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Saving Natural Resources with Extractive Heterogeneous-Azeotropic Distillation

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Efficient processes save natural resources, e.g. chemicals, energy carriers. The Extractive Heterogeneous Azeotropic Distillation (EHAD) is an efficient, novel process for the separation of highly non-ideal liquid mixtures. On the one hand, it consumes less energy than any other separation process and on the other hand the separated compounds of highly non-ideal mixtures can be reused. The EHAD contributes to the saving of natural resources and sustainability. The efficiency of the EHAD is presented on the separation of three highly non-ideal quaternary mixtures of fine chemistry and printing company origins. In this work, the comparison of the efficiency of different separation technologies are compared based on their energy consumptions. It is concluded that the EHAD based separation technology needs the least energy among the investigated alternatives and also enables the recovery and reuse of precious organic compounds.

1. Introduction

It is our obligation to save the natural resources for the next generations. The engineers and engineering can do a lot for the completion of this aim with designing and implementing more efficient processes, technologies. The saving of natural resources is in strong correlation with sustainability (Klemes, 2015). The natural resources can be saved if we consume less energy and recover to recycle chemicals. The pharmaceutical industry and printing companies consume a lot of different organic solvents containing water as well. It is important to note that these solvents arise at the outflow of the technologies as highly non-ideal liquid mixtures containing alcohols, esters, halogenated compounds, ketones and almost always water.

There are incentives to create solvent free technologies but in many cases it is technologically not feasible and the only way for saving the natural resources is their recovery and recycle. For process water use there are such targeting techniques (Saw et al. 2010) that are capable to determine the minimum amount of fresh material/water use via maximizing reuse and recycle but such techniques are not developed for organic solvents. As a consequence efficient process are to be designed for their recovery. Such an efficient novel design is the Extractive Heterogeneous-Azeotropic Distillation (EHAD) that can separate highly non-ideal multicomponent mixtures in a simple and efficient way and as a consequence natural resources (energy and chemical compounds) can be saved.

1.1 Extractive Heterogeneous-Azeotropic Distillation

Szanyi (2005) has developed and proposed a new distillation based process for the separation of highly non-ideal liquid mixtures, the Extractive Heterogeneous-Azeotropic Distillation. If highly non-ideal mixtures are to be separated where both homogeneous and heterogeneous azeotropes are also present this novel hybrid tool is capable to the separation of such ternary and quaternary mixtures. This new hybrid separation tool, first published by Szanyi et al. (2004), combines the advantages of the extractive and the heterogeneous azeotropic distillations. Figure 1 shows the EHAD. To the top of the column a component is fed that has both entrainer and extractive agent functions. In the mixtures, investigated in this work, this component is always the water, called extra water. In the top of the column a two phase product is obtained and a phase split, decanter is applied. Therefore, this unit operation is a kind of hybrid separation tool. The top product is a heterogeneous azeotrope

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which are always minimum boiling ones. Depending on the density circumstances, the organic rich phase is either the upper or lower product as long as the opposite is the water rich phase that is applied as reflux. The bottom product is a one phase product.

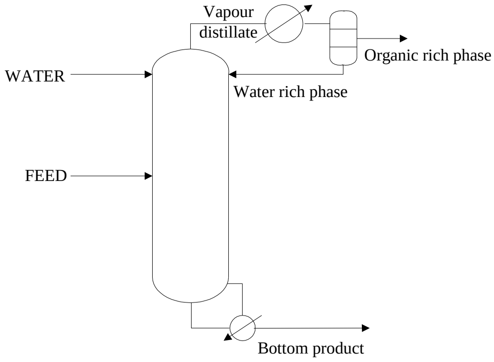

Figure 1: The Extractive heterogeneous-azeotropic distillation

Extractive heterogeneous-azeotropic distillation (EHAD) differs from the heteroextractive distillation that has been first studied by Wijesinghe (1985). Hilmen (2000) has described also the heteroextractive distillation in detail, however, in the case of EHAD no new azeotrope is formed, namely the extractive agent/entrainer is water and this component is already present in the mixtures studied. On the other hand, the extractive and relative volatility changing effect of the autoentrainer/extractive agent is fully utilized and there is no rectifying section in the column. Since heterogeneous azeotropy is absolutely needed to the right operation of EHAD, a hybrid separation tool, water should be used in EHAD as extractive agent. The extractive process of EHAD works within one distillation region of the complex diagram, and the distillation boundaries are crossed by the liquid-liquid phase splitting in the heterogeneous region. On the other hand, the application of extra water as extractive agent/entrainer corresponds to the basic principle of the "green chemistry" (Anastas and Warner, 1998) since no new material is added to the mixture for the sake of proper separation.

Figure 2 presents the separation of a ternary mixture (e.g. ethanol, ethyl-acetate, water) with EHAD. The azetropes, the limited solubility area and the separatricies are presented. The operating line of EHAD column is a straight line. Water addition as extractive separating agent is also presented. The dashed line presents the operation of column "C" and the dashed line with dotes presents the phase separator. D, distillate, B, bottom products and R, the reflux are also presented. Other separation alternatives of this mixture have been studied by Toth (2019).

The EHAD can separate, however, quaternary mixtures as well but for the sake of understanding the operation of EHAD should be presented in the form of a tetraeder, that is, it should be presented in the space. EHAD is capable of separating liquid mixtures containing minimum and/or maximum boiling azetropes. However, the heterogeneous azetropes form only minimum boiling azeotropes and among the homogeneous azeotropes there are more minimum boiling azeotropes and this study is focusing on the separation of quaternary liquid mixtures containing only minimum boiling homogeneous and heterogeneous azeotropes. On the other hand, the industrial mixtures selected as case studies are containing only minimum boiling azetropes.

2. Motivating case studies

The three selected quaternary mixtures of industrial origin are presented in Table 1. ETOH – ethanol; ETAC – ethyl acetate; MEK – methyl ethyl ketone; IPAC – iso-propyl acetate.

The selected mixtures contain binary and ternary azeotropes. Mixtures 1 and 2 are similar as far as the number of azeotropes is considered. It is the aim of this research work to show that the number of azeotropes influences the separation structure based on EHAD. However, Mixture 3, printing company origin, is more complicated having more azeotropes.

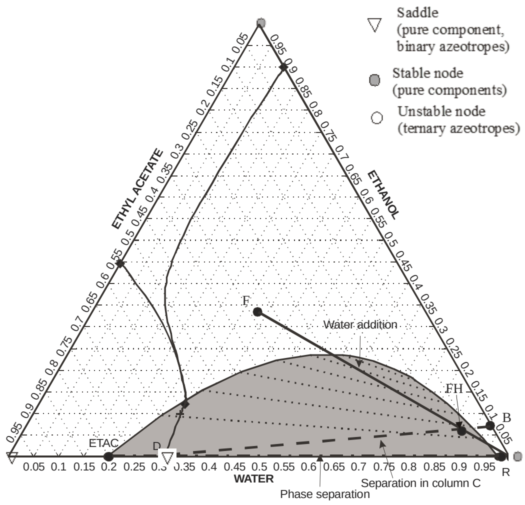

Figure 2: Water – Ethyl acetate – Ethanol diagram (immiscible region is the shaded area, the azeotropes are stable points indicated with black points, F feed, FH feed with extractive agent, water, D distillate, B bottom product)

Table 1: Ternary liquid mixtures of industrial origin

Mixture	1	2	3
Compounds	Water (1) – ETOH (2) – ETAC (3) – IPAC (4)	Water (1) – ETOH (2) – ETAC (3) – IPAC (4)	Water(1) – ETOH (2) – ETAC (3) – MEK (4)
Binary azetropes	(1)-(2); (1)-(3); (1)- (4); (2)-(3); (2)-(4)	(1)-(2); (1)-(3); (1)- (4); (2)-(3); (2)-(4)	(1)-(2); (1)-(3); (1)-(4); (2)-(3); (2)-(4); (3)-(4)
Ternary azeotropes	(1)-(2)-(3); (1)-(2)-(4)	(1)-(2)-(3); (1)-(2)-(4)	(1)-(2)-(3); (1)-(2)-(4); (1)- (3)-(4)

For the separation of Mixtures 1, 2 a solution has been developed by Raab (2001), see Figure 3. This separation technology consists of nine (!) units, seven distillation columns, two extractors and different recycles.

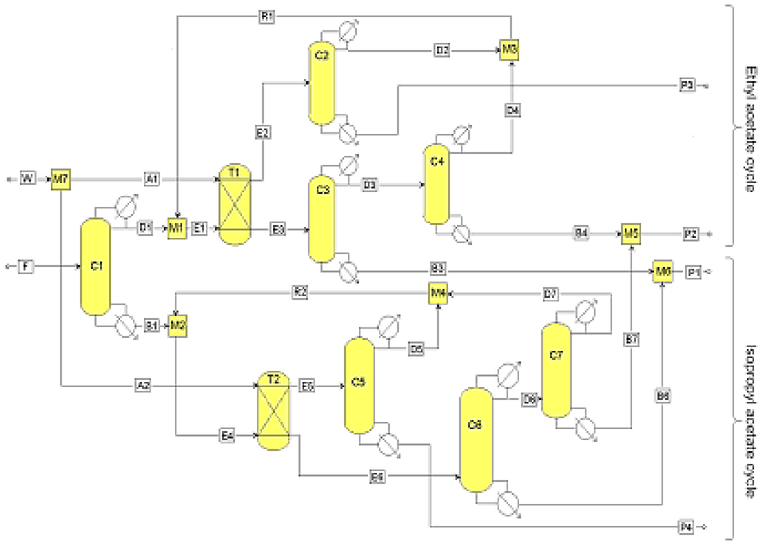

Figure 3: The separation scheme of the ternary-cut-system (W, P2 = water, F = feed, P1 = ethanol, P3 = ethyl acetate, P4 = isopropyl acetate)

Mizsey (1991) has developed a so called two column system (Figure 4) that belongs also to the hybrid separation structures. It has the same idea like the EHAD that heteroazeotrop should be formed in the top of the first column. Water addition to the phase separator is used to obtain proper hetero-azeotrop formation. The two column system separates into binary mixtures of the quaternary ones. Stefankovics (1992) has verified experimentally the operation of the two column system.

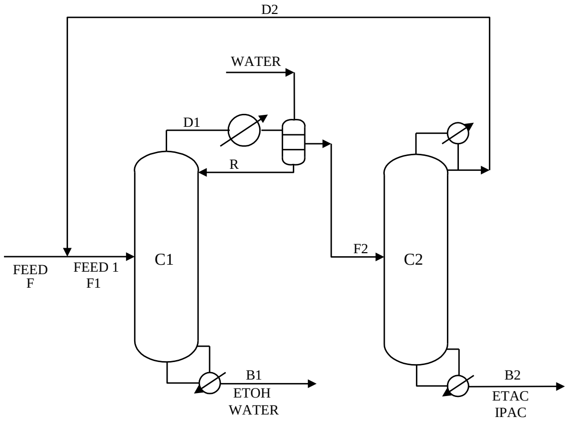

Figure 4: Two-column system

2.1 Solution of the motivating case studies with the proper use of EHAD

After studying the vapor-liquid-liquid equilibria, a simple separation structure can be designed based on the right application of the EHAD as presented in Figure 5.

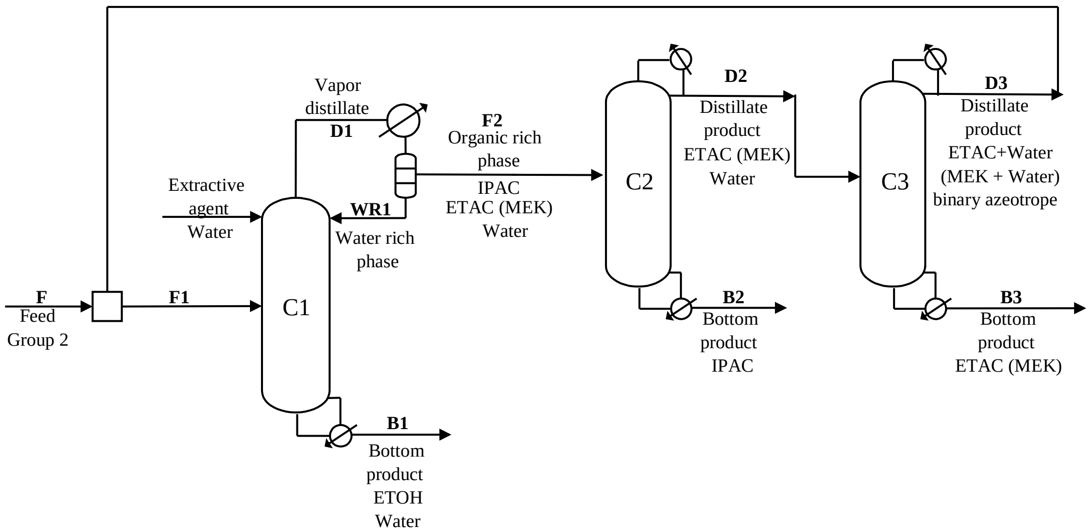

Figure 5: EHAD based structure for the separation of Mixtures 1 and 2

The VLLE (vapor-liquid-liquid equilibria) data and the operation of this EHAD based separation structure (Figure 5) are shown in the 3-dimensional tetrahedral diagram (Figure 6) where the types of the azetropes are also indicated (stable, unstable, saddle). In this case the separatricies divide the solution space into three distinct distillation regions. The first region is generated by the two heterogeneous binary azeotropes, the second one with the two ethanol acetate binary azeotropes, and the last one with the water ethanol azeotropes. Every region contains two ternary azeotropes. The shaded area marks the immiscibility region. The operating lines of the EHAD, column C1 and the phase separator are described. The water as the autoentrainer helps both to cross the separation boundaries and to change the relative volatilities. This double effect makes the desired separation possible. The recycle stream from the second ordinary distillation column contains the azeotrope of ETAC (or MEK) and water.

Benko et al. (2006) have studied the different process alternatives - terner cut, two column structure, EHAD based structure - developed for the separation of Mixtures 1 and 2 with life cycle assessment and economic tools. They have concluded that all the three separation structures are more economic than the incineration and replacement of the organic compounds but the life cycle analysis has proved that only the EHAD based structure is competitive.

The straight lines represent the operating lines of the distillation columns. The separation of the ethanol-water mixture is not included since it is a well-known problem having different solutions.

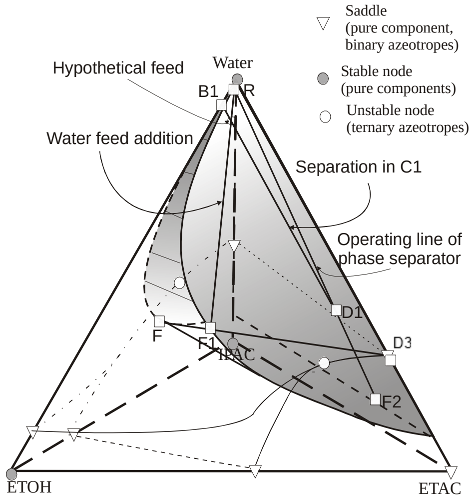

Figure 6: VLLE representation of Mixture 1 and its EHAD based separation in Figure 5 (immiscible region is the shaded area)

In the case of Mixture 3, due to its different VLLE behavior, the separation structure developed for Mixtures 1 and 2 cannot be applied and a different structure is developed using two EHADs (Figure 7). The system also works if iso-propyl alcohol is used instead of ethanol. The VLLE data are presented in Figure 8.

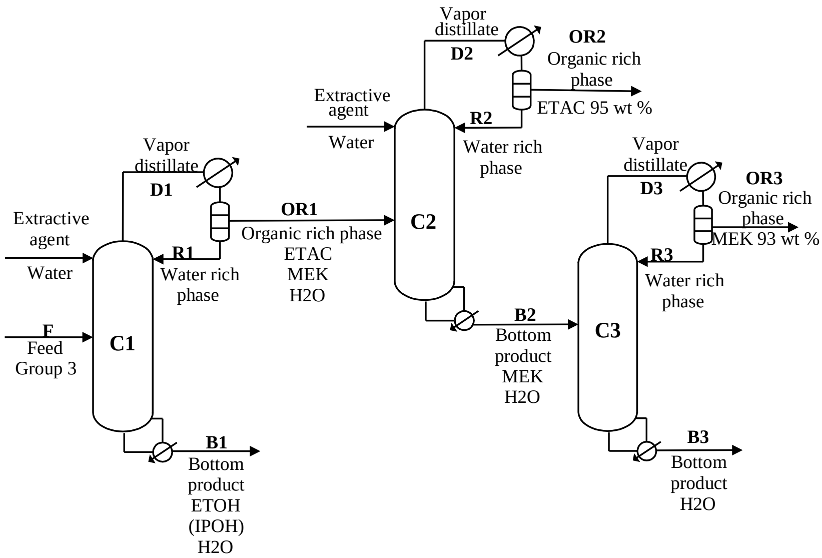

Figure 7: Separation structure for Mixture 3 with two EHAD

3. Results

For the sake of saving natural resources the recovery of organic compounds of highly non-ideal mixtures, three separation process are designed and tested. In this work the efficiencies of the different separation structures are measured according to their energy consumption (Table 2).
The results clearly present the powerful feature of the EHAD based separation schemes for the separation of highly non-ideal mixtures that help save natural resources, that is, solvent recycle with less energy consumption.

Table 2: Ternary liquid mixtures of industrial origin

	EHAD based [MW]	Two-column-system [MW]	Ternary cut system [MW]
Mixture 1	12.04	57.86	23.26
Mixture 2	14.62	35.44	21.17
Mixture 3	21.17	65.17	--

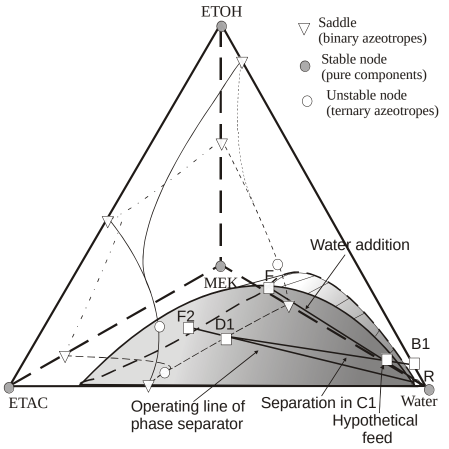

Figure 8: VLLE data and the operating lines of the columns in Figure 7

4. Conclusions

There are powerful process design tools, so called targeting methods, that can determine the maximal recovery/recycle for energy or material. With their application the minimal utility or fresh material consumption and as a consequence the natural resources can be also saved. However, in the case of organic materials/liquids/solvents there is currently no such tool and the possible solution is that the process design should focus on the development of more and more efficient processes that can complete this goal, that is, saving natural resources.

EHAD is the result of the continuous process development where the merits of the rectification, extraction and phase split are applied resulting in a powerful hybrid separation method that enables the efficient recovery of organic liquids, usually solvents from their highly non-ideal mixture. The case studies presented here demonstrate that the innovation and design of more and more efficient processes can result in a separation technology based on EHAD that simply allows the separation and recycle of precious organic liquids minimizing the amount of fresh liquid needs and as a consequence saving natural resources.

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