NOVEL HYBRID PROCESSES FOR SOLVENT RECOVERY

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ABSTRACT

Three hybrid separation processes are developed and recommended for solvent recovery from highly non-ideal quaternary mixtures obtained in printing companies. The procedures are tested on two different solvent mixtures.

The first process (ternary-cut-system) splits mixture 1 into two ternary mixtures which are separated later in subsequent units into components of the purity needed. The second separation process is based on two coupled distillation columns (two-column-system) which can cope with the separation of both mixtures into two binary mixtures that are to be separated further with common methods.

The third separation process is developed merging the extractor and distillation units into a process based on extractive distillation using water as extractive agent (integrated-system). This integrated-system can separate both mixtures into components of the prescribed purity or into binary mixtures and proves to be the simplest arrangement and consumes the lest energy among the three ones.

The separation processes are verified experimentally and the agreements between the simulated and measured data prove to be rather favorable.

INTRODUCTION

The chemical engineers are faced with the important problems of the solvent recovery which minimizes the burden upon the environment due to the exhaustive use of solvents and the emission associated with the incineration of the used solvents. The solvent recovery is also economically beneficial but the saving always depends on the different, usually country specific, prices.

In printing companies the following typical quaternary waste mixtures of different solvents are often produced, mixture 1: ethanol (ETOH) 30w%, ethyl acetate (EtAC) 25w%, isopropyl acetate (IPAC) 20w%, water (H2O) 20w%, and mixture 2: ethanol 23w%, ethyl acetate 32w%, methyl-ethyl-ketone (MEK) 28w%, and water 13w%. There are some accompanying components in less than 5w%, which are neglected in this study. The two mixtures are highly non-ideal ones and they form several binary and ternary azeotropes making the separation to a quite complex problem (Tables 1-4 [3]). The synthesis for possible separation processes is a complex engineering activity but there are some powerful tools to overcome this problem.

Among several synthesis strategy, Rev et al. and Mizsey et al. [1,2] have also recommended a framework for designing feasible schemes of multicomponent azeotropic distillation. This procedure recommends to study in detail the vapour-liquid-liquid equilibrium data to explore immiscibility regions, azeotropic points of binary and ternary ones, and separatrices for ternary and quaternary regions. On the behalf of the VLLE data the set of feasible separation structures can be explored. This procedure is followed and new separation technologies are developed.

Table 1, Binary azeotropes of mixture 1

	t	H2O	ETOH	ETAC	IPAC
	[°C]	[w%]	[w%]	[w%]	[w%]
H2O - ETOH	78.17	4	96	0	0
H2O - ETAC	70.38	8.5	0	91.53	0
H2O - IPAC	76.6	10.6	0	0	89.4
ETOH - ETAC	71.81	0	31	69	0
ETOH - IPAC	76.8	0	53	0	47

Table 2, Ternary azeotropes of mixture 1

	t	H2O	ETOH	ETAC	IPAC
	[°C]	[w%]	[w%]	[w%]	[w%]
H2O - ETOH - ETAC	70.2	9	8.4	82.6	0
H2O - ETOH - IPAC	74.8	9.8	19.4	0	70.8

Table 3, Binary azeotropes of mixture 2

	t	H2O	ETOH	EtAC	MEK
	[°C]	[w%]	[w%]	[w%]	[w%]
EtAC -H2O	70.4	8.5	0	91.53	0
ETOH- EtAC	71.8	0	31	69	0
MEK-H2O	73.3	12.7	0	0	87.3
ETOH-MEK	74.1	0	39	0	61
EtAC -MEK	77	0	0	82	18
ETOH-H2O	78.1	4	96	0	0

Table 4, Ternary azeotropes of mixture 2

	t	H2O	ETOH	EtAC	MEK
	[°C]	[w%]	[w%]	[w%]	[w%]
ETOH- EtAC -H2O	70.2	3	8.4	82.6	0
ETOH -MEK-H2O	73.2	11	14	0	75

DISCUSSION OF THE HYBRID SEPARATION PROCESSES

After studying the complex non-ideal VLLE nature of the two mixtures to be recovered, it becomes clear that the mixtures cannot be separated with he use of common distillation units, a combination of different type of separation units, hybrid separation processes are needed. Three separation processes are designed with the help of a synthesis strategy [1,2]: the ternary-cut-system, the two-column-system, tested already previously for mixture 2 [1,2], and the integrated system based on extractive distillation. The simulations are completed with the ASPEN PLUS flowsheeting package, the VLLE method used is the Uniquac thermodynamic property package with UNIFAC estimation for the non-measured data. Its databank is based on the DECHEMA Chemistry Data Series, Dortmund DataBank e.g. [7].

The Ternary-cut Process

The VLLE data of mixture 1 indicates that a ternary azeotrope (ethanol, ethyl-acetate, water) of minimum boiling point is existing and can be obtained as distillate in case of common distillation. According to the analysis of the system it is possible to cut the quaternary mixture into two ternary mixtures (ternary-cut): ETAC-ETOH-H2O and IPAC-ETOH-H2O. In the following the two ternary mixtures can be processed separately in two similar cycles (Figure 1) The cycles consist of one extractor and three distillation columns, respectively.

The VLLE data, azeotropes, separation boundaries, and the operating lines of the two cycles are shown in Figures 2,3. It can be seen that the extractor units play a key role in each cycles and internal recycles are also needed to improve the efficiency of the solvent recovery.

The Two-Column System

The system has been already earlier synthesized and tested for mixture 2 [4,1,2]. Two coupled distillation columns and a three-phase flash where extra water is added are applied in this system. With the use of the two-column system it is possible to separate the quaternary mixtures into two binary fractions (H2O+ETOH and ETAC+MEK) which can be further separated with common distillation tools into components of the prescribed purity. The physical insight of this system and its operation have been also explained [1,2] The necessity of the phase-separation is due to a separation boundary in the VLLE and the extra water addition can help to overcome on this boundary (Figure 4).

In this work the two-column system is tested for mixture 1 (Figure 5) and proves to be successful again to separate the quaternary mixture into two binary ones (H2O+ETOH and ETAC+IPAC). The separation of the two binary mixtures is not studied in detail but to recover the individual components more separation units are needed

The Integrated System

In the third step of this evolutionary process synthesis, the fact is utilized that water is always used in the previous hybrid separation processes to exploit the advantage of the immiscibility regions allowing the step over separation boundaries. As a consequence an integrated separation technology, the integrated-system, is designed based on extractive distillation unit with water as extractive agent. The system integrates the distillation and the extraction or the water addition in the phase-separator of the previous systems. The use of the extractive distillation unit proves to be a multifunctional unit and allows a significant simplification of the previous separation systems.

In case of mixture 1 it becomes possible to separate the quaternary mixture in four distillation columns into the components of the prescribed purity (Figure 6). Figure 7 shows the VLLE data for columns 2 and 3 and also their splitting lines.

In case of mixture 2 an easier separation of the quaternary mixture is possible into the two binary mixtures (H2O+ETOH and ETAC+MEK) compared to the two column-system. Later on it will be proved that it consumes also less energy.

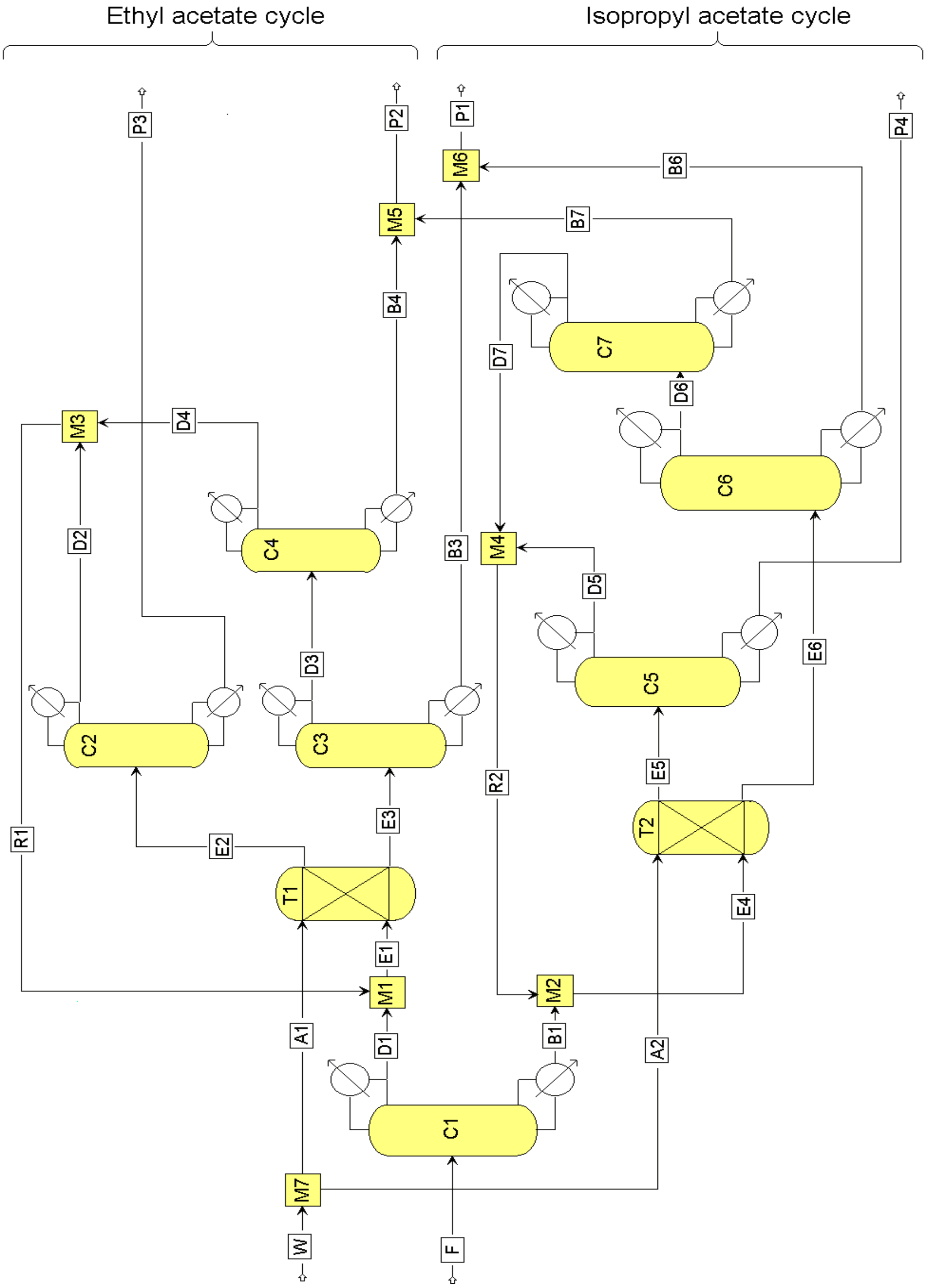

Figure 1. The separation scheme of the ternary-cut-system
(W, P2 = H2O, F = feed, P1 = ETOH, P3 = ETAC, P4 = IPAC)

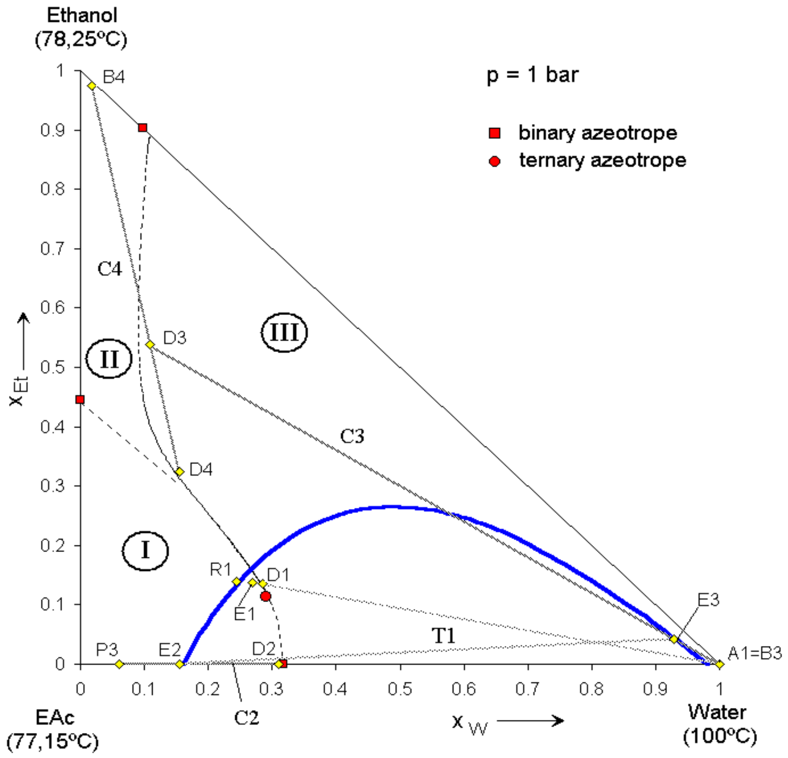

Figure 2. The VLLE data and representation of the ETAC cycle (ternary-cut-system)

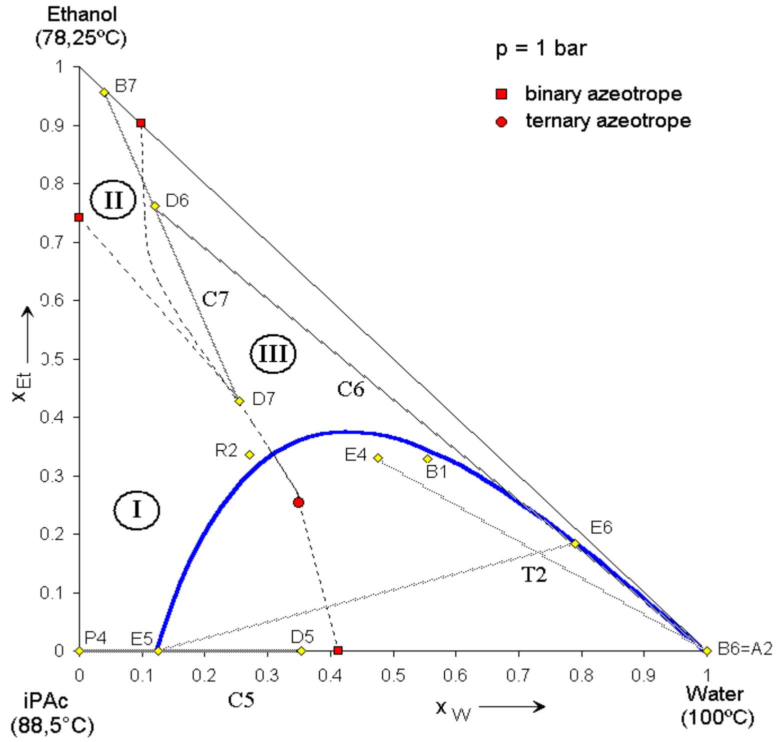

Figure 3. The VLLE data and representation of the IPAC cycle (ternary-cut-system)

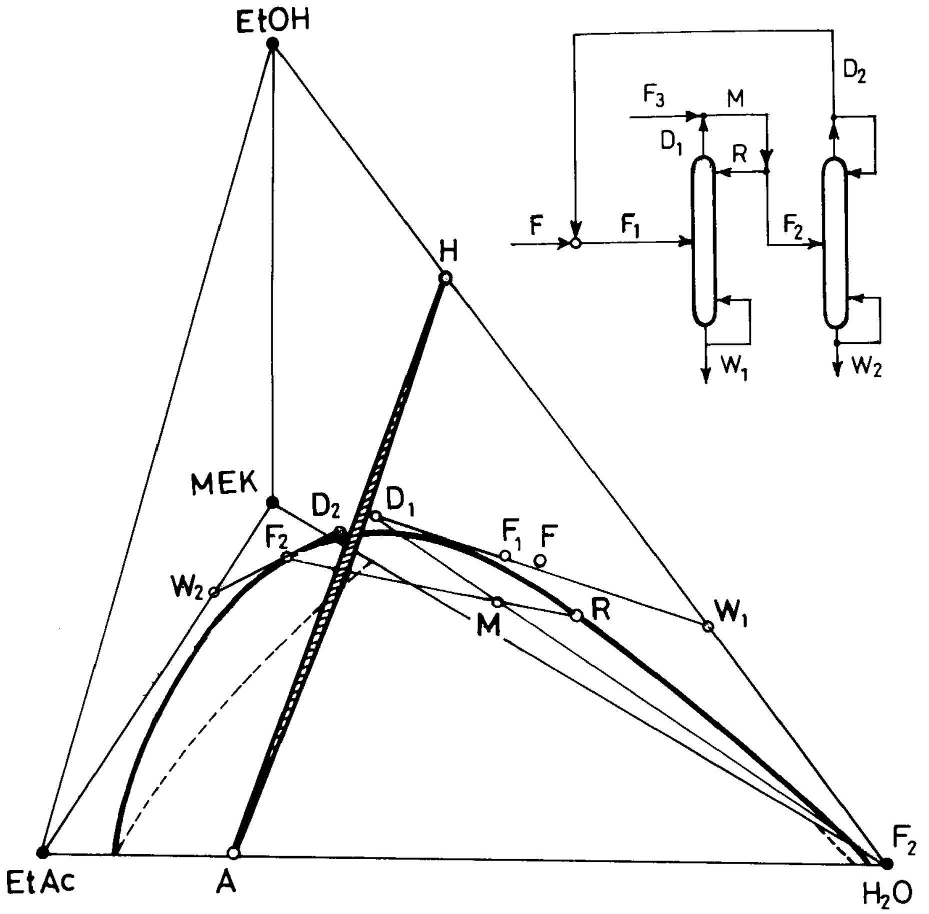

FIgure 4, The VLLE of mixture 2 and the operation of the two-column system

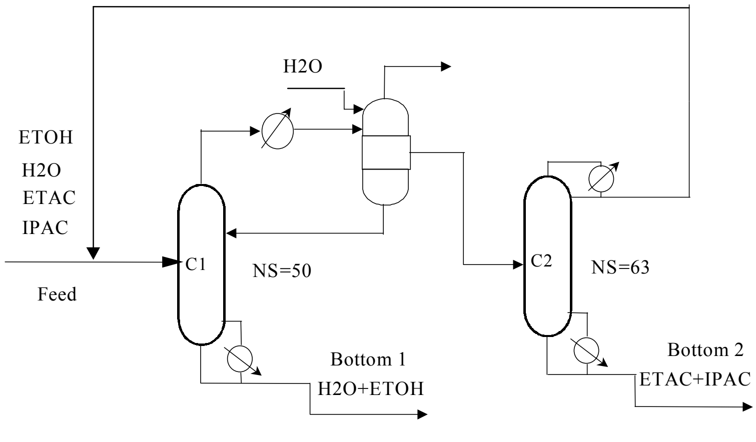

Figure 5. Two-column-system for the separation of quaternary mixtures

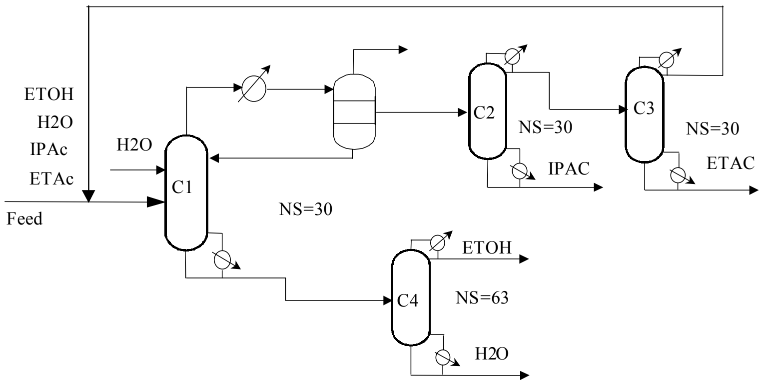

Figure 6. Integrated-system based on extractive distillation

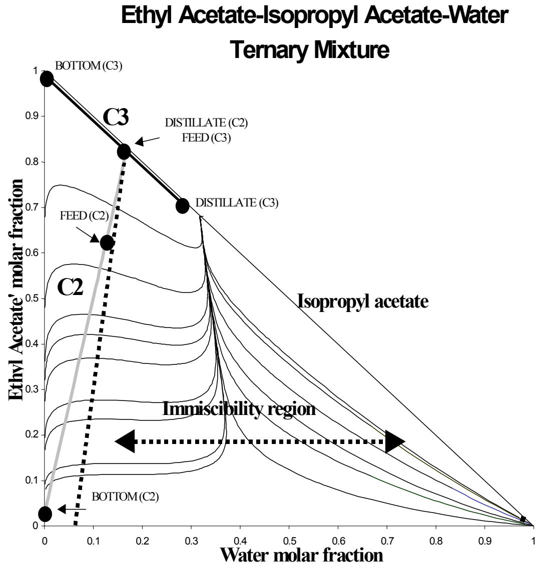

Figure 7, The VLLE data and representations of columns 2 and 3

COMPARISON OF THE ENERGY CONSUMPTION

The three separation systems are investigated from the points of operation and energy consumption. The integrated-system is the simplest one and it is the easier to realize and operate. The total energy consumption (heating and cooling) of the three systems are also determined and compared. The new integrated solvent recovery technology using hybrid equipment proves to be not only the simplest but also the most attractive for the energy consumption (Table 3). Among the cost comparison it is indicated if the costs relate only for such separation when only binary mixtures are obtained (e.g. two-column system). In spite it can be concluded that the integrated-system based on extractive distillation proves to be the cheapest and simplest among the three. The separation of mixture 2 in the integrated-system into two binary products consumes less energy than the same separation with the two-column system, too.

According to estimations, the savings of the solvent recovery depends on the actual, usually country specific, prices and range between 70-95%. The energy consumption could be further minimized (Szitkai et al., 2001) if membrane separation technology is combined with distillation for the ethanol-water separation (Figure 6, Column 4) and this option is considered in our research group as possible further process improvement.

Table 3. Comparison of separation technologies (Feed = 100 kmol/h)

	Integrated-system [MW]	Two-column-system [MW]	Ternary-cut-system [MW]
Mixture 1	10.7	25.1*	23.3
Mixture 2	14.6*	23.8*	—

* only binary products are obtained

EXPERIMENTAL INVESTIGATIONS

All the three separation processes are verified fully or partially by laboratory experiments corresponding to the circumstances found by simulations. The internal diameter of the columns are always 3 cm, the column internal is always structured packing.

First, the core of the of the ternary-cut-system, column 1 (C1), (Fig. 1), in which the split of mixture 1 takes place into two ternary products, is tested experimentally. Steady-state continuous distillation is carried out for 6.5 hours controlling the column according to the typical top temperature. The distillate and bottom products are analyzed and compared with the simulation data (Table 4). The comparison of the simulated and measured data shows a good agreement (Raab, 2001) which proves both the accuracy of the selected UNIQUAC thermodynamic property package and the simulation procedure.

Table 4. Comparison of measured and simulated data of C1 of the ternary-cut-system for mixture 1

	Feed w%	Simulated data w%		Measured data w%	
		Distillate	Bottom	Distillate	Bottom
Water	21	8.3	26.9	8.9	29.7
ETOH	32	10.0	40.6	8.6	39.9
ETAC	26	81.3	0.6	82.1	0.2
IPAC	21	0.4	31.9	0.4	30.2

Secondly, the two-column-system is verified experimentally in two coupled laboratory columns for mixture 2. The results are compared with the simulated ones and they are in good agreement (Figure 5).

The third process, the integrated-system based on extractive distillation is also verified by experiment. The most critical part of the system, the extractive distillation is measured in the laboratory column. Three and a half hours continuous operation is carried out and the results are compared with the simulated ones. The agreement is good (Figure 6).

Table 5. Comparison of measured and simulated data of the two-column-system for mixture 2

	Feed w%	Simulated data w%		Measured data w%	
		Bottom 1	Bottom 2	Bottom 1	Bottom 2
Water	36	84.91	0	83.9	0
ETOH	26	14.76	0.05	13.1	0.5
ETAC	19	0.03	49.13	1.1	48.9
MEK	19	0.29	50.81	1.9	50.6

Table 6. Comparison of measured and simulated data of the extractive distillation of the integrated-system for mixture 1

	Feed w%	Simulated data w%		Measured data w%	
		Bottom 1	Bottom 2	Bottom 1	Bottom 2
Water	21	2.7	96.1	2.8	95.8
ETOH	32	0	3.9	0	4.2
ETAC	26	55.0	0	53.2	0
MEK	21	42,3	0	44,0	0

CONCLUSIONS

The successful application of the integrated-system obtained with evolutionary steps allows significant simplification and improves economic features of the separation of non-ideal mixtures typical for solvent recovery. By reason of the applied evolutionary synthesis strategy a generalisation of the extractive distillation based processing is outlined for the separation of non-ideal mixtures containing heterogeneous azeotropes.

Experiments show good agreement between the simulated and measured data that also supports the accuracy of the three solvent recovery processes. The developed solvent recovery processes can realise significant saving and reduction of the burden upon the environment.

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