plates according to measurement carried out by Methanol-Water mixture (Toth et al., 2017). The solvent feed enters at the middle of the column. The water is pumped in the top of the column, as EHAD philosophy requires (Toth et al.,

2017). The column heating is controlled with a 0.3 kW efficiency heating basket, the phase separator has atmospheric conditions. The flow leaving the condenser goes to a phase split (Toth et al., 2016a). The lower, organic rich phase is taken away as product (Toth et al., 2017; Toth et al., 2016a). The upper, water rich phase goes back into the column as reflux flow (Toth et al., 2017). The organic content of the feed (F), distillate (D), bottom product (W) are measured with Shimadzu GC2010Plus+AOC-20 autosampler gas chromatograph with a CP-SIL-5CB column connected to a flame ionization detector, EGB HS 600. Headspace apparatus is used for sample preparation. The water content is measured with Hanna HI 904 coulometric Karl Fischer titrator (Toth et al., 2017). EHAD experiments are completed on laboratory column shown in **Fig. 4**.

Total Annual Cost (TAC) of the optimized EHAD separations is calculated according to the cost equations of Douglas (Douglas, 1988) with current M&S index (Toth et al., 2017). 10-year amortization of investment cost is presumed for the TAC estimation. Steam and water consumptions are calculated for estimation of operating cost and 8000 work hours/year continuous operation is assumed. Equation 1 shows the function of the calculation of the total annual cost (Toth and Mizsey, 2015).

$$Total\ Annual\ Cost\ (\$/year) = \frac{Capital\ cost}{years\ of\ amortization} + Operation\ cost \tag{1}$$

3. Results and discussion

3.1 Results of Mixture I separation

The compositions and the optimized data of both configurations of Mixture I can be compared with the same Chloroform purity (99.5 m/m%) in **Table 1**. The lower, organic phase (D-LP) is presented.

As it can be seen both configuration can separate this quaternary mixture. Configuration (2) should be used, because its lower reboiler duty (Q_{RD}) and same beside Chloroform purity is achieved with lower column size, although more water addition is needed. The better water percent is also confirming the

efficiency of extractive effect of EHAD method. In the following, only the results of Configuration (2) is presented.

The separation is verified with laboratory experiment. The reboiler duty value is 300 W in flowsheet environment too. Three experiments are taken out, the average of results can be seen in **Table 2**, which represent the simulated and measured results of EHAD. Average compositions error is 5% and flow rate error is 3%. The reflux ratio is 2.

The comparison shows the accuracy also in both cases, D and W. It can be seen the organic phase of distillate stream is ~30% of feed mixture, so the other aim is reached, which is the concentration of used solvent. **Table 3** introduces the complete separation of Mixture I.

It can be seen, the reboiler duties of second and third columns are significant. **Fig. 5** shows the reboiler duty together with the minimal water consumption in the function of the total number of theoretical stages. The water is fed in the top of the column and quaternary mixture is fed in the middle of the column. These curves are good accordance with experienced in EHAD separations of ternary and quaternary mixtures with minimum boiling azeotropes (Toth et al., 2016a). The influence of number of stages and reboiler duties on the total annual costs can also be seen in **Fig. 5**.

3.2 Results of Mixture II separation

Table 4 introduces the measured and simulated results of EHAD column. Three laboratory experiments are taken out with Mixture II. Average compositions error is 6% and flow rate error is 2%. The reflux ratio is 4.

It can be seen the experiment and simulation results are in good accordance. **Table 5** shows the optimized product compositions of separation of Mixture II.

It can be stated, EHAD technique is capable for separation of Water-Ethyl Acetate-Chloroform-Ethanol quaternary mixture too. **Fig. 6** shows the minimal water consumption and the Q_{RD} in the function of the total number of theoretical stages and the influence of reboiler duties and number of stages on the TAC.

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3.3 Comparison and evaluation of two quaternary mixtures separation

Table 6 shows the reboiler and condenser duties and it introduces the Total Annual Cost of EHAD column.

It can be seen, the duty can be reduced with heat integration and greater extent in the case of Mixture I and the separation of Mixture II is more expensive, in all categories.

It can be concluded, in the case of maximum boiling azeotrope mixtures, there is tendency between the number of azeotropic points and the minimal water consumption for separation (see Supplementary part, Szanyi (2005), **Fig. 5** and **Fig. 6**). If the mixture has more azeotropic points, the water requirement for separation will be higher. The cost of separation is also influenced by the number of azeotropic points containing the mixture, but other factors also influence the TAC. The operating cost generates the most significant part of the TAC, within this the steam cost, as it can be seen in **Table 6**.

4. Conclusions

The applicability and effectiveness of extractive heterogeneous-azeotropic distillation are investigated on two non-ideal mixtures. The simulations are verified with experiments proving the accuracy of modelling. EHAD has benefit in the case of separation of three or more component mixtures, containing heterogeneous azeotropes. The clear advantage of EHAD compared to extractive distillation is the separation efficiency of heterogeneous azeotropes. A column and a phase separator are enough for breaking azeotrope pairs. The method clearly shows that the EHAD means a powerful tool for the separation of highly non-ideal mixtures containing maximum boiling azeotropes and water.

Acknowledgements

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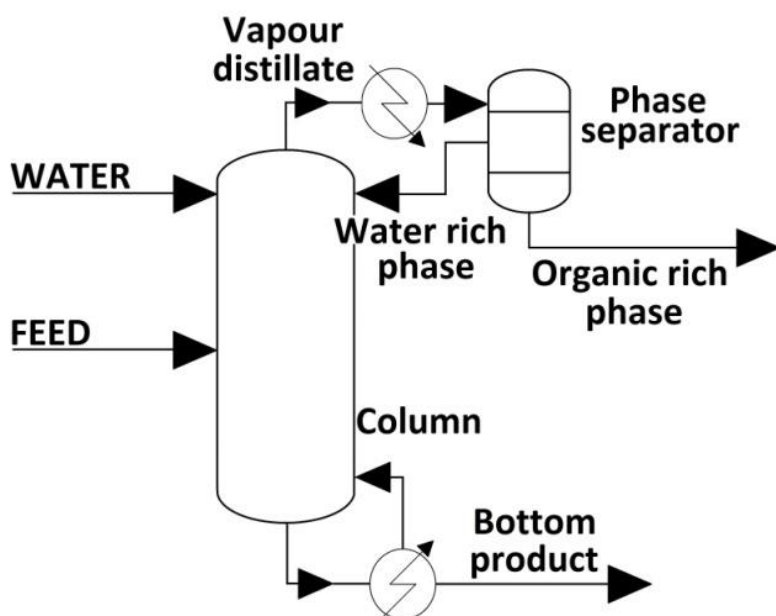
Fig. 1 Schema of EHAD if the mixture contains maximum boiling azeotrope

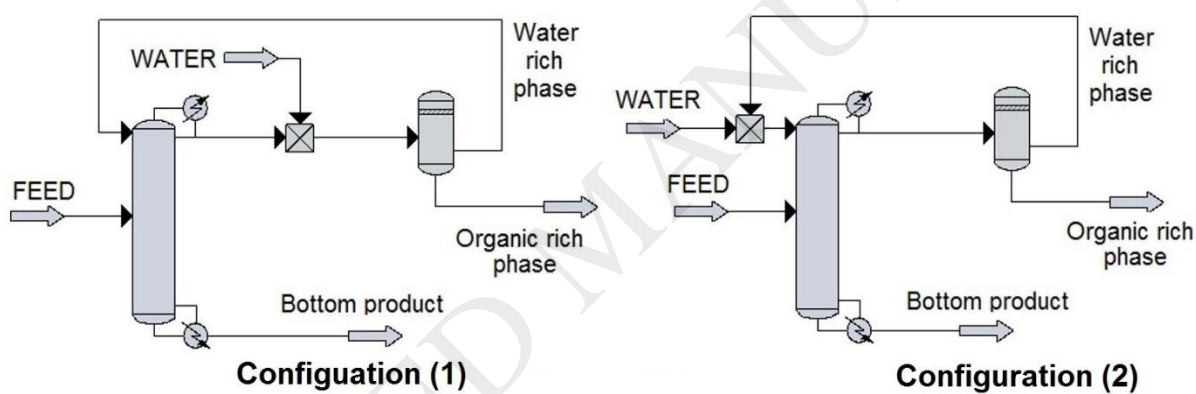**Fig. 2** The schematic figures of simulated EHAD in the case of maximum boiling azeotropes
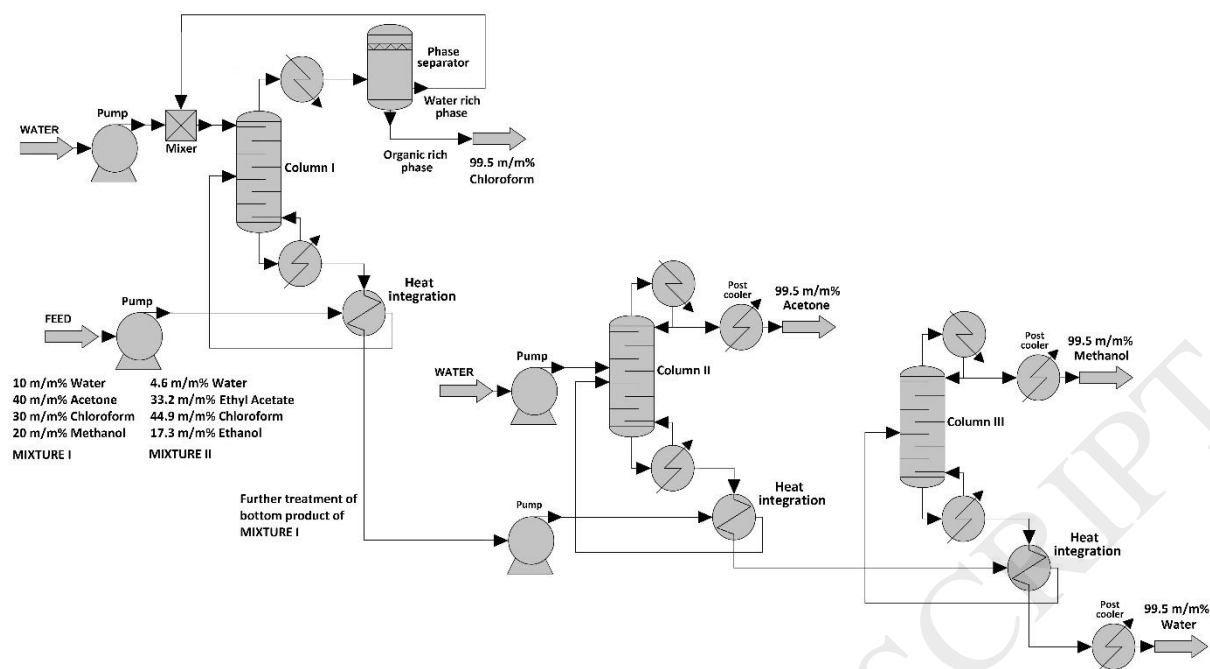
Fig. 3 Separation schema of Water-Acetone-Chloroform-Methanol (Mixture I) and Water-Ethyl Acetate-Chloroform-Ethanol (Mixture II)
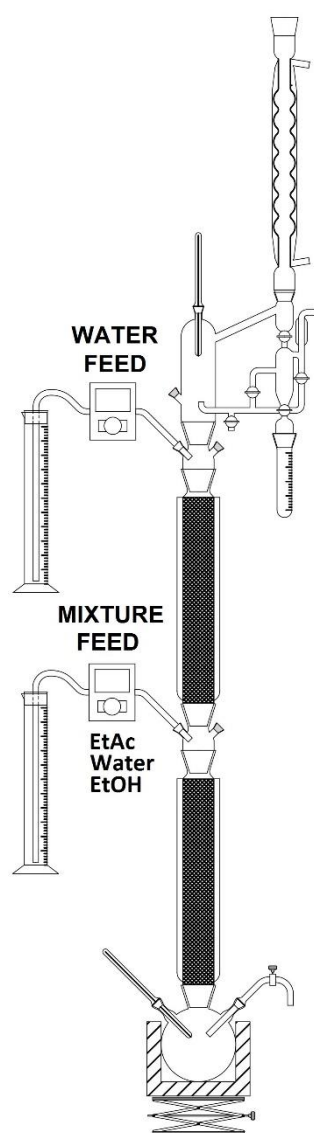
Fig. 4 Extractive heterogeneous distillation column of laboratorial size (Andre, 2016)
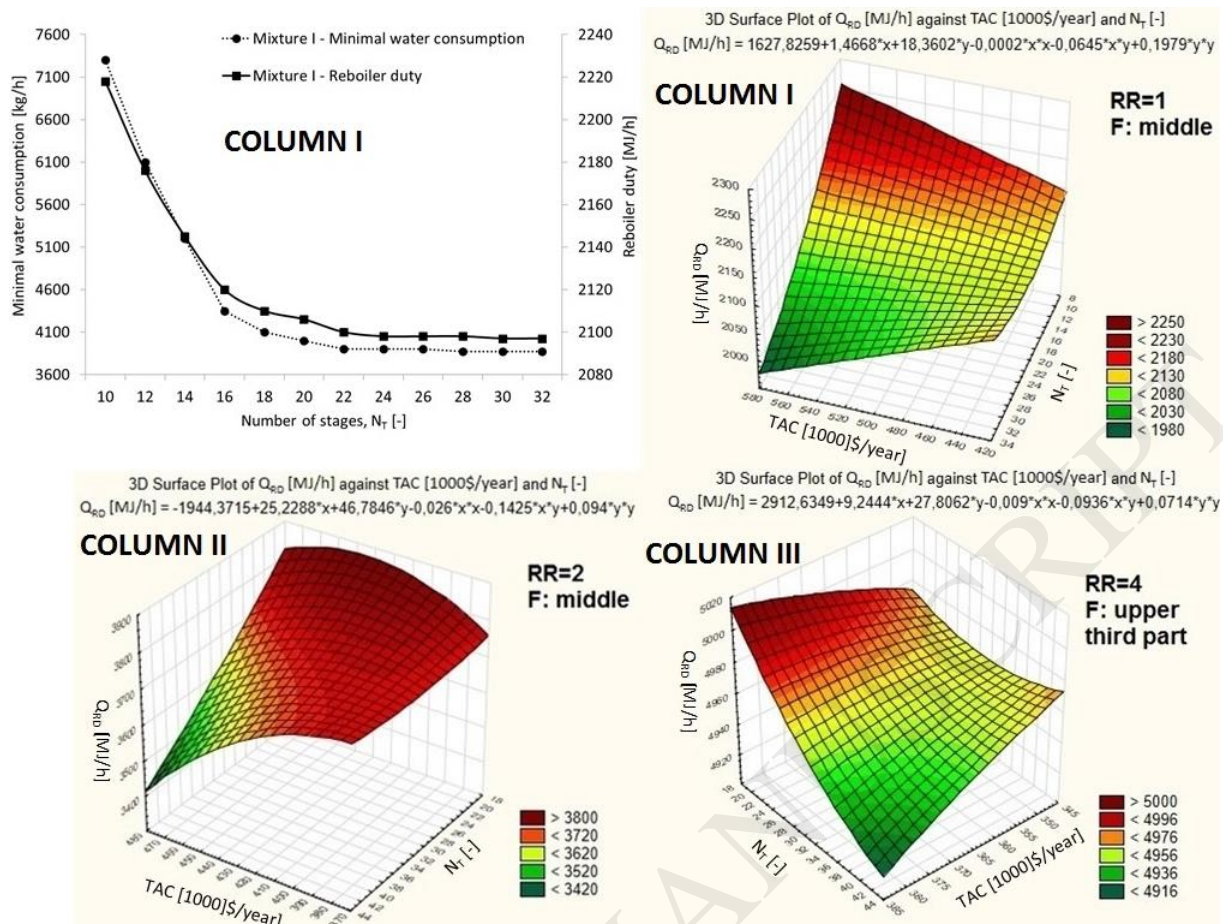
Fig. 5 Reboiler duty and minimal water consumption in the function of stages (Mixture I, Column I, top left corner) and influence of the number of stages and reboiler duties on the TAC in separation of Mixture I
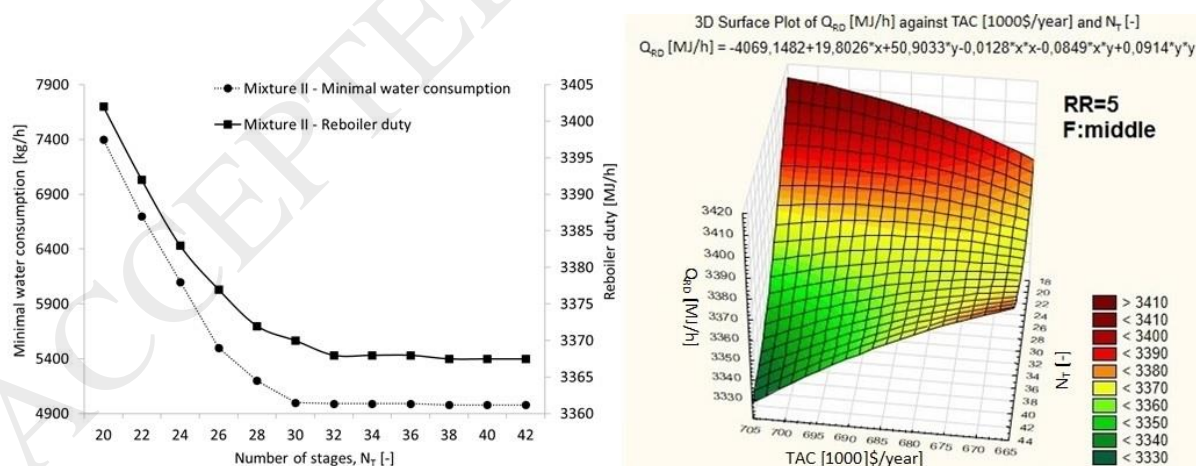
Fig. 6 Reboiler duty and minimal water consumption in the function of stages (Mixture II, left) and influence of the number of stages and reboiler duties on the TAC in separation of Mixture II (right)

Table 1 Comparison of output weight percent and optimized parameters of Configuration (1) and Configuration (2) (Mixture I)

| Mixture I	Mixture	Water	Configuration (1)		Configuration (2)	
	F	F	D-LP	W	D-LP	W
Water [m/m%]	10	100	0.29	69.45	0.14	74.86
Acetone [m/m%]	40	0	0.21	19.2	0.36	16.1
Chloroform [m/m%]	30	0	99.5	0.1	99.5	0.1
Methanol [m/m%]	20	0	1.8E-11	11.25	1.9E-14	8.94
N_{Total} [-]			30		20	
N_{Feed} [-]			15		10	
RR [-]			-		1	
$F_{Mixture}$ [kg/h]			1000		1000	
F_{Water} [kg/h]			3000		4000	
T_{LLVF} [°C]			20		20	
T_{HI} [°C]			50		50	
p_{LLVF} [bar]			1		1	
Q_{RD} [MJ/h]			2234		2106	

Table 2 Comparison of simulated and measured data for Mixture I in the case of Configuration (2)

Mixture I	Feed		Simulated data		Measured data	
	Mixture	Water	D-LP	W	D-LP	W
Water [m/m%]	10	100	0.18	72.66	0.17	73.01
Acetone [m/m%]	40	0	0.32	17.41	0.30	17.12
Chloroform [m/m%]	30	0	99.50	0.1	99.53	0.11
Methanol [m/m%]	20	0	1.8E-14	9.83	0.001	9.76
Stream [kg/h]	0.25	0.88	0.08	0.95	0.08	0.96
T [°C]	20	20	20	71.6	20	72.1

Table 3 Optimized simulation results of Mixture I

Mixture I	Column I	Column II	Column III
N_{Total} [-]	20	36	30
N_{Feed} [-]	10	18	20
N_{Water} [-]	1	10	
p_{Feed} [bar]	1	1	1
RR [-]	1.0	2.0	4.0
$Q_{Condenser}$ [MJ/h]	-1746	-3336	-4596
$Q_{Reboiler}$ [MJ/h]	2106	3750	4962
$Q_{Post\ cooler}$ [MJ/h]		-177	-963
Mixture I	F	F	F
Water [m/m%]	10	74.9	91.6
Acetone [m/m%]	40	16.1	0.1
Chloroform [m/m%]	30	0.1	3.0E-03
Methanol [m/m%]	20	8.9	8.3
Mixture stream [kg/h]	1000	4190	4516
Water stream [kg/h]	4000	1000	0
Temperature [°C]	50.0	70.0	80.0
Mixture I	D-LP	D	D
Water [m/m%]	0.1	0.1	0.0
Acetone [m/m%]	0.4	99.5	0.5
Chloroform [m/m%]	99.5	0.4	3.7E-06
Methanol [m/m%]	1.9E-14	1.5E-03	99.5
Mixture stream [kg/h]	310	674	360
Temperature [°C]	20.0	55.9	63.8
Mixture I	W	W	W
Water [m/m%]	74.9	91.6	99.5
Acetone [m/m%]	16.1	0.1	0.1
Chloroform [m/m%]	0.1	3.0E-03	2.0E-18
Methanol [m/m%]	8.9	8.3	0.4
Mixture stream [kg/h]	4190	4516	4156
Temperature [°C]	71.6	92.3	99.1

Table 4 Comparison of simulated and measured data for Mixture II in the case of Configuration (2)

Mixture II	Feed		Simulated data		Measured data	
	Mixture	Water	D-LP	W	D-LP	W
Water [m/m%]	4.6	100	0.50	87.73	0.46	88.14
Ethyl Acetate [m/m%]	33.2	0	1.9E-05	9.26	7.5E-04	9.18
Chloroform [m/m%]	44.9	0	99.50	0.10	99.54	0.12
Ethanol [m/m%]	17.3	0	5.7E-06	2.91	1.1E-04	2.56
Stream [kg/h]	0.25	1.50	0.12	1.51	0.12	1.52
T [°C]	20	20	20	72.1	20	72.8

Table 5 Output weight percent and parameters of optimized Mixture II separation (Configuration (2)

Mixture II	F - Mixture	F - Water	D-LP	W
Water [m/m%]	4.6	100	0.50	85.64
Ethyl Acetate [m/m%]	33.2	0	1.9E-05	9.36
Chloroform [m/m%]	44.9	0	99.50	0.10
Ethanol [m/m%]	17.3	0	5.7E-06	4.90
N_{Total} [-]			30	
N_{Feed} [-]			15	
RR [-]			5	
$F_{Mixture}$ [kg/h]			1000	
F_{Water} [kg/h]			5000	
T_{LLVF} [°C]			20	
T_{HI} [°C]			55	
p_{LLVF} [bar]			1	
Q_{RD} [MJ/h]			3370	

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Table 6 Comparison of Total Annual Cost (TAC) and effect of heat integration (HI) of EHAD columns

TAC and HI effect of EHAD column		Mixture I	Mixture II
Investment cost [1000$/year]	Column	31	48
	Reboiler	20	32
	Condenser+LLVF	10	27
	Total	61	107
Operating cost [1000$/year]	Steam	292	442
	Water	79	121
	Total	371	563
Total Annual Cost (TAC)		432	670
Q-DIST$_{Reboiler}$ [MJ/h]	Basic	2576	3534
	Heat integration (HI)	2106	3002
	Difference [%]	-18	-15
Q-DIST$_{Condenser}$ [MJ/h]	Basic	-1987	-3021
	Heat integration (HI)	-1746	-2754
	Difference [%]	-12	-9