

Separation of Mixture Containing Maximum Boiling Azeotrope with Extractive Heterogeneous-Azeotropic Distillation

Andras Jozsef Toth^{a,*}, Botond Szilagyi^a, Eniko Haaz^a, Szabolcs Solti^b, Tibor Nagy^a, Ariella Janka Tarjani^a, Nora Valentinyi^a, Peter Mizsey^{a,c}

^aEnvironmental and Process Engineering Research Group, Department of Chemical and Environmental Process Engineering, Budapest University of Technology and Economics, H-1111, Budapest, Budafoki Street 8., Hungary

^bSzelence Kamionmoso, Ipartelep, H-2431, Szabadegyhaza, Hungary

^cInstitute of Chemistry, Faculty of Material Science and Engineering, Department of Fine Chemicals and Environmental Technology, University of Miskolc, H-3515, Miskolc, Egyetemvaros C/1 108., Hungary
andras86@kkft.bme.hu

Separation of highly non-ideal mixtures with the use of extractive heterogeneous-azeotropic distillation (EHAD) has been successful in the last few years. In contrast, most researches have focused on mixtures with containing minimal boiling homoazeotropes. Despite the fact that maximum boiling azeotropes are fewer in numbers it is important to examine if the use of EHAD method is viable. It is important to note that the EHAD method does not exclude maximum boiling azeotropes despite the fact that these types of azeotropes can not be heterogeneous. In the fine chemical industry, large amounts of used solvent have to be disposed, in many cases with incineration. Because of the high cost it is advisable to concentrate and dehydrate of the liquid wastes. The work is motivated by an industrial environmental problem, which is concentration and dehydration of used, waste solvent contains maximal boiling azeotrope in one step with EHAD. The separation of highly non-ideal Water-Acetone-Chloroform-Methanol quaternary mixture is investigated and optimized in professional flowsheet environment. The aim is to reach as clear as possible bottom product in water compound in order to few distillate product has to be burned. Two slightly different constructions of separations are examined. It can be concluded the computer simulations and experimental verification are proved the separation efficiency of EHAD in first case of maximal boiling azeotrope mixture.

1. Introduction

If such non-ideal mixtures are to be separated where both homogeneous and heterogeneous azeotropes are also presents, a new hybrid tool devoted to the separation of such quaternary mixtures, the so-called extractive heterogeneous-azeotropic distillation (EHAD) can be applied (Szanyi et al., 2004a, Toth et al., 2017; Toth et al., 2016). This new hybrid separation tool combines the advantages of the extractive and the heterogeneous azeotropic distillations (Szanyi et al., 2004a, Toth, 2015). The 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 since no new azeotrope is formed and the extractive and relative volatility changing effect of the autoentrainer is fully utilized (Mizsey et al., 2002). On the other hand, rectification is also taking place while EHAD is applied. The extractive process works along one distillation 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. It combined two of the best separation methods for non-ideal mixtures, extraction and distillation. Also combined in a way that it remained a continuous technology (Toth et al., 2017). Although there are fewer in numbers in some parts of the industry it can be used efficiently. In the case of minimal boiling azeotropes EHAD has been already examined in more research works. The aim of this paper is to investigate one mixture from fine chemical industry, which contains maximal boiling azeotrope. Usually the maximum boiling azeotropes contain chloroform, which is used as a solvent in many industries. Separation of

mixtures that contain chloroform is a complex and expensive. Pressure-swing and extractive distillation can be used as viable separation method (Luyben, 2013). Figure 1 shows the EHAD column in the case of separation of maximal boiling azeotrope.

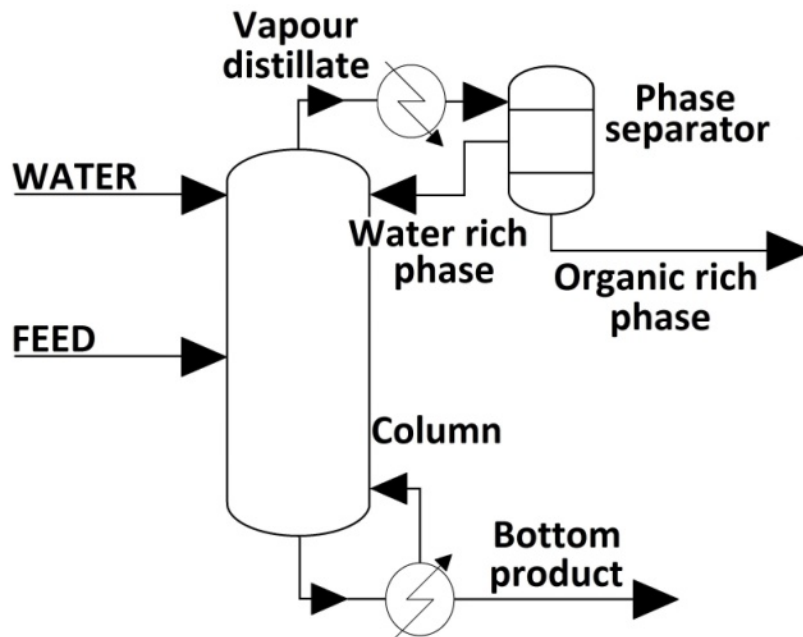


Figure 1: Schema of EHAD if the mixture contains maximal boiling azeotrope

2. Material and methods

10 m/m% Water, 40 m/m% Acetone, 30% Chloroform and 20 m/m% Methanol mixture is used for evaluation, which is a used, waste solvent from fine chemical industry. The aim is to removal the water content from this quaternary mixture and to split it into two binary pairs, Acetone-Chloroform as the organic rich phase in the phase separator (D, see Table 1) and Water content with minimal Methanol as bottom product (W).

The compounds of the examined quaternary mixture form binary and ternary azeotropes as well. Table 1 shows the binary azeotropes of this mixture with UNIQUAC parameters ($U_{ij}-U_{ji}$ and $U_{ji}-U_{ii}$) the residue curve maps of ternary Chloroform-Acetone-Water and Chloroform-Methanol-Water mixtures can be seen in Figure 2 and Figure 3.

Table 1: Binary and ternary azeotropes of the examined mixture (Gmehling et al., 1994; Marsden, 1954)

	x_1 [m/m%]	x_2 [m/m%]	x_3 [m/m%]	x_4 [m/m%]	T [°C]	$U_{ij}-U_{ji}$	$U_{ji}-U_{ii}$
Chloroform(1)+ Methanol(2)	87.5	12.5	-	-	53.5	1283.44	-263.693
Chloroform(1)+ Acetone(3)	79.5	-	20.5	-	64.5	535.401	-555.939
Methanol(2)+ Acetone(3)	-	12.0	88.0	-	56.4	95.259	-10.377
Chloroform(1)+ Methanol(2)+ Acetone(3)	20.9	42.9	36.2	-	57.1		
Chloroform(1)+ Water(4)	97.5	-	-	2.5	56.1	24130.7	-6966.24

Chloroform/Acetone/Water By UNIQ

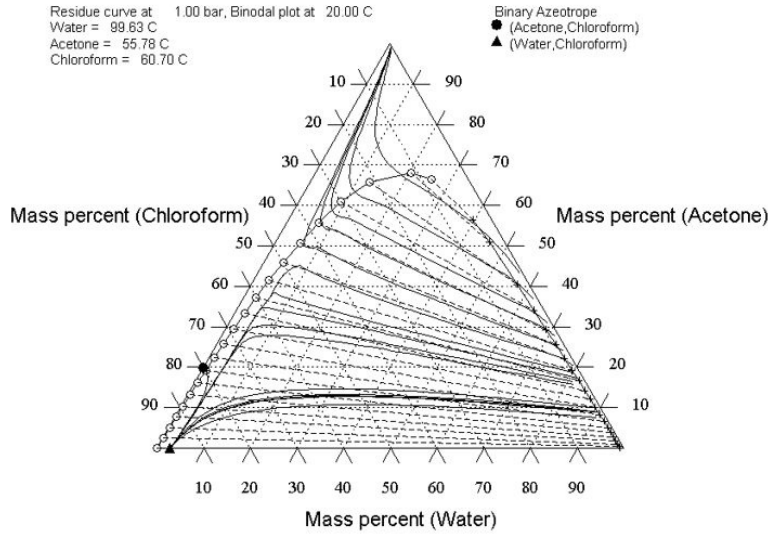


Figure 2: Ternary plot of Chloroform-Acetone-Water mixture

Chloroform/Methanol/Water By UNIQ

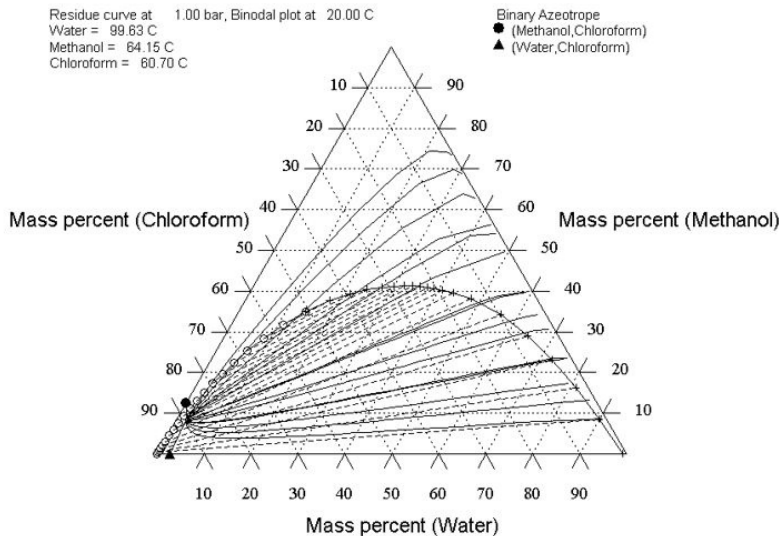


Figure 3: Ternary plot of Chloroform-Methanol-water mixture

It can be seen the Acetone-Chloroform-Methanol-Water quaternary mixture forms five azeotrope: one maximal boiling homogeneous azeotrope (Acetone-Chloroform), two minimal boiling homogeneous azeotrope (Methanol-Acetone, Methanol-Chloroform), one minimal boiling heterogeneous azeotrope (Chloroform-Water), one ternary azeotrope (Acetone-Methanol-Chloroform). The mixture has 2 stable nodes (pure Water component and Acetone-Chloroform maximal 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).

As it can be seen the fully separate the quaternary mixture complex separation method is needed.

Professional flowsheet simulator (ChemCAD) are carried out before 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-Gocłowska and Malanowski, 2001). Also mentioned that two slightly different constructions are used, as it can be seen in Figure 4. The Construction 1 is used to evaluate the effect only of water the addition. The Construction 2 (b) is identical to the real EHAD constructions. Continuous operations are investigated (Yimin et al., 2017).

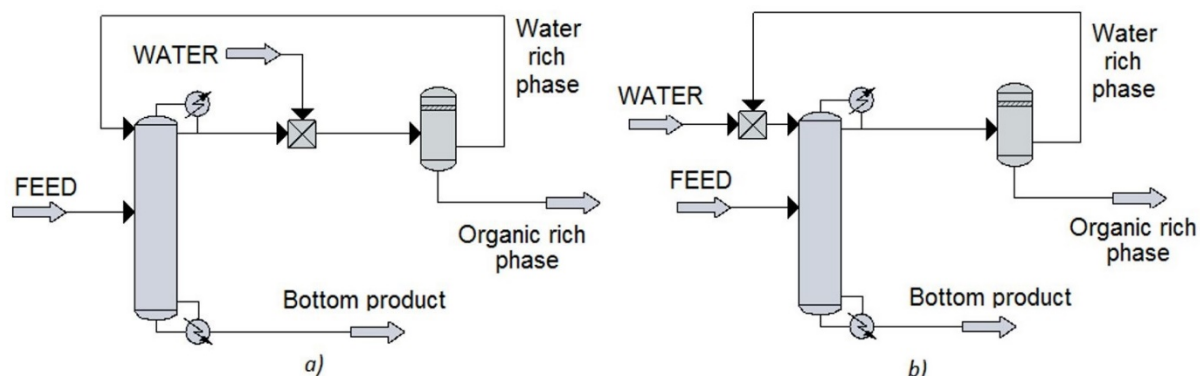


Figure 4: The schematic figures of simulated EHAD in the case of maximal boiling azeotropes

The difference between the two constructions is the place of feed of the extractive water. In the case of Construction (1) the water addition is achieved into mixer between mixer and phase separator. The maximal flooding of the top of column and the effect of water addition can be investigated with Construction (1). After that, the real EHAD column can be investigated with Construction (2)

The following parameters are optimized during the simulations:

- number of theoretical trays of the distillation column (N_{Total}),
- feed tray location (N_{Feed}),
- reflux ratio (R),
- water mass flow (F_{Water}),
- temperature of phase separator (T_{LLVF}),
- pressure of phase separator (p_{LLVF}).

For both configurations the optimal parameters have to be found settings with which the best separation under the current conditions are obtained. In both of the construction the feed parameters are the following: mass flow: 1000 kg/h; feed temperature 20 °C; pressure 1 bar. K-values model is UNIQUAC and the Global Phase Option is V/L/L/S because of the highly non-ideal mixture and SCDS columns are applied. During the parameter optimization the aim is to achieve as pure as possible binary mixture in the bottom product of the distillation column and the phase separator.

The EHAD column is examined experimentally in laboratory apparatus. The main parameters of the column are the following: structured packing, internal diameters of 40 mm. The column has 10 theoretical plates according to a measurement carried out by methanol-water mixture. The solvent feed enters at the middle of the column. The water is fed in the top of the column, as EHAD philosophy requires. The column heating is controlled with a 300 W efficiency heating basket, the phase separator has atmospheric conditions. The flow leaving the condenser goes to a phase split. The lower, organic rich phase is taken away. The upper, water rich phase goes back into the column as reflux (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).

3. Results and discussion

The compositions of both configurations can be compared in Table 2. It can be seen, Configuration (2) is achieved better results in bottom fraction and distillate too.

Table 3 shows the optimized data of both configurations.

Although higher column and more water addition are needed in the case of Configuration (2), this setting should be used, because the EHAD column can separate the quaternary mixture into two binary phases. The better water percent is also confirming the utility of extractive effect of EHAD method.

The second separation (Configuration (2)) is verified with laboratory experiment. The feed composition of mixture is selected according to the industrial separation problem. Q_b value is 300 W in flowsheet environment too. Three experiments are taken out, the average of results can be seen in Table 4, which represent the simulated and measured results of EHAD. Average compositions error is 5% and flow rate error is 3%. The reflux ratio is 5.

Table 2: Comparison of output weight percent of Configuration (1) and Configuration (2)

	F-Mixture	F-Water	Config. (1) D	Config. (1) W	Config. (2) D	Config. (2) W
Water [m/m%]	10	100	5.3	99.2	0.7	99.8
Acetone [m/m%]	40	0	50.8	0.1	53.8	0.1
Chloroform [m/m%]	30	0	43.9	1.4E-17	45.5	2.4E-21
Methanol [m/m%]	20	0	8.4E-09	0.7	7.4E-06	0.1

Table 3: Optimized parameter of Configuration (1) and Configuration (2)

	Configuration (1)	Configuration (2)
N_{Total} [-]	20	25
N_{Feed} [-]	10	5
R [-]	-	1
F_{Water} [kg/h]	2000	3000
T_{LLVF} [°C]	20	20
p_{LLVF} [bar]	1	1

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

	Feed Mixture	Feed Water	Simulated data		Measured data	
			D	W	D	W
Water [m/m%]	10	100	0.3	99.8	1.0	99.7
Acetone [m/m%]	40	0	53.5	0.1	54.1	0.2
Chloroform [m/m%]	30	0	46.2	2.6E-13	44.9	2.4E-5
Methanol [m/m%]	20	0	9.8E-09	0.1	4.5E-05	0.1
Stream [kg/h]	0.25	1.25	0.05	1.45	0.07	1.43
T [°C]	20	20	60.5	99.4	61.3	99.1

The comparison shows the accuracy also in both cases, D and W. It can be seen the distillate stream is 20% of feed mixture, so the other aim is reached, which is the concentration of used solvent.

4. Conclusions

The applicability and effectiveness of extractive heterogeneous-azeotropic distillation is investigated on a non-ideal mixture with simulations and experiments verifying the accuracy of modelling. The method clearly shows that the EHAD means a powerful tool for the separation of highly non-ideal mixtures containing maximal boiling azeotrope and water.

High purity Water-Methanol binary mixture can be achieved easily. In the case of the Acetone-Chloroform mixture it is harder to achieve high purity, however the initial amount of waste solvent can be concentrated to one fifth. The results show the importance of the critical application of vapour-liquid-liquid equilibrium data and if it is about fine chemical production the experimental verification has paramount importance. The application of the EHAD allows also the simplification of the separation schemes and the separation reduces the energy requirements of the distillation and opens new horizons for the separation of non-ideal mixtures saving energy, money and natural resources.

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References

- Abrams D.S., Prausnitz J.M., 1975, Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems, *AIChE Journal*, 21, 116-128.
- Egner K., Gaube J., Pfennig A., 1999, GEQUAC, an excess Gibbs energy model describing associating and nonassociating liquid mixtures by a new model concept for functional groups, *Fluid Phase Equilibria*, 158–160, 381-389.
- Gmehling J., Menke J., Krafczyk J., Fischer K., 1994, *Azeotropic Data*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, New York, Basel, Cambridge, Tokyo.
- Luyben W.L., 2013, Comparison of extractive distillation and pressure-swing distillation for acetone/chloroform separation, *Computers & Chemical Engineering*, 50, 1-7.
- Marsden C., 1954, *Solvents and allied substances manual: with solubility chart*, Cleaver-Hume Press.
- Mizsey P., Szanyi A., Raab A., Manczinger J., Fonyo Z., 2002, Intensification of a solvent recovery technology through the use of hybrid equipment, in: Johan, G., Jan van, S. (Eds.), *Computer Aided Chemical Engineering*, Elsevier, pp. 121-126.
- Sabri N.H., Anwaruddin H., Badhrulhisham A.A., 2017, Modelling and Simulation of Multi-vessel Batch Distillation Column, *Chemical Engineering Transactions*, 56, 1135-1140.
- Skiborowski M., Harwardt A., Marquardt W., 2013, Conceptual design of distillation-based hybrid separation processes, *Annual Review of Chemical and Biomolecular Engineering*, 4, 45-68.
- Skiborowski M., Harwardt A., Marquardt W., 2014, Conceptual Design of Azeotropic Distillation Processes - Chapter 8, in: Gorak, A., Sorensen, E. (Eds.), *Distillation: Fundamentals and Principles*. Academic Press, Aachen, p. 321.
- Szanyi A., Mizsey P., Fonyo Z., 2004a, Novel hybrid separation processes for solvent recovery based on positioning the extractive heterogeneous-azeotropic distillation, *Chemical Engineering and Processing: Process Intensification*, 43, 327-338.
- Szanyi A., Mizsey P., Fonyo Z., 2004b, Optimization of non-ideal separation structures based on extractive heterogeneous azeotropic distillation, *Industrial and Engineering Chemistry Research*, 43, 8269-8274.
- Szanyi A., Mizsey P., Fonyo Z., 2005, Separation of highly non-ideal quaternary mixtures with extractive heterogeneous-azeotropic distillation, *Chemical and Biochemical Engineering Quarterly*, 19, 111-121.
- Toth A. J., 2015, *Liquid Waste Treatment with Physicochemical Tools for Environmental Protection*, PhD Thesis, Budapest University of Technology and Economics, Budapest.
- Toth A.J., Haaz E., Nagy T., Tari R. Tarjani A.J., Fozér D., Szanyi A., Koczka K.-A., Racz L., Ugro G., Mizsey P., 2017, Evaluation of the accuracy of modelling the separation of highly non-ideal mixtures: extractive heterogeneous-azeotropic distillation, in: Espuña, A., Graells, M., Puigjaner, L. (Eds.), *Computer Aided Chemical Engineering*. Elsevier, pp. 241-246.
- Toth A.J., Szanyi A., Haaz E., Mizsey P., 2016, Separation of Process Wastewater with Extractive Heterogeneous-Azeotropic Distillation, *Hungarian Journal of Industry and Chemistry*, 44, 29-32.
- Wiśniewska-Gocłowska B., Malanowski S.X.K., 2001, A new modification of the UNIQUAC equation including temperature dependent parameters, *Fluid Phase Equilibria*, 180, 103-113.
- Yimin Z., Guoli J., Zhuoyun N., Jiansheng G., 2017, A Closed-loop Identification Method based on AIC and Its Application in the Distillation Column Reactor of Ethanol/Water System, *Chemical Engineering Transactions*, 62, 187-192.