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INVESTIGATION OF ACETIC ACID DEHYDRATION BY VARIOUS METHODS

Chavdar Chilev[1,2], Farida Darkrim Lamari[2],
Moussa Dicko[2], Evgeni Simeonov[1]

[1] *University of Chemical Technology and Metallurgy*
8 Kl. Ohridski, 1756 Sofia, Bulgaria
[2] *LSPM CNRS Université Paris 13*
Sorbonne Paris Cité, Inst. Galilée,
Av. J.-B. Clément 93430 Villetaneuse, France
E-mail: cchilev@abv.bg

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ABSTRACT

Some separation methods for acetic acid dehydration, such as azeotropic distillation, extractive distillation and hybrid extraction/distillation process (HEDP) are investigated and further analyzed. In order to optimize the separation process, different separation agents were investigated. The phase equilibria (vapor-liquid and vapor-liquid-liquid) of the ternary system acetic acid/water/separating agent are analyzed in order to choose an appropriate thermodynamic model suitable for the simulation of the system. The results show that the azeotropic distillation is the most undesirable dehydration method among the three separation processes investigated. Almost similar results are obtained using the extractive distillation and HEDP. The latter is energetically more favorable, but the extractive distillation requires less equipment and control operations costs. Therefore, HEDP using methyl tert-butyl ether as an extraction agent is the most promising separation method for the system studied.

Keywords: heterogeneous azeotropic distillation, extractive distillation, hybrid extraction/distillation process, acetic acid dehydration, numerical simulation.

INTRODUCTION

Acetic acid is the most widely used aliphatic carbonic acid. It is frequently used as a solvent in the manufacture of cellulose acetate or many pharmaceutical products. But acetic acid coexists often with an amount of water. Because a high-purity acetic acid is needed in industry, separating acetic acid and water is an urgent challenge. Separation of pure water from dilute solution of HAc/W in the concentration range of 1 % to 30 % acetic acid by simple rectification is almost impossible as the mixture relative volatility in this range approaches unity. It would then require towers with large number of stages which would be operated at high reflux ratio and require high energy operating costs [1]. In order to separate a binary mixture which is difficult or impossible to separate by ordinary means, a third component term, the so-called separating agent is added. It alters the relative volatility of the original constituents thus permitting the separation. The addition of a separating agent, which is generally immiscible with water permits to separate the HAc/W mixture by heterogeneous azeotropic distillation, as already reported in the literature [1]. In order to use azeotropic distillation for the separation of HAc/W, the process contains a dehydration column, a decanter, and a stripping column. Pure acetic acid is brought to the bottom of the column while water leaves the column from the head mixed with the separating agent (entrainer). The latter must be further separated from water before being re-used. The effects of the entrainer flowrate, feed tray locations (both for main feed and entrainer feed) into the acetic acid purification process were investigated.

Extractive distillation is a multicomponent-rectifi-

cation method similar in purpose to azeotropic distillation. This method is used since more than 50 years [2] in the separation of aromatic, alcohol, olefin/paraffin, cycloalkanes/paraffin, carboxylic acids/water mixtures, etc. In the extractive distillation process, the separating agent is not vaporized and thus the energy consumption is relatively low. Therefore, it is an attractive method for acetic acid dehydration and has been studied by Berg [3, 4]. The process flowsheet contains an extractive-distillation column and an ordinary distillation column. The influence of the total solvent (extractive agent) flowrate and the reflux ratio on the separation process is studied.

The hybrid extraction/distillation process is a separation approach that combines an extraction column and an azeotropic distillation process. This process design is considered to be comparatively effective because of the lower total energy required [5, 6]. In this work, the total numbers of trays, the feed tray locations, and the extraction solvent flow rate into the extraction column are the most important design parameters which are integrated into the optimization procedure.

In this work, many approaches including, heterogeneous azeotropic distillation, extractive distillation and hybrid extraction/distillation process are investigated to design the most suitable HAc dehydration process with the lowest total annual cost. The separating agent choice affects strongly the process efficiency. Therefore, different separating agents would be investigated in order to minimize the total annual cost.

SIMULATION PROCEDURE

Separating agents' selection

Different types of an organic solvent may be considered. A low boiling solvent such as ether or chloroform which may be further easily separated from the concentrated acid after the liquid/liquid extraction or distillation operations can be used. The intermediate boiling solvents such as isobutyl acetate (IBA) which may be used as azeotropic withdrawing agents and separated from the concentrated acid according to the method of azeotropic distillation can be an option. Intermediate boiling solvents in which the water in the solvent/acid/water mixture is removed through extraction by azeotropic distillation can be chosen as well. The solvents of a boiling point sufficiently higher than that of the acetic acid can be also used. In this case the acetic acid obtained by extractive distillation or extraction from the liquid phase may be removed from the solvent by conventional distillation.

Ethylene dichloride was one of the first entrainers used in the process of azeotropic distillation [5]. Later Othmer [7, 8] and Tanaka [9] used normal propyl acetate and normal butyl acetate for acetic acid dehydration process. Luyben [10] proposed vinyl acetate for academic studies. The typical examples of effective agents in Berg's patent [3, 4] include ethyl n-valerate, 4-methyl-2-pentanone, methyl propionate, hexyl acetate, 2-methyl hexanone-5, diisobutyl ketone, hexyl formate, 2-octanone, 4-methyl-2-pentanone, diethyl malonate, 2-undecanone, 2,4-pentanedione, propiophenone, 4-methyl pentyl acetate, ethyl n-valerate, amyl propionate, propyl caproate, ethylene glycol diacetate, triacetin and isophorone. Three entrainers were used by Chien [11] and isobutyl acetate was found the best one for energy cost reduction. Therefore, in this work, vinyl acetate (VA), isobutyl acetate (IBA), methyl acetate (MA), ethyl acetate (EA) and methyl tert-butyl ether (MTBE) were selected to participate in the heterogeneous azeotropic distillation via ChemCAD simulation.

The solvent (extractive agent) is the core of extractive distillation. It is well-known that the selection of a suitable solvent plays an important role in the economical design of extractive distillation. The extractive agents should boil at temperature higher than those of the liquids being separated without forming azeotropes with them. Adiponitrile and sulfolane, acetophenone, heptanoic acid, nitrobenzene, octanoic acid, ethylene glycol diacetate, dimethyl acetamide, etc. typical examples [3, 4] of effective agents for dehydration of acetic acid by extractive distillation. In terms of selectivity, recoverability, density, chemical reactivity, viscosity, vapor pressure and freezing point, toxicity, cost, and so on, adiponitrile and sulfolane are selected as extractive solvents to run the simulation and to analyze the effect of different extractive solvents on the extractive distillation process.

Several low boiling extractive agents are used to separate HAc/W mixture system by liquid/liquid (L/L) extraction. Characteristics like solubility in water, extraction capacity, distribution coefficients, azeotrope compositions, price, availability and requirements in terms of environmental and health protection must be taken into account for the purpose of this selection.

Table 1. Extraction agents for the separation of acetic acid from water.

Name	Average distribution coefficient, kg kg^{-1}	Density, kg m^{-3}	Enthalpy of vaporization, kJ kg^{-1}	Boiling Point, °C	Azeotrope	
					Water, mass %	T, °C
Methyl-tert.-butyl ether, MTBE	0.75	740	322	55	4	52.6
Ethyl acetate, EAC	0.84	900	395	76.7	8.47	70.4
Vinilacetat, VAC	0.78	934	379	72.5	7.3	66
Isopropilacetat, IPA	0.55	877	361	88.6	10.5	76.5
Isobutilacetat, IBA	0.65	871.2	309	116.5	16.5	87.4
n- propilacetat, PAC	0.5	891	336	101.6	13.2	82.2
Methylpropilketon, MPK	0.97	810	384	102.3	19.5	83.3

Table 1 shows a selection of extractive agents suitable for the recovery of acetic acid. The average distribution coefficients do not differ essentially from one another. As a result, all the extractive agents listed in the table must be equivalently considered with regard to the extraction. The energy consumption depends on the vaporization enthalpy of the azeotropic mixture, which is determined by the water content in the azeotrope. Thus, the energy consumption in case of EAC or MTBE use as extraction agents ought to be the lowest. If ethyl acetate is used, there is a considerable reciprocal solubility with water. The immiscibility gap is relatively small, so that the feed concentration of 30 mass % should not be exceeded for safe extraction work. On the other hand, the immiscibility gap in case of MTBE/HAc/W system is better pronounced, while the reciprocal solubility is lower. Feed mixtures with acetic-acid concentrations of up to 40 mass % can, therefore, be reprocessed using MTBE extractive agent.

According to literature [6] IBA dissolves completely acetic acid in the liquid phase and hence the extraction process is possible. Subsequent separation of the IBA and the acetic acid is very difficult. Usually, the separation is carried out in a rectification column. In this case it is practically impossible, since IBA and acetic acid have very close boiling temperatures. VAC is an extractive agent suitable for the recovery of acetic acid because it dissolves acetic acid and the subsequent separation is easy by conventional distillation. Kürüm [12] evaluated 34 types of possible entrainers for acetic acid dehydration with extraction followed by azeotropic distillation and concluded that EA, diisopropyl ether and MTBE are the most promising entrainers. Therefore VAC, EAC and MTBE have been selected as solvents in the hybrid extraction/distillation process.

Fluid phase equilibrium

Simulation of the phase equilibria data referring to HAc/W mixture (vapor-liquid-VL and vapor-liquid-liquid-VLL equilibrium) was carried out in order to investigate accurately the separation required by heterogeneous azeotropic distillation, extractive distillation and hybrid extraction/distillation process. It was done on the ground of thermodynamic model (NRTL) using MatLAB software. The liquid-liquid equilibrium (LLE) of the ternary system elucidated. It reproduced correctly the immiscibility gap and the tie-lines slopes. The second virial coefficient model (equation of state)

Table 2. Comparison between predicted data by NRTL before the optimization with experiments.

Components	Experimental data		NRTL model	
	Azeotropic composition, mass %	Temperature, °C	Azeotropic composition, mass %	Temperature, °C
H_2O-VAC	(9.0,91.0)	66.7	(11.1,88.9)	62.0
H_2O-EA	(8.47,91.53)	70.4	(12.1,87.9)	70.81
H_2O-IBA	(19.53,80.47)	87.5	(23.0,77.0)	81.33
H_2O-MA	(3.36,96.64)	56.3	(3.0,97.0)	56.19
H_2O-MTBE	(4.0,96.0)	52.6	(4.8,95.2)	50.89

Table 3. NRTL parameters after the optimization.

System HAC-W-MTBE			
Component$i$	HAC	HAC	W
Component$j$	W	MTBE	MTBE
a_{ij}	0	0	0
a_{ji}	0	0	0
b_{ij}	-307.16	-47.36	1307.33
b_{ji}	597.97	-113.15	707.56
α_{ij}	0.3	0.3	0.3
System HAC-W-EA			
Component$i$	HAC	HAC	W
Component$j$	W	EA	EA
a_{ij}	-1.9763	0	9.4632
a_{ji}	3.3293	0	-3.7198
b_{ij}	609.8886	-235.279	-1705.68
b_{ji}	-723.8881	515.8212	1286.123
α_{ij}	0.3	0.3	0.2
System HAC-W-IBA			
Component$i$	HAC	HAC	W
Component$j$	W	IBA	IBA
a_{ij}	0	0	0
a_{ji}	0	0	0
b_{ij}	-211.31	90.268	756.356
b_{ji}	652.995	194.416	389.609
α_{ij}	0.3	0.3	0.2
System HAC-W-MA			
Component$i$	HAC	HAC	W
Component$j$	W	MA	MA
a_{ij}	0	0	0
a_{ji}	0	0	0
b_{ij}	-211.31	-239.246	860.256
b_{ji}	652.995	415.27	442.401
α_{ij}	0.3	0.3	0.383
System HAC-W-VAC			
Component$i$	HAC	HAC	W
Component$j$	W	VAC	VAC
a_{ij}	-1.9763	0	0
a_{ji}	3.3293	0	0
b_{ij}	609.8886	38.385	1064.6
b_{ji}	-723.8881	189.2358	215.7
α_{ij}	0.3	0.3	0.2

of Hayden-O'Connell was used [13] to take into account the dimerization of HAC in the vapor phase. The model was implanted into ChemCAD program with the application of MatLab software.

The NRTL parameters for water and MA were obtained from ChemCad data bank. The data predicted by NRTL using these parameters and experimental results of Gmehling[14] were very close to each other. The set of NRTL parameters for HAc/W/IBA reported from Chien[11] and the other NRTL parameters obtained from Wang[15] and Gau[16] did not give satisfactory results in comparison with experimental one [15] (see Table 2).

Thus, a procedure for these parameters optimization was developed on the ground of MatLAB software. The set of NRTL parameters obtained described very well the VL binary system and the LL ternary system. These NRTL parameters are listed in Table 3.

Table 4 illustrates the comparison between the experimental values of the azeotropic compositions and the temperatures of the systems [15] and the data predicted by the NRTL model. Small differences between these two sets of data were found.

SIMULATION METODS AND DISCUSSION

In other to simulate the extraction columns, the module liquid/liquid extraction (EXTR) in ChemCAD 6.3.1 software was used. This module calculates the heat and material balance of a stagewise contact of two immiscible liquid mixtures. EXTR permits up to five feeds and six products. This unit allows up to 300 stages and accommodates stage efficiencies. The EXTR module uses the Newton-Raphson simultaneous convergence technique for its solution.

In other to simulate the distillation (azeotropic, extractive and ordinary) columns the SCDS module in ChemCAD 6.3.1 software was used. SCDS is a rigorous multi-stage vapor-liquid equilibrium module which simulates any single column calculation including distillation columns, absorbers, reboiled absorbers and strippers. Side products and side heaters/coolers can also be modeled rigorously by SCDS. Murphree's tray efficiency can be input and simulated by SCDS. This module handles columns with unlimited stages, five feed streams, and four side products. The rigorous simulation of the multiphase (two-phase or three-phase) distillation systems can be performed. If the calculation concerns a three-phase system, the user has the option to decant one of the liquid phases in the condenser, while refluxing the other. SCDS is mainly designed to simulate non-ideal K-value chemical systems. It uses a Newton-Raphson convergence method and calculates rigorously the derivatives of each equation.

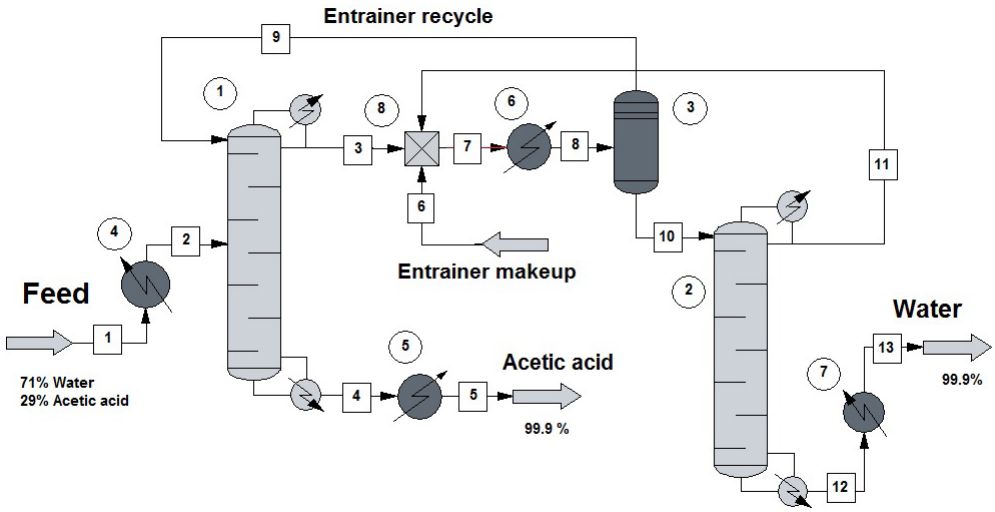

Fig. 1. Heterogeneous azeotropic distillation.

Heterogeneous Azeotropic Distillation

Fig. 1 shows the flowsheet of HAc/W dehydration system by azeotropic distillation.

The dehydration column 1 is a heterogeneous azeotropic distillation column (HADC) which can be designed to obtain high-purity acetic acid at the bottom (stream 4) while releasing minimum-boiling entrainer-water azeotrope as distillate at the top of the column (stream 3). Since the entrainer-water azeotrope is heterogeneous, it can be sent to a decanter (3) to form two liquid phases. The organic phase (light phase) will be refluxed back to the azeotropic column via entrainer recycle stream 9 in order to provide enough entrainer inside the column. The aqueous phase (stream 10) containing water mostly will be sent into a stripping column (SC) 2 to reduce further the entrainer residue in water, thus forming the by-product at the bottom (stream 12). The distillate of the stripping column (stream 11) is the entrainer-water azeotrope which can be recycled back into the decanter via mixture 9.

Two operating modes of HADC were investigated. In the first case, HADC worked as a stripping column, *i.e.* without reflux and the entainer was fed to the first tray. This option was the most economically advantageous because no cooling water was required in the condenser. This saved the utility cost in cooling step. Numerical optimization was carried out in this case to determine the optimum entrainer's amount and the main feed tray location. Fig. 2 illustrates the influence of the IBA mass flow on the bottom acetic acid stream.

Furthermore, Fig. 2 shows the loss of acetic acid related to the amount of IBA. The increase of the separating agent amount resulted in a linear increase of the amount of extracted pure acetic acid. There was no convergence in the calculation algorithm in case the entrainer flow increased over 300000 kg h^{-1}. The second type of optimization was related to the main mixture feed tray location. The numerical experiments showed that the decrease of the feed tray separation increased the HAc output. Fig. 3 shows the results of this optimization using IBA.

The decrease of the number of the main feed trays increased the HAc mass flow. There were no convergent calculations in case the number of the feed trays was reduced to less than 5. Thus, if the HADC worked as a stripping column, the loss of acetic acid was significant.

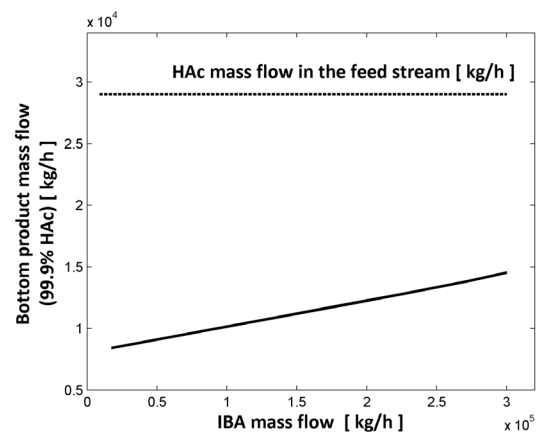

Fig. 2. Influence of the IBA mass flow on the bottoms acetic acid stream.

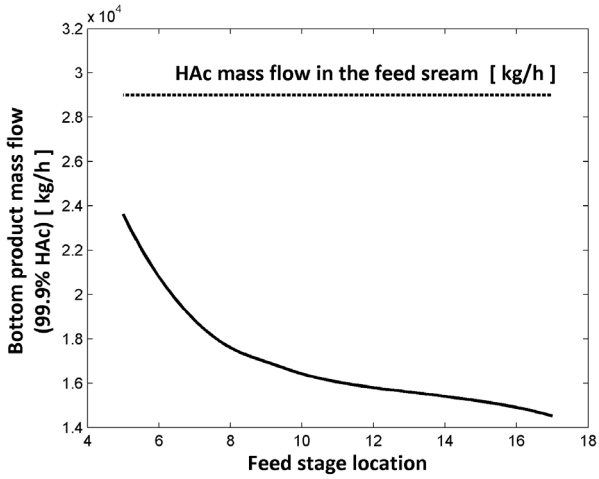

Fig. 3. Influence main feed tray location on the bottom HADC flow (acetic acid).

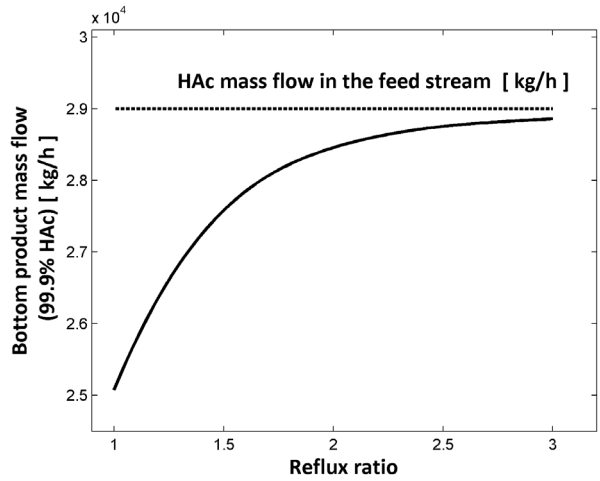

Fig. 4. Bottom product mass flows depending on the reflux ratio.

So a reflux flow (working mode 2 of HADC) was added. An optimization aiming to determine the optimal reflux ratio in terms of loss of HAc at the top of the column was performed. The results are presented in Fig. 4. It shows that the optimum reflux ratio is equal to 3, i.e. substantially all of the acetic acid in the feed stream is extracted. An additional optimization procedure for determining the central feed tray location and the entrainer feed tray location was then performed. The results show that the change in the number of central feed trays affects negatively the separation. By changing the entrainer feed tray location similar results were obtained, but the concentration and temperature profiles of the column were unstable and there is low tolerance calculation. Using IBA, the central feed tray number was found equal to 17, while the tray number for the entainer feed stream was found equal to 2. Analogous optimization procedures were performed with the other 4 separating agent. Table 5 shows the final results for acetic acid dehydration by azeotropic distillation using five separating agents. It is evident that IBA and MTBE are the most suitable entrainers for acetic acid dehydration by azeotropic distillation. A small loss of HAc (i.e. the produce of HAcis greatest) was obtained using these two entrainers. The total energy consumption of IBA was much lower than that in MTBE case. Therefore, using IBA as an industrial entrainer is more favorable than MTBE. From the entrainer loss viewpoint, MTBE is more favorable than IBA. The comparison of MTBE and IBA shows it is better to choose the entrainer that forms an azeotrope of higher water content (see Table 4). This means that the entrainer is more able to carry water to the top of the column. Hence, IBA is found a better entrainer when compared to MTBE. The results of the numerical experiments using both IBA and MTBE are almost similar. IBA is more suitable according to this study as well.

Table 4. Comparison between data predicted by NRTL model after the optimization with experiments.

Components	Experimental data		NRTL model	
	Azeotropic composition, mass %	Temperature, °C	Azeotropic composition, mass %	Temperature, °C
H_2O-VAC	(9.0,91.0)	66.7	(9.2,90.8)	66.58
H_2O-EA	(8.47,91.53)	70.4	(12.1,87.9)	70.81
H_2O-IBA	(19.53,80.47)	87.5	(19.5,80.5)	87.58
H_2O-MA	(3.36,96.64)	56.3	(3.0,97.0)	56.19
H_2O-MTBE	(4.0,96.0)	52.6	(3.6,96.4)	52.59

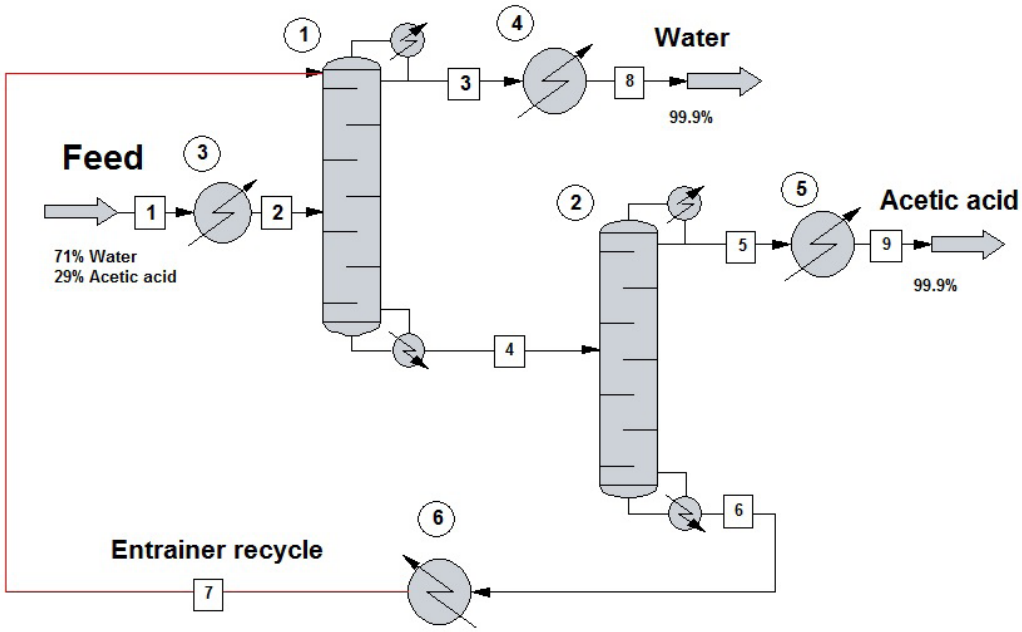

Fig. 5. Extractive distillation flowsheet.

Extractive distillation

Fig. 5 shows the flowsheet for HAc/W system dehydration by extractive distillation.

The extractive distillation column 1 (EDC) can be designed to obtain high-purity water as a distillate at the top of the column (stream 3) and HAc/solvent mixture at the bottom (stream 4). The interaction between HAc and the separating agent is mainly determined by physical forces resulting in Van der Waals and hydrogen bonding. Therefore the HAc/solvent mixture can be separated with the application of the conventional distillation column 2. The pure HAc is obtained as a distillate at the top of the column (stream 5). The solvent used forms the product at the bottom of column 2 (stream 6) and is refluxed back to the EDC.

Two modes of EDC were tested. In the first one, EDC operates as a stripping column, *i.e.* without reflux. Thus the solvent is fed to the first plate. In order to determine the optimal amount of the extractive agent, the numerical optimization was carried out. The results indicate that HAc is removed completely from the bottom product of column 1 in a wide range of the extractive agent content. But the increase in mass flow of the extractive agent promotes the separation of water in the distillate. Since the latter is a mixture of water and the extractive agent then the amount of the separating agent in the distillate represents an extractive agent loss. Therefore the distillate should concentrate all the water (99.99 %) in order to minimize the loss of separating agent.

Fig. 6 shows the separated amount of water in the distillate versus the mass flow of sulfolane. Practically, all of the water from the feed mixture is separated under

Table 5. Final results using different entrainers.

	IBA	EA	MA	VAC	MTBE
Total number of trays of the HADC	30	30	30	30	30
Total number of trays for the stripping column	10	6	6	6	6
Acetic acid 99.9 mass %, kg h^{-1}	28 954	28 808	28 923	28 896	28 946
Total heating [MW]	312.14	313.14	376.14	343.64	377.14
Total cooling [MW]	-312.41	-313.66	-375.93	-343.04	-377.76
Loss of acetic acid, kg h^{-1}	75.8	220.8	115.7	133.4	82.7
Loss of the entrainer, kg h^{-1}	3.3	19.9	27.5	40.7	1.1

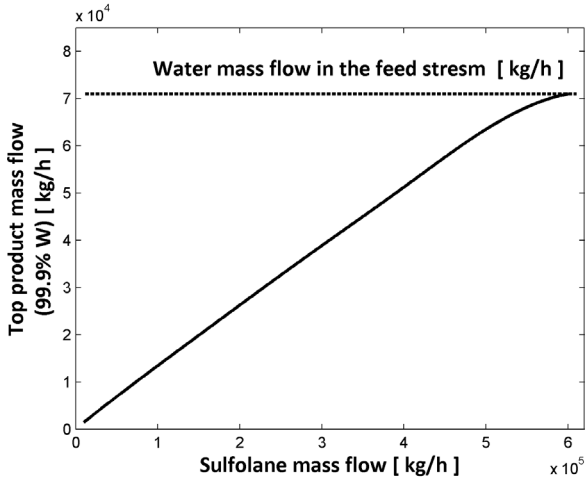

Fig. 6. Influence of the mass flow of sulfolane on the water mass flow in the distillate.

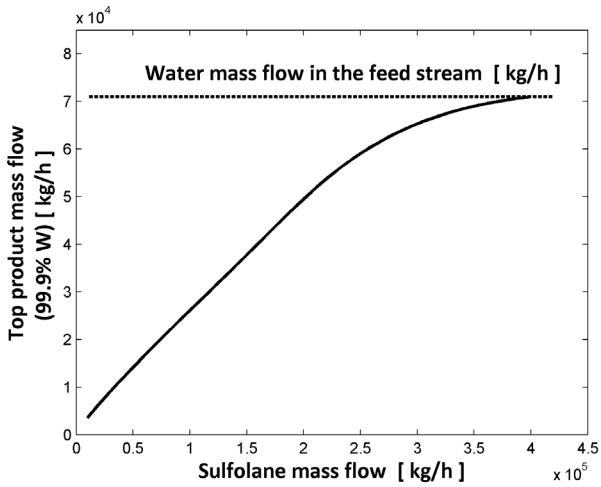

Fig. 7. Water removed in the distillate versus the mass flow of sulfolane at a reflux ratio 1.

sulfolane mass flow of 600000 kg h^{-1}, but the maximum reached purity of water is 98 %. This leads to large amounts of sulfolane lost in the distillate. To minimize them, the second mode of operation of the EDC is then investigated. This mode is associated with the addition of

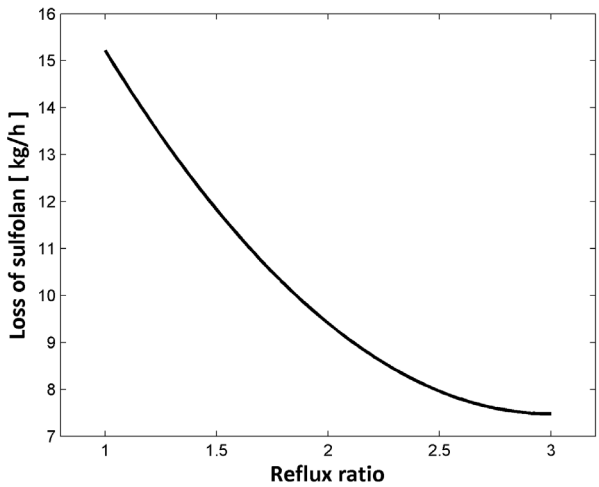

Fig. 8. Loss of sulfolane versus a reflux ratio.

a reflux at the top of the column. In this case, the solvent is fed to plate 3. Fig. 7 shows that under a reflux ratio of 1 and third feed plate for sulfolane, water is removed completely in case of a solvent flow at 400000 kg h^{-1}. Although the water purity is 99.9 %, the sulfolane loss is relatively high because its feed mass flow is very high.

Fig. 8 represents sulfolane loss depending on the reflux ratio. At a reflux ratio equal to 3 the minimum loss of sulfolane becomes 7.5 kg h^{-1}.

Any subsequent increase of the reflux ratio provokes deterioration in the separation of the feed mixture. As a final result, the optimal conditions for the extractive column using sulfolane correspond to a total number plate of 30, a number of the central feed plate of 17, a number of solvent feed plates of 3, solvent mass flow of 400 000 kgh^{-1} and a reflux ratio of 3. The same type of optimization procedures was performed when a second separating agent was used. Table 6 presents the final results referring to acetic acid dehydration by an extractive distillation using two solvents. It is evident that the required purity of the final product (99,99 % HAC) is

Table 6. Final results using different solvents.

	Sulfolane	Adiponitrile
Total number of trays of the HADC	30	30
Total number of trays for the stripping column	20	20
Acetic acid 99.9 mass%, kg h^{-1}	28956	28 955
Total heating [MW]	250.02	274.02
Total cooling [MW]	-250.32	-273.5
Loss of acetic acid, kg h^{-1}	45.2	45.04
Loss of the solvent, kg h^{-1}	7.48	0.86

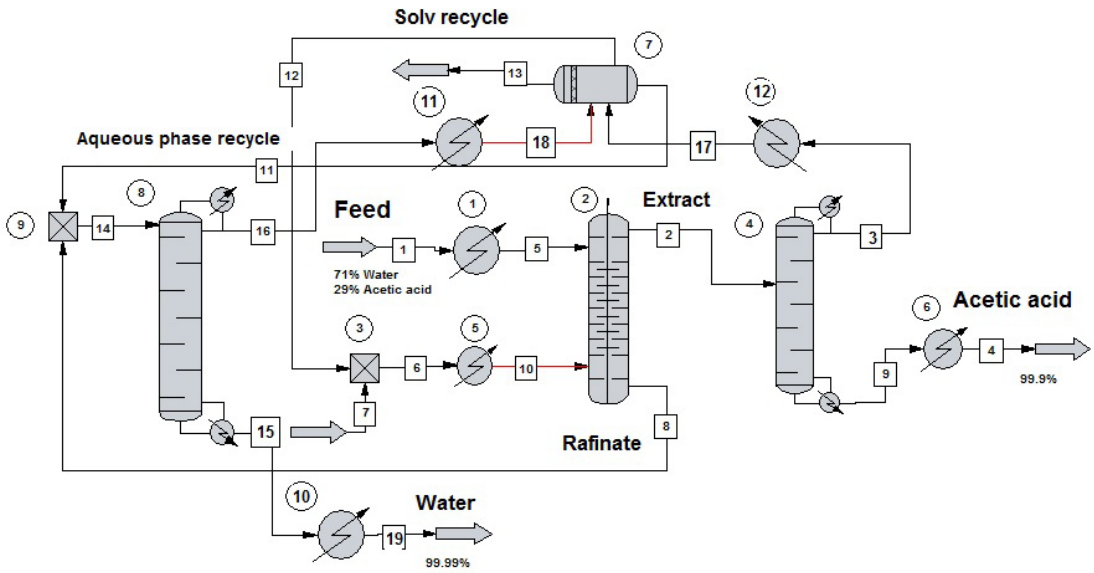

Fig. 9. Hybrid extraction/distillation process.

achieved. The results show in terms of thermal balance that the heat loss is about 10 % higher when adiponitrile is used. But as practically there is no solvent loss, addition of fresh adiponitrile is not required.

Hybrid extraction/distillation process

The hybrid extraction/distillation process (HEDP) envisages liquid/liquid extraction through an azeotropic distillation. Fig. 9 shows the flowsheet of the HEDP. Three extraction agents, VAC, EA and MTBE are selected to perform the process. The raffinate of extraction column 2 (stream 2) contains predominantly water and a small amount of HAc. In fact the water forms the by-product through a stripping column 8 (the so-called water column). There high-purity water is obtained as a bottom product (stream 15). The extract contains predominantly HAc and a solvent (stream 2), which is directed to an azeotropic dehydration column 4 to obtain high-purity HAc as a bottom product (stream 9). The two distillates of azeotropic column 4 (stream 3) and water column 8 (stream 16) are heterogeneous forming two phases in decanter 7. The organic phase contains mostly the solvent (stream 12). It is recycled to use the solvent used repeatedly in the extraction column. The composition of the aqueous phase (stream 11) is almost the same as that of the raffinate, and which is why it is mixed with it (by mixture 9) to feed the stripping column. The numerical experiments show that using EA as an extractive agent at 40°C and 20 trays in an extractor are optimal parameters for this process. Fig. 10 illustrates the optimization study described. Total acetic acid recovery from the feed mixture is achieved in case of 200 000 kg h^{-1} EA. Similar studies with the other separating agents are carried out to determine the

Table 7. Final results using different extractive agents.

	EA	VAC	MTBE
Total number of trays of the extraction column	20	20	8
Total number of trays of the dehydration column	20	20	20
Total number of trays for the stripping column	6	6	8
Acetic acid 99.9 mass %, kg h^{-1}	28 965	28 932	29 257*
Total heating [MW]	89.36	117.19	64.81
Total cooling [MW]	-89.35	-118.13	-64.41
Loss of acetic acid, kg h^{-1}	37.9	71	35.3
Loss of the extraction agent, kg h^{-1}	35	3	$3e^{-12}$

*acetic acid 99.00 mass %

parameters of the extractor. Table 7 shows the final results obtained in case of HAc dehydration by HEDP in presence of different extractive agents. It is evident that the three extractive agents are effective, *i.e.* they separate successfully HAc/W mixture. Using VAC, instead of EA and MTBE, results in HAc loss which is two times higher. The advantage of EA compared to MTBE refers to HAc purity which is 99.99 mass %, while MTBE leads to purity of 99.00 mass %. However, the total energy consumption of MTBE is 30 % lower than that of EA. The separating agent's loss is when VAC is used, while in the case of MTBE there is nearly no loss. Thus, VAC is recommended when high HAc purity (99.99 mass %) is required. The use of MTBE is energetically more favorable without extractive agent loss. This makes it a more advantageous industrial extractive agent when HAc purity of up to 99.0 mass % is required.

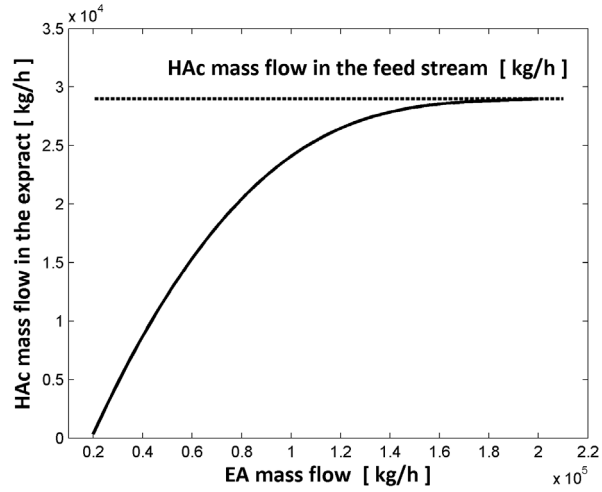

Fig. 10. Influence of the mass flow of EA over the HAc extraction.

Comparison of the Three Separation Methods

Several separating agents were used in the three separation methods. Table 8 summarizes the total optimal results concerning HAc dehydration. It is seen that the HAc/W system is successfully separated by using the methods studied as the final products obtained are high purity. In terms of the HAc loss, the best results are obtained by using HEDP. The latter is followed in the line by the extractive distillation. The separating agent loss is small and observed only in case of azeotropic distillation. From energetic viewpoint, HEDP is the most advantageous method. In terms of equipment costs and process conducting stability, the extractive distillation shows the best performance. In this case, there are only two columns and four heat exchangers, while the other methods require a decanter and more heat exchangers. It is evident that the azeotropic distillation is the least advantageous dehydration method. Similar results are obtained in case of HEDP and extractive distillation application. But HEDP is energetically more favorable, while the extractive distillation requires less equipment and control operations costs. Therefore, HEDP appears to be the most advantageous dehydration method.

CONCLUSIONS

Azeotropic distillation, extractive distillation and hybrid extraction/distillation process were investigated to separate HAc/W mixtures. Rigorous process simulation was performed to find the optimum design and operating conditions. An optimization of NRTL param-

Table 8. Final results for the three methods of HAc dehydration.

Separation method	Azeotropic distillation	Extractive distillation	Hybrid extraction/distillation process
Separating agent	IBA	Adiponitrile	MTBE
Total number of trays of the extraction column	-	-	8
Total number of trays of the dehydration column	30	30	20
Total number of trays for the stripping column	10	20	8
Acetic acid 99.9 mass %, kg h^{-1}	28 954	28955	29 257
Total heating [MW]	312.14	274.02	64.81
Total cooling [MW]	-312.41	-273.5	-64.41
Loss of acetic acid, kg h^{-1}	75.8	45	35.3
Loss of the extraction agent, kg h^{-1}	3.3	0.86	3e-12

eters for each of the acetic acid/water/separating agent systems was carried out. All methods studied can avoid the tangent point by using a separating agent. Thus the energy requirements were reduced.

Five entrainers (IBA, EA, MA, VAC, MTBE) were investigated in case of HAc/W mixture separation by an azeotropic distillation. The simulation results showed that isobutyl acetate is most suitable entrainer. In case of IBA application the total number of plates in case of HADC was 30, acetic acid of 99.9 mass % - purity was obtained, the total energy of 624.55 MW was required, the acetic acid loss was of 78.8 kg h^{-1}, while that of the solvent was 3.3 kg h^{-1}.

The dehydration of HAc/W by extractive distillation was carried out using two extractive agents (sulfolane and adiponitrile). The results showed that adiponitrile was the most advantageous extractive agent. The optimal conditions in this case referred to total number of plates of 30, acetic acid of 99.9 mass % - purity, total energy requirement of 574.52 MW, solvent mass flow of 400 000 kg h^{-1}, acetic acid loss of 45.04 kg h^{-1} and solvent loss of 0.86 kg h^{-1}. The technological flowsheet of HAc dehydration by HEDP using three separating agents (EA, VAC, MTBE) was simulated. The best results were obtained in case of MTBE. The total number of plates of the extraction column was 20, acetic acid of 99.9 mass % - purity was obtained, the total energy requirement was 29.22 MW, the acetic acid loss was 35 kg h^{-1}, while that of the solvent was $3e^{-12}$ kg h^{-1}.

The comparative consideration of the three methods studied shows that the azeotropic distillationis is the least advantageous method. The other two methods give similar results but HEDP is energetically more favorable, while the extractive distillation requires less equipment and control operations costs. Consequently, HEDP appears to be the best acetic acid dehydration method.

Furthermore, the methodology applied can be further adapted for various LL systems associated with azeotropic complex formation, whose separation by conventional methods is not satisfactory from an economic point of view.

Acknowledgements

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