Complexities of the design of distillation based separation: extractive heterogeneous-azeotropic distillation

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Abstract

The distillation based separation can be extremely complex if highly non-ideal mixtures are to be separated. In spite of different successfully applied unit operations there is still possibility to improve distillation technique and widen its toolbar. A new improvement in this area is the introduction of the extractive heterogeneous-azeotropic distillation. This unit operation includes the merits of the extractive and heterogeneous-azeotropic distillations in one unit without an extra material addition. In spite of the complexity of this unit operation it can be efficiently applied and complex separation technologies can be simplified with its application.

The separations of ternary and quaternary mixtures from the fine chemical industry show both in the modelled and the experimental results that the extractive heterogeneous-azeotropic distillation can be successfully applied.

The comparison of the modelled and experimental results in the case of concentrations close to high and/or zero purity concentrations shows differences between modelled and measured values. This highlights the paramount importance of the experiments if special extra fine chemicals with almost no impurities e.g. pharmacopoeial quality are to be produced by special distillation technique.

Keywords

complexities of design, non-ideal mixtures, extractive heterogeneous-azeotropic distillation

1. Introduction

Distillation is the most widespread separation process in the chemical industry. The components of a liquid mixture are separated on the basis of the difference in their volatilities. As the energy demand of the distillation is very high, the optimal design and operation of the process are important questions, both economically and environmentally [1].

If the separation of highly non-ideal mixtures should be made, that is quite often in fine chemical industries, where the separation of usually azeotropic mixtures and then fine chemical quality should be produced, it is extremely difficult to pay significant attention to the energetic and environmental issues. Such highly non-ideal mixtures usually contain different kinds of alcohols, esters, aldehydes, ethers and water. These compounds already predict that serious problems arise at their distillation based separation.

The separation of an ethanol, ethyl acetate, isopropyl acetate and water containing quaternary mixture from the fine chemical industry [2] called the attention of the necessity for the development of the distillation based separation that comprises the merits of different separation solutions.

A new hybrid separation alternative, the so called extractive heterogeneous-azeotropic distillation (EHAD) introduced by Szanyi et al. [3-5] and Szanyi [6] that combines the advantages of the extractive and the heterogeneous-azeotropic distillations (Figure 1). The heterogeneous-azeotropic option assumes that water is present in the mixture and limited immiscibility exists.

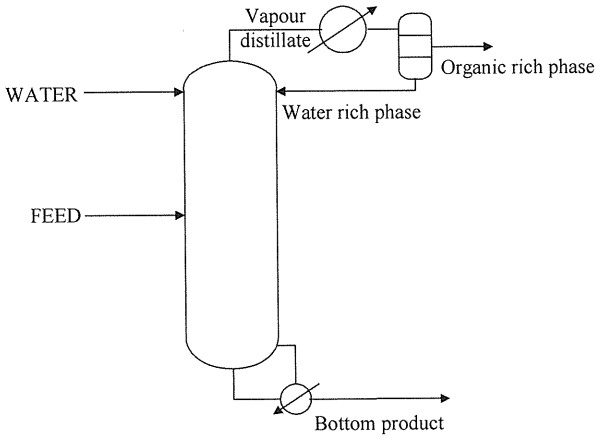

Figure 1 The extractive heterogeneous-azeotropic distillation

The EHAD differs from the heteroextractive distillation [7] since no new azeotrope is formed, namely the extractive agent/entrainer is water and this component is already present in the mixtures to be separated. Moreover, the extractive and relative volatility changing effect of the autoentrainer/extractive agent is fully utilized and there is no rectifying section in the column [6].

The efficiency of the EHAD can be represented with the motivating case study. This was first solved with a separation system of nine units, distillation columns and extractors [8]. With the application of the EHAD it could be simplified to four units (Figure 2) [2].

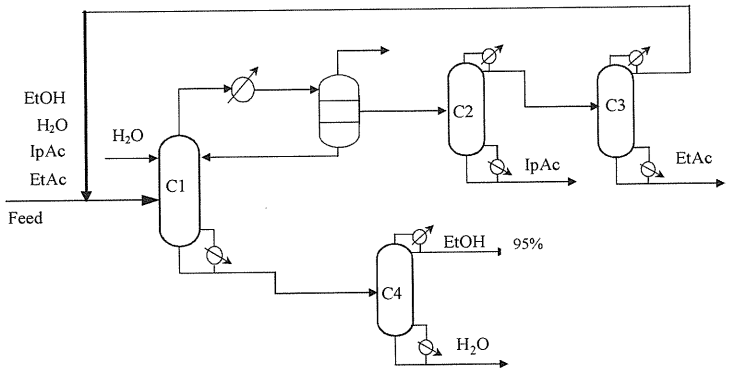

Figure 2 Solution of the motivating example with EHAD

Among the products there is the ethanol of 95 w/w% purity, so below the azeotropic point. In our investigation we considered the current industrial praxis where the dewatering of the ethanol can be completed with molecular sieve.
If fine purity is required e.g. biofuel or pharmacopoeial application further unit operations might be needed, e.g. rectification again.

2. Results and discussion

The applicability and effectiveness of extractive heterogeneous distillation is tested with computer simulations and experimentally. The test includes also the investigation of the accuracy of computer modelling.
First a terner mixture is selected: methanol (MEOH), ethyl-acetate (ETAC) and water. Before the experiments computer simulations are carried out with ChemCAD 6.4.2 [9] to reduce the required number of experiments and to find promising separation alternatives. Moreover, the optimal reflux ratio, the mass- and bottom flow rates, heating and cooling requirements can be also determined knowing the measured heat flow in the column. As an equilibrium model for the calculation of the highly non-ideal vapour-liquid equilibria the UNIQUAC method [10-13] is applied. If binary pairs are existing, where no UNIQUAC data are available, the UNIFAC method [14] is applied.
Since the EHAD works with limited immiscibility besides the vapour-liquid equilibria, liquid-liquid equilibria should be also calculated, that is, vapour-liquid-liquid (VLL) equilibria. The mentioned equilibrium models (UNIQUAC, UNIFAC) both have VLL equilibria option.

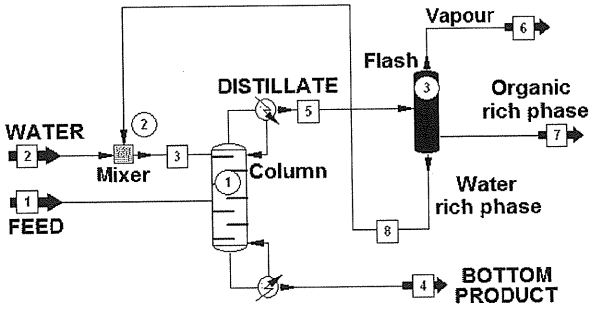

Figure 3 ChemCAD model for the separation of the ternary mixture

The operation of the EHAD and the complexities of the ternary mixture are shown in Figure 3 calculated with ChemCAD. There are two binary azeotropes, one

homogeneous and on heterogeneous. The operating lines show the operation of the EHAD. The entrainer, water, addition is also presented.
To save time and material first extensive simulation works should be completed. The simulation prepares and predicts the experiments. The experiments are completed on a laboratory apparatus shown in Figure 4.

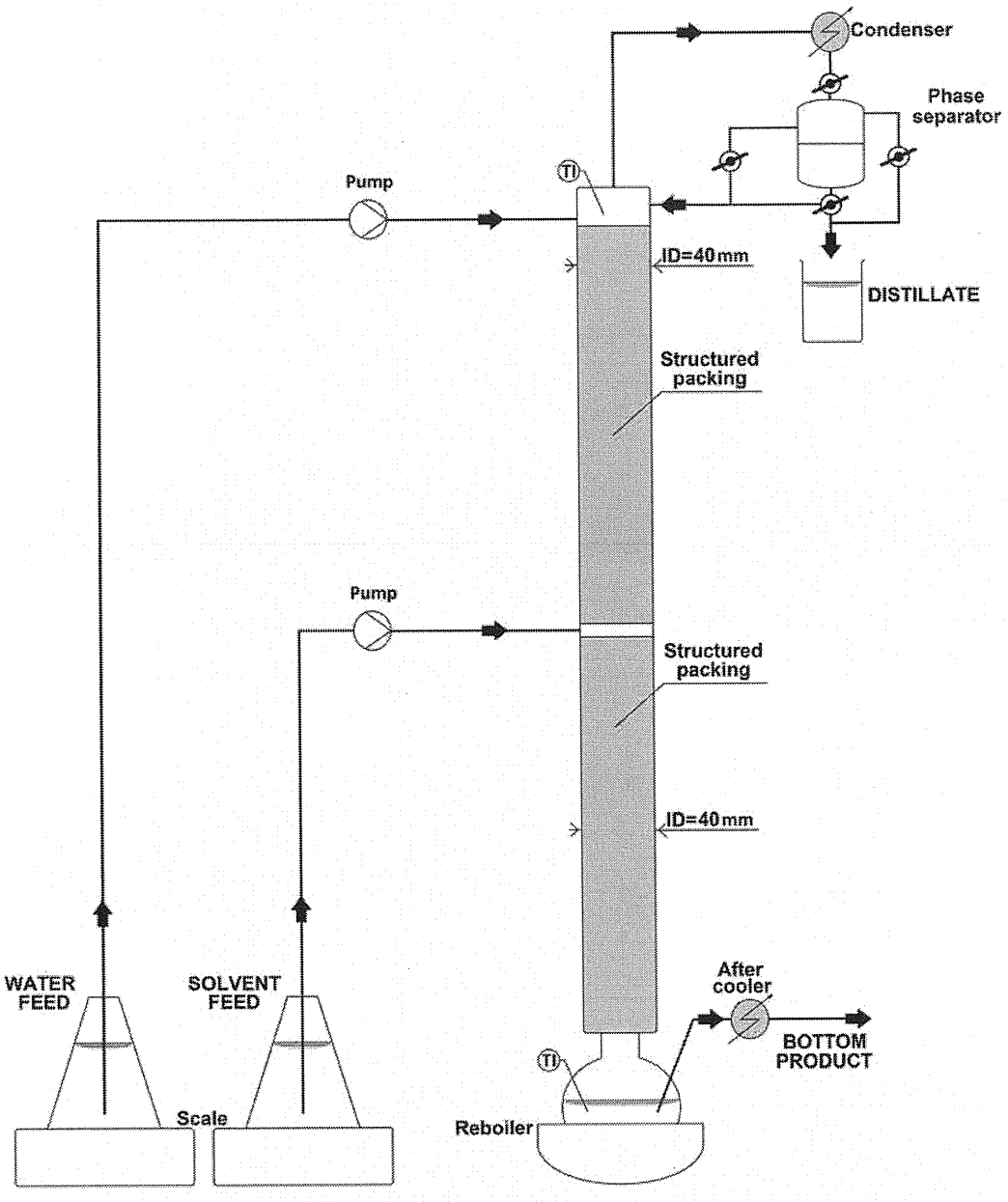

Figure 4 Extractive heterogeneous distillation column of laboratorial size

The modelling results are tested in laboratory experimental conditions. The main parameters of the experimental column are the following: structured packing, internal diameters of 40 mm. The column has 40 theoretical plates. (According to measurement carried out by methanol-water mixture.) The feed is not preheated and it is pumped in the middle of the column and the flow value is kept at 0.25 kg/h. The entrainer (water) is pumped in the top of the column and the flow value is kept at 1.23

kg/h. The column heating is controlled with a 300 W efficiency heating basket. The flow leaving the condenser goes to a phase split. The upper, organic reach phase is taken away. The lower, water rich phase goes back into the EHAD column as reflux. The content of the feed (F), distillate (D), bottom product (W) are measured with Shimadzu GC-14B gas chromatograph with a CP-SIL-5CB column connected to a flame ionization detector.

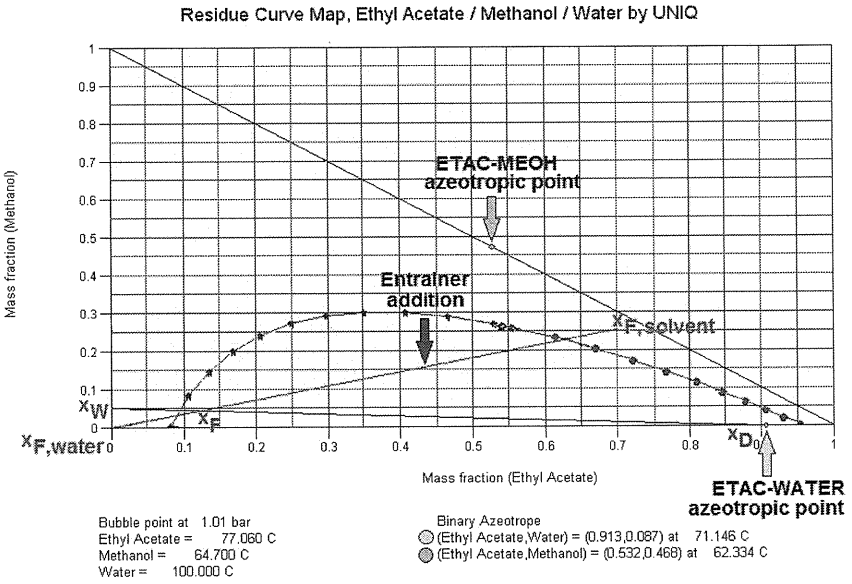

Figure 5 Calculated equilibria and operating lines of the EHAD

In Table 1 we can see the measured and calculated results. The comparison pays special attention to those regions where the measured and calculated concentrations are close to zero. This is usually a pretty uncertain region.

Table 1 Comparison of measured and simulated data for the ternary mixture

	Feed	Simulated data w %		Measured data w %	
	w %	D - top phase	W	D - top phase	W
Water	4	3.6	94.7	5.3	94.6
MEOH	26	0.102	5.2	0.227	5.4
ETAC	70	96.3	0.1	94.5	b.d.l.

b. d. l.: below detection limit

For instance at the production of extreme fine chemical, industrial examples show that this uncertainty can be even critical when only calculations are considered and this uncertainty underline the importance of the experiments.
The comparison of our previous modelling also strengthens this result [2]. These measurements and calculations were made for quaternary mixtures like in the case of the motivating example ethanol, ethyl acetate, isopropyl acetate and water and ethanol, ethyl acetate, methyl ethyl ketone and water.

3. Conclusions

The application of the extractive heterogeneous-azeotropic distillation improves significantly the possibilities for the separation of highly non-ideal mixtures. It opens

new areas for the design of distillation based systems. Difficult multicomponent separations can be easily and cost effective solved with the EHAD.
Modelling and experimental results show good agreement for the EHAD. Our results obtained on EHAD experiments and industrial distillation problems that close to zero concentrations e.g. pharmacopoeial purity the modelling cannot always deliver reliable results and the experiments and proper analytics have paramount importance.

Acknowledgements
The authors would like to acknowledge the financial help of TÁMOP-4.2.2.A-11/1/KONV-2012-0072 and KMR - 12-1-2012-0066.

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