

Heterogeneous Distillation of the System Water-Acetic Acid-p-Xylene: Study of its Fluid Phase Equilibria, Micro-Pilot Column Experimental Results and Computer Simulation

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The separation of the binary mixture water-acetic acid by direct distillation is not suitable for industrial applications because of the presence of a tangent pinch on the pure water end. The problem is overcome via heterogeneous azeotropic distillation adding a third component, the entrainer, generally immiscible with water. With particular reference to terephthalic acid production process, we selected p-xylene being both a good entrainer and the principal raw material for the terephthalic acid production.

The phase equilibria (vapor-liquid and vapor-liquid-liquid) of the ternary system water/acetic acid/p-xylene were analysed in order to choose a right thermodynamic model suitable for the simulation of this system. The simulations obtained by SIMSCI PRO II software adopting the Lyngby modified UNIFAC equation to calculate the activity coefficients and the Hayden-O'Connell correlation to take into account the acetic acid association gave very satisfactory results. As further check, some experimental data were produced by a continuous micro-pilot distillation column, 5 m height with 15 trays. These data, successfully simulated, showed the possibility to use p-xylene as entrainer. A new system based on two operative column for this separation is then proposed. The first column, without entrainer, is used to bring the composition of the distillate near the tangent pinch, while the second one is used to complete the separation.

1. Introduction

The water/acetic acid separation is an important operation in different industries, as cellulose acetate production or in the terephthalic and isophthalic acids synthesis processes. Even if acetic acid (AcAc) and water (W) system does not form azeotrope at atmospheric pressure, it shows a tangent pinch on the pure water end making very expensive their separation by direct distillation. The addition of an entrainer generally immiscible with water permits to separate the W/AcAc mixture by heterogeneous azeotropic distillation, as already reported in literature (Wilgado 1996): water is brought by the third component to the head of the column while acetic acid leaves the column from the bottom mixed with the entrainer from which must be separated before to be re-used. Several kind of entrainers were proposed, for example ethyl acetate, n-butyl acetate, vinyl acetate or iso-butyl acetate. These entrainers are all suitable for recovering acetic acid from water but are potential contaminants when acetic acid has to be recycled in the main production process. The use of p-xylene (p-xyl) as entrainer is here proposed with the particular reference to the industrial terephthalic acid production, being this chemical already present in the process as main reactant. p-Xylene can work as water's entrainer and can be directly recyclable with acetic acid to the main process without any further purification because it is the principal raw material of the terephthalic acid production. This solution has been already proposed in a recent paper (Wang and Huang, 2012), where particular attention is devoted to the control strategy of the distillation plant, while in the present paper is also reported a detailed study of the phase equilibria involved in connection with the separation results.

In order to accurately investigate the separation of water/ acetic acid mixture by heterogeneous azeotropic distillation using p-xylene, our main purpose was the right simulation of the phase equilibria data of this

system (vapor-liquid and vapor-liquid-liquid equilibria) by a selection of a predicting thermodynamic model (UNIFAC) using PRO II software by Simulation Science. Some experimental data were produced by a continuous micro-pilot distillation column, 5 m height with 15 trays (Carvoli, 1987) in order to verify both the separation and their right simulation. Finally, on the base of this verified simulation, a new system based on two operative columns for this separation is then proposed. The first column, without entrainer, is used to bring the composition of the distillate near the tangent pinch, while the second one is used to complete the separation. The whole system is discussed.

All the compositions are expressed in term of liquid molar fraction x_i or vapor molar fraction y_i , being $i = W, AcAc$ or $p\text{-xyl}$. If the compositions are referred to a particular stream ($F =$ feed of the mixture $W/AcAc$, $dist =$ distillate, $res =$ residue), these labels are inserted.

2. $W/AcAc/p\text{-xyl}$ system study

The vapor pressures of water, acetic acid and p-xylene were calculated using the equation and the parameters of the PRO II database. The normal boiling temperatures that characterize the $W/AcAc/p\text{-xyl}$ system are those of the pure components (i.e. 100, 118 and 138 °C for water, acetic acid and p-xylene respectively) and those of two azeotropic binary mixtures. In Table 1 the normal boiling temperatures and the composition that characterize these azeotropic mixtures are reported, both experimental from literature (Horsely, 1962) and calculated using the thermodynamic model discussed hereinafter.

The fluid phase equilibria data available in literature concerning water, acetic acid and p-xylene have been carefully considered in order to select a suitable thermodynamic model able to reproduce the system. The calculation of the activity coefficients by predictive models and of the fugacity of the different components has been in this way taken into account. The binary vapor-liquid equilibria (VLE) water/acetic acid (Ito and Yoshida, 1963) and acetic acid/p-xylene (Marek, 1955) were simulated using temperature dependent Lingby modified UNIFAC (Fredenslund, 1987), modified UNIFAC in the following, for the activity coefficients calculations. In Figures 1a and 1b the comparisons between experimental and calculated data of the two systems are shown (dotted lines). A better reproducibility of the data is obtained adopting the Hayden-O'Connell (HOC) (Hayden 1975) second virial coefficient model for taking into account the acetic acid association in vapor phase (continuous lines in Figure 1a and 1b). Liquid-liquid equilibrium (LLE) experimental data at the boiling temperatures of the ternary system were published (Murugova, 1971). The comparisons between experimental and calculated data using both standard UNIFAC (Fredeslund, 1975) and modified UNIFAC (Fredeslund 1987) were calculated and this last model well reproduces the immiscibility gap and the tie-lines slopes, on the contrary of standard UNIFAC. The comparison between predicted data (using modified UNIFAC and HOC correlation) and experimental (Murugova, 1971) data for vapor-liquid-liquid equilibria of the system has been performed too, confirming the satisfactory overlapping of the different values. On the basis on this study the thermodynamic model modified UNIFAC with HOC correlation was chosen as a sound foundation of our work. Moreover, as explained in the next paragraph, it was decided to perform an experimental test on a micropilot distillation column to further verify this preliminary conclusion.

Table 1: Normal boiling temperatures and azeotropic composition of the mixtures $AcAc/p\text{-xyl}$ and $W/p\text{-xyl}$

System	Experimental		Calculated	
	T(°C)	$x_{p\text{-xyl}}$	T(°C)	$x_{p\text{-xyl}}$
$AcAc/p\text{-xyl}$	115.25	0.18	114.2	0.223
$W/p\text{-xyl}$	92.7	0.24	92.3	---

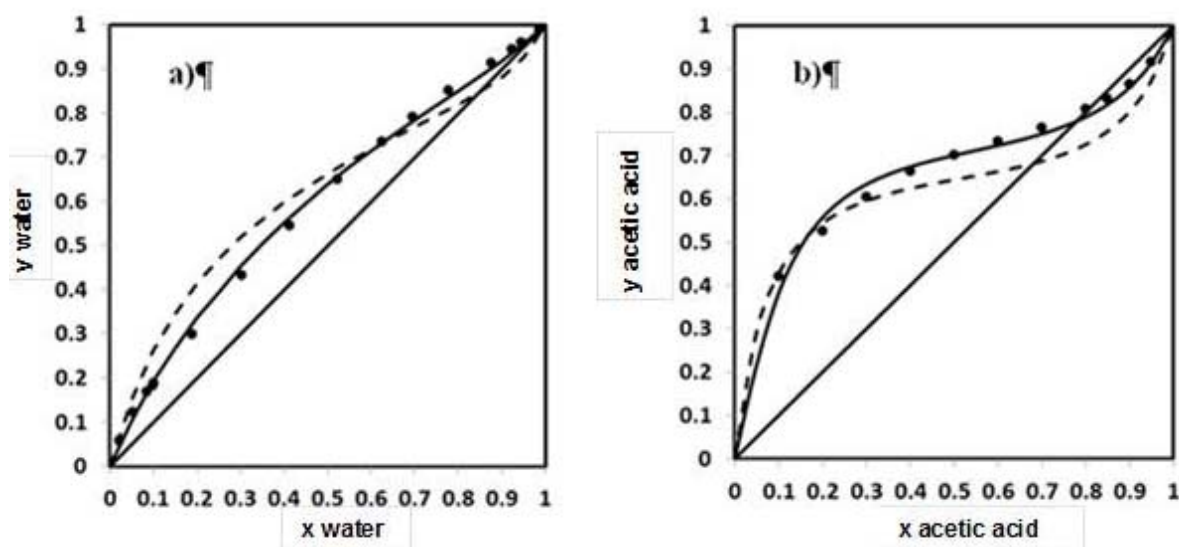


Figure 1: VLE calculation of a) W/AcAc and b) AcAc/p-xyl using modified UNIFAC, using HOC correlation (solid line) or not (dotted line). Black points represent the experimental data.

3. Experimental micro-pilot distillation column

A distillation run was performed in a pyrex micropilot column plant (Normschliff, control unit Mod. DEST-STAR IV). The height of this column is 5 m for a total of 15 trays; it is thermally insulated by a vacuum gap and through a silver shield. The internal diameter of the column is 5 cm. The reboiler at the bottom has a capacity of 2 L. The resulting thermal loss was about 850 kJ h^{-1} being approximately the 30 % of the total exchanged heat. The mixture W/AcAc was fed at the tray number 5 from the bottom while the entrainer (p-xylene) at the top tray of the column. Water content in the samples was determined by Karl-Fisher titration; low acetic acid content ($< 2 \text{ \%}_{\text{wt}}$) was determined by titration using KOH 0.1 M and phenolphthalein as indicator. The AcAc and p-xyl concentration of all the samples was determined by gas-chromatography. The simulations of this column were carried out using PROII Version 8.3 by Simulation Science (SimSci). The computer program add-on ternary_VLE of PRO II was used for generating equilibria phase diagrams and distillation curves to compare with the experimental data. The computer program used for the micro-pilot simulations was based on the CHEMDIST algorithm of PRO II. The total trays efficiency of the column was estimated equal to 0.55, in agreement with that previously verified by the same authors (Carvoli 1987) using the same distillation column with another vapor-liquid-liquid equilibrium system (benzene, cyclohexane, sulpholane and water).

The operative parameters and the experimental and simulated results of this run are reported in Table 2.

Table 2: Experimental/simulated results of the micro-column distillation run; molar reflux ratio=1.0, feed flow= 1.75 L h^{-1} at $68 \text{ }^{\circ}\text{C}$; p-xyl flow= 3.67 L h^{-1} at $20 \text{ }^{\circ}\text{C}$; distillate flow= 0.81 L h^{-1} ; residue flow= 4.61 L h^{-1}

	Feed			Distillate			Residue			$T_{\text{dist}} \text{ (}^{\circ}\text{C)}$	$T_{\text{res}} \text{ (}^{\circ}\text{C)}$
	X_{W}	X_{AcAc}	$X_{\text{p-xyl}}$	X_{W}	X_{AcAc}	$X_{\text{p-xyl}}$	X_{W}	X_{AcAc}	$X_{\text{p-xyl}}$		
Experimental	0.32	0.68	0	0.704	0.055	0.241	0.008	0.498	0.494	93	116
Simulated	0.32	0.68	0	0.693	0.074	0.233	0.03	0.495	0.475	92	115

The results obtained show the actual efficiency of the p-xylene as entrainer, in particular the quantity of water obtained in the residue stream is satisfactory (0.8 %). The amount of acetic acid in the distillate (5.5 %) can be further lowered by changing the various operating parameters (reflux ratio in particular). The simulation of this run gave a good reproducibility of all the experimental compositions, confirming our right thermodynamic approach.

After this experimental verification of the effectiveness of p-xylene as entrainer and the correctness of the simulation of this system, an optimized industrial solution for the separation of the mixture water-acetic acid will be proposed in the next paragraph.

4. Process optimization

As shown in Figure 1-a, the vapor-liquid equilibrium diagram for the system water-acetic acid can be divided into two main zones. The first part of the diagram in fact, for concentrations of water until about 70%, allow a convenient separation by direct distillation of the mixture. For higher water concentration the presence of a tangent pinch on the pure water end makes essential the use of an entrainer. Starting from these considerations, it is proposed an optimization of the entire process thanks to two distillation columns. The first column of direct distillation has the purpose of bringing the mixture W/AcAc in the distillate stream, from various possible feeding compositions, near to the pinch point of the diagram while in the residue a stream of pure AcAc can be obtained. The distillate of the first column is sent in the second column, where by an extractive distillation with p-xyl it is possible to obtain AcAc/p-xyl in the bottom and W/p-xyl at the top of the column. p-Xyl is then easily separated and recycled at the top of the column; the outgoing flows of acetic acid from the bottom of the first and second column are then merged and sent back to the manufacturing process of terephthalic acid. The scheme of this process is reported in Figure 2.

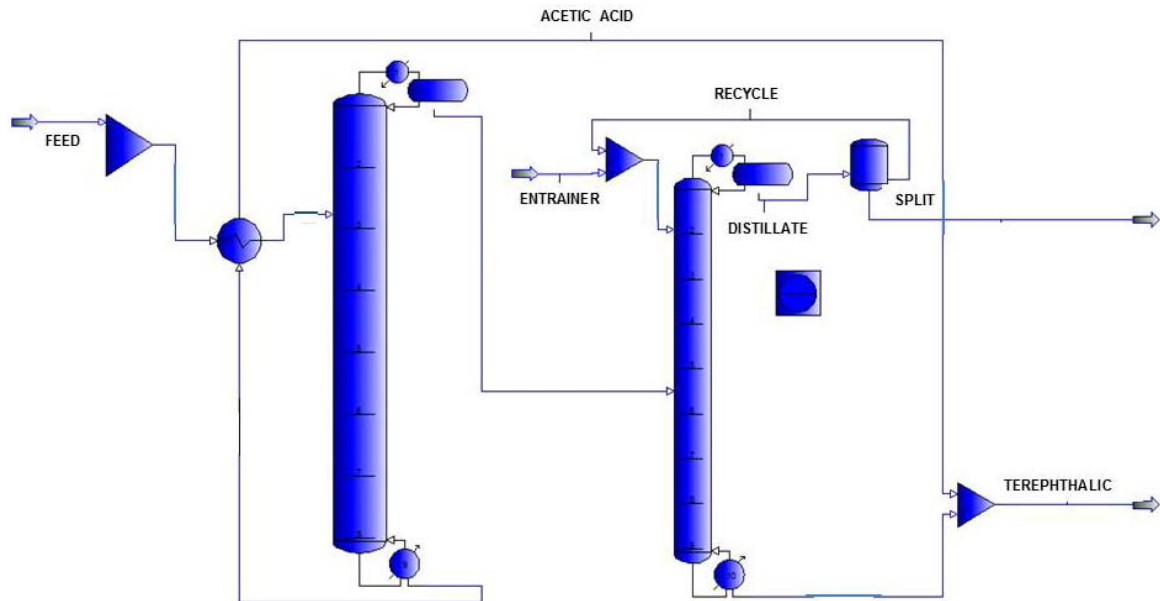


Figure 2: General process layout for the W/AcAc mixture separation in the production plant of terephthalic acid

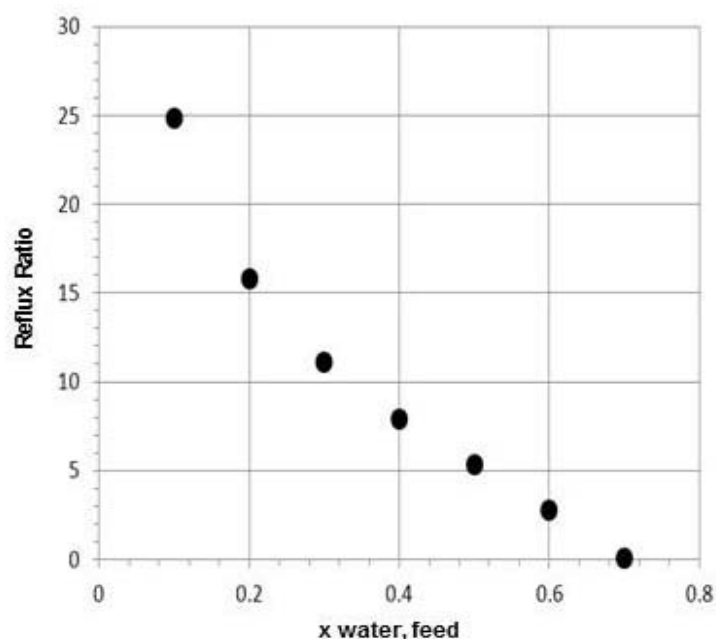


Figure 3: First direct distillation column: reflux ratio required to obtain $x_W=0.74$ in the distillate stream vs. feed composition

The first distillation column is used to obtain a direct separation without the use of p-xyl, with the aim of approaching in the distillate flow the composition of the W/AcAc pinch point. It was investigated an 8 stages distillation column, fed with a stream of $26.62 \text{ kmol h}^{-1}$ (equivalent to 1000 L h^{-1}) having 7 different compositions, characterized by a molar fraction of water from 0.1 to 0.7. All the mixtures were fed to the boiling point and the specifications of simulation were set regarding the compositions of the distillate and residue: in particular it was set a composition of water in the distillate equal to 0.74 and equal to 0.02 in the residue. The parameter obtained is the reflux ratio required to achieve such separation. The following figure shows the results:

The results obtained demonstrate how it is possible with a column of 8 ideal stages to reach the composition specifications desired. The smaller the amount of water in the feed is, the greater the reflux ratio must be.

Following the process layout reported in figure 2, a feed has been hypothesized equal to $26.62 \text{ kmol h}^{-1}$ with a concentration of water and acetic acid equimolar. The molar reflux ration used for the first direct distillation column and the second extractive one were 5.7 and 8 respectively. The value of 5.7 was selected on the basis of the study reported in figure 3 while the value of 8 was selected in order to obtain a satisfactory separation in the extractive column using a not so high number of trays (8). In Table 3 the main streams flows and compositions are reported.

Table 3: Simulated results of the two columns separation plant; feed flow= $26.62 \text{ kmol h}^{-1}$ at $65 \text{ }^\circ\text{C}$ ($x_W=0.5$, $x_{AcAc}=0.5$); p-xyl flow= 6.6 kmol h^{-1} at $52 \text{ }^\circ\text{C}$

Direct distillation column (T1)				Extractive distillation column (T2)			
dist (kmol h^{-1})	$x_{\text{dist, AcAc}}$	res (kmol h^{-1})	$x_{\text{res, W}}$	dist (kmol h^{-1})	$x_{\text{dist, AcAc}}$	res (kmol h^{-1})	$x_{\text{res, W}}$
17.7	0.26	8.9	0.02	17.73	0.029	6.58	0.025

The extractive column T2 is fed with a quantity of p-xyl corresponding to 26 % molar of the total (p-xyl plus mixture W/AcAc). This amount is sufficient to maintain the composition in the column of the two azeotropes W/p-xyl and AcAc/p-xyl and then to act as entrainer. The total flow of p-xyl in the column is obtained by a mixing of a small fresh stream (2.3 kmol h^{-1}) and a recycled one (4.31 kmol h^{-1} , $x_{p-xyl}=0.984$) coming from the top of the column. The second flow outcoming from the splitting (operating at $25 \text{ }^\circ\text{C}$) at

the top of the column is a flow of water with a low amount of AcAc ($x_{AcAc} = 0.034$). The residue of column T2 is monophasic with a composition $x_{W} = 0.025$. This flow is merged with the outgoing residue by column T1, obtaining a suitable composition ($x_{AcAc} = 0.83$, $x_{p-xy} = 0.148$) to be directly sent to the system production of terephthalic acid. Summarizing, in this two columns based separation plant, for $13.31 \text{ kmol h}^{-1}$ of acetic acid incoming, 0.458 are lost with the outward flow of water (< 3 %), while the rest is recovered successfully.

Conclusion

p-Xylene was proposed as entrainer for the extractive distillation of the mixture water/acetic acid. On the basis of the study of the vapor-liquid and vapor-liquid-liquid equilibrium data of this ternary system a right thermodynamic model has been selected. In this approach the modified UNIFAC model was used for the calculation of activity coefficients and HOC correlation was taken into account for the calculation of the components fugacity. An experimental run performed on a 15 trays column was successfully conducted and simulated.

Based on these first results, a two columns distillation plant was proposed and simulated. The data collected confirm the possibility to use p-xylene as entrainer obtaining the desired separation of the water/acetic acid mixture.

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