

## Simulation of the Water-Acetic Acid Separation via Distillation Using Different Entrainers: an Economic Comparison

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Diluted solutions of acetic acid (AA) in water (W) are a typical side stream in several production processes including terephthalic acid synthesis, acetyl cellulose manufacture and biochemical processes. Since AA is typically in the range of 10 to 40 % by weight in W, for most companies it is profitable to recover and recycle it as a solvent (Dylewski, 1980). Among the separation processes, distillation is the most adopted because of its flexibility and the relatively low cost compared to other technologies such as membrane separation or pervaporation. The challenge in the separation of W and AA through simple distillation is to find in the volatility of AA in the lower range of concentration, which tends to the unit (Ito and Yoshida, 1963). In other words, even if the mixture is never azeotropic, the equilibrium diagram exhibits a pinch point on the pure water end. An entrainer, either with lower or higher boiling point compared to the two main components, alters the volatilities of W and AA, modifying their activity coefficients and improving the separation. However, the introduction of a third component usually requires a second distillation unit to recover the entrainer (Wang and Huang, 2012).

Among the entrainers proposed in the literature, AA esters are common for their efficiency. For instance, Chien et al. (2004) report a bottom product composition with 99.9 % acetic acid for ethyl, iso-butyl and n-ethyl acetate for molar ratios AA/W of 1:1 with only one distillation step. In the context of the terephthalic acid production process, we recently demonstrated that the use of p-xylene is profitable because of its availability in-situ (Pirola et al., 2013).

We study the W-AA separation with different entrainers (e.g. p-xylene, ethyl acetate, propyl acetate and butyl acetate) and survey alternative configurations including a pre-reactor to synthesize the entrainer in-situ, and an intensified reactive distillation. We selected an algorithm based on the Guthrie equations to calculate the cost of both CAPEX and OPEX (Guthrie, 1969) with the simulation software PRO/II 9.3. The data confirm that propyl acetate is a practical and economical alternative to methyl acetate for the acetic acid recovery from water, and the p-xylene avoids introducing an extraneous component as an entrainer.

### 1. Introduction

Distillation is one of the most common unit operations. It is a separation method based on the different boiling point of the substances to split, in which a mixture of two or more components is brought to the boiling point through several stages of condensation/evaporation. There are, however, systems that deviates from ideality. Azeotropes are typical examples of this deviation, but also cases in which one of the components has a high decrease in volatility when the molar ratio of the other component approaches the unit. The latter situation occurs in the water/acetic acid (W/AA) system, in which, AA is not easily separated when it is highly diluted in water, i.e. on the pure water end the equilibrium diagram exhibits a pinch point (Huang et al., 2013). In such cases, an entrainer is typically used. It is a third substance added to the mixture which modifies the volatility of the two components forming the azeotrope. W/AA mixtures are a side stream of the terephthalic acid production process. The oxidation of p-xylene in AA as a solvent yields terephthalic acid, in the presence of a

variety of catalysts, such as cobalt and manganese salts or heavy metal bromides at 200°C and 28 bar (Speight, 2002). After the separation of terephthalic acid, which is further purified, the wastewater is a mixture of AA and W, with a AA concentration of ~35% by mass, which is almost an equimolar mixture. AA recovery is essential to contain the costs, in particular when it is used in large quantities as a solvent. In literature there are several examples of the distillation of the W/AA mixture with different entrainers, i.e. vinyl acetate (Luyben and Tyreus, 1998), ethyl acetate (Pham et al., 1990) or butyl acetate (Li, 2011), concerning either a dynamic or a economic optimization. In a previous paper (Pirola et al., 2014) we investigate the possibility to use p-xylene (PX) as an entrainer because of its availability in the terephthalic acid manufacturing process and its low solubility in water. Moreover, a robust optimization work was carried out (Corbetta et al., 2016) to find the best column configuration which minimizes the total annual cost (TAC). Scientific literature lacks of a direct comparison of the different column configurations, as well as the type of entrainer. The aim of the present work is to find the most economical solution among the several proposed in literature for the distillation of W/AA mixtures through process simulation with PRO/II 9.3 (static simulation software) and an economic comparison. The data of a single column without entrainer are the baseline for the comparison of different scenarios. We focus on four entrainers: PX, ethyl acetate (EA), propyl acetate (PA) butyl acetate (BA). We selected the most suitable thermodynamic system for each simulation and minimized the TAC in each scenario. for carrying out the calculation.

## 2. Experimental

### 2.1 Simulations

In the manuscript we adopt the following abbreviations: x for the liquid molar fraction, D for the distillate stream, B for the bottom stream exiting the column and WW for the wastewater stream, i.e. the water-rich liquid of the distillate. WW is sent to disposal, while the organic part, rich in entrainer, is recycled. For example  $x_{WW,AA}$  corresponds to the molar fraction of acetic acid (AA) in the wastewater (WW) stream. We used PRO/II 9.3 software for all the simulations. It is a static simulator of chemical processes in which we implemented a pseudo FORTRAN based code that calculates both the operative (OPEX) and the capital costs (CAPEX) of the unit operation under study. In particular, we compared four different systems in a single column configuration with different entrainers: i) p-xylene (PX) (SIM1); ii) methyl acetate (SIM2); iii) propyl acetate (SIM3) and iv) butyl acetate (SIM4). We used the UNIQUAC model for the calculation of the components activity in all the simulations, and the Hayden O-Connel (1975) correlation in SIM 2-4 to calculate the vapour fugacities of the components in order to account for the AA association. We didn't use the correlation in SIM1 because we regressed the parameters of UNIQUAC equation directly from experimental data using a robust model (Pirola et al. 2014). All the simulations were carried out looking at both minimizing the amount of W in the bottom stream (that will be recycled back to the reaction section), and the amount of AA in the distillate flow. The typical flowsheet is reported in Figure 1.

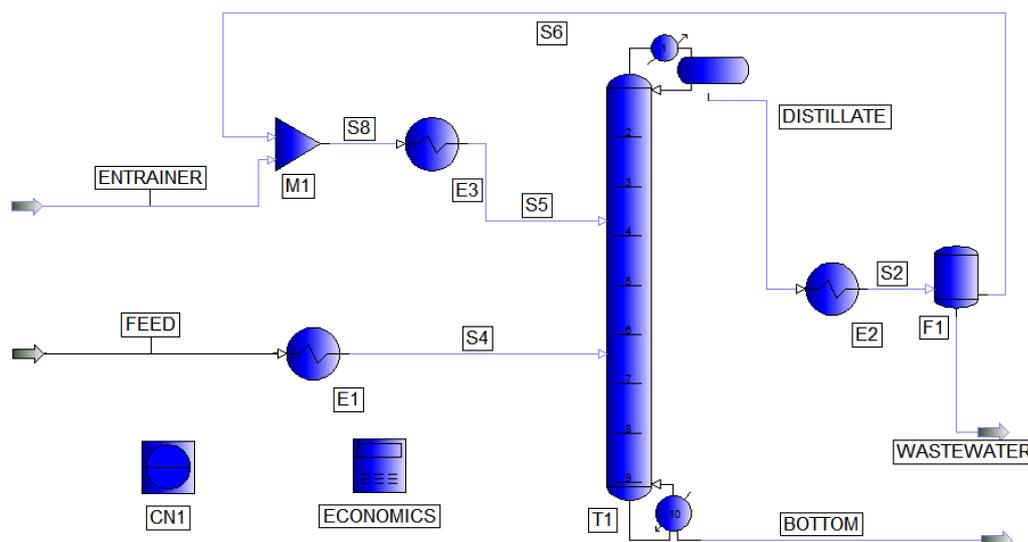


Figure 1: Scheme of the process used in PRO/II

The distillation column was optimized considering the concentration of AA at the bottom of the column ( $x_{B,AA} > 0.95$ ) and the concentration of W in the wastewater stream ( $x_{WW,W} > 0.98$ ) as simulation specifications. The variables were the condenser and reboiler duties. Moreover, we simulated the distillation of W and AA using the following parameters set (see Figure 1):

- 1) Heat exchangers E1 and E3 heat stream FEED and S8, respectively, to a temperature 30 K lower than the column tray, in which each stream enters. The purpose is to set a temperature that does not perturbate the temperature profile of the column. We adopted  $U_D = 370 \text{ W m}^{-2} \text{ K}^{-1}$  as the overall heat transfer coefficient.
- 2) The unit F1 is a decanter that works at atmospheric pressure and 298 K. It splits the distillate in two streams: WW and S6. WW contains mostly wastewater, while in S6 the entrainer is more concentrates and is then recycled back to the column. The cost of WW treatment is similar in all scenarios, therefore we did not consider it for the aim of comparison. We adopted  $U_D = 370 \text{ W m}^{-2} \text{ K}^{-1}$  as the overall heat transfer coefficient.
- 3) CN1 is a variable controller used to modify the flowrate of ENTRAINER stream (which is the make-up of fresh entrainer), in order to have a molar ratio between the entrainer (in S5) and water (in S8) equal to the azeotropic one. The composition of the azeotropes W/entrainer are reported in Table 1:

Table 1: azeotropic composition for the mixture water/entrainer at atmospheric pressure (Horsley, 1962)

Entrainer	$x_W$ , azeotrope
PX	0.76
EA	0.33
PA	0.52
BA	0.62

- 4) The distillation column is a sieve tray column, operating at 760 torr and with a pressure drop of 25 torr per tray. We selected a kettle type reboiler (conventional). The condenser operates at the boiling point, i.e. no subcooled D is obtained. The spacing between trays is constant and equal to 0.6096 m.
- 5) ECONOMICS is a calculator in which CAPEX and OPEX are computed.

We evaluated both CAPEX and OPEX using, as costing technique, the Guthrie method (1969 and 1974). This method relates all costs back to the cost of equipment purchased evaluated for some base conditions (bare module costs). Several factors (equipment type, operating pressure, constructions material, etc.) are adopted to correct the costs at base conditions to costs at specific conditions.

According with the Guthrie method the equipment cost was calculated with equation 1:

$$C_{BM} = C_p^0 (B_1 + B_2 F_M F_P) \quad \text{Eq.1}$$

In which  $C_p^0$  is the cost of the module at basic conditions,  $B_1$  and  $B_2$  are the constants for bare module factor,  $F_M$  is the material factor for the equipment and  $F_P$  is the pressure factor.  $C_p^0$  was calculated as:

$$\log_{10} C_p^0 = K_1 + K_2 \log_{10}(A) - K_3 (\log_{10}(A))^2 \quad \text{Eq.2}$$

where  $K_1$ ,  $K_2$ , and  $K_3$  are the parameters of the equipment unit considered, while  $A$  is the capacity (tank volume, heat exchanger area, column volume...). For all units the building material was stainless steel. The pressure factor was considered always equal to 1 because the operating pressure of each unit is lower than 5 barg.

The volume of the vessel F1, used for the separation of the aqueous phase, was calculated considering the flowrate of S2 and an average residence time of 30 minutes. Heat exchangers E1, E2 and E3 were considered as fixed tube units, with two tubes and one shell passes. The utility used as heating stream was steam at medium pressure (10 barg and 184°C). The cooling stream used in the column condenser is water at 25°C.

The cost of distillation column was evaluated considering it as composed by an empty vessel, several sieves (in function of the entrainer) and two heat exchangers (condenser and reboiler). Capital cost of sieve was calculated using equation 3:

$$C_{BM} = C_p^0 N F_{BM} F_q \quad \text{Eq.3}$$

where  $C_p^0$  is the cost of the sieve at basic conditions,  $N$  is the number of trays,  $F_{BM}$  the bare module factor and  $F_q$  is a quantity factor for trays given by:

$$\log_{10}F_q = 0.4771 + 0.08516 \log_{10}N - 0.3473(\log_{10}N)^2 \quad \text{Eq.4}$$

where  $N$  is the number of trays. Since all trays work in single liquid phase, the average tray efficiency was considered equal to 70%.

The condenser was a fixed tube unit while the reboiler a kettle reboiler. The condenser utility was water at 20°C while the reboiler utility was steam at medium pressure (10 barg and 184°C).

According to Turton (2012) most equipment in a chemical plant has a life of 9.5 years with a no salvage value, for this reason we consider a depreciation time of 9.5 years. All the costs were actualized to 2014 using the CEPCI index. All the parameters used are reported in Table 2.

Table 2: Equipment constants for the calculation of CAPEX

Equipment	Unit	$K_1$	$K_2$	$K_3$	$B_1$	$B_2$	$F_M$	$F_{BM}$	A
Tank	F1	3.4974	0.4485	0.1074	2.25	1.82	3.1	-	$m^3$
Heat Exchanger - Fixed Tube	E1,	4.3247	-0.3030	0.1634	1.63	1.66	2.7	-	$m^2$
	E2,								
	E3,								
CONDENSER									
Heat Exchanger - Kettle Reboiler	REBOILER	4.4646	-0.5277	0.3955	1.63	1.66	2.7	-	$m^2$
Distillation Column - Column	T1	3.4974	0.4485	0.1074	2.25	1.82	3.1	-	$m^3$
Distillation Column - Sieve	T1	2.9949	0.4465	0.3961	-	-	-	1.8	$m^2$

OPEX were calculated considering high pressure steam, cooling water and entrainer make-up stream flowrate. The annual operating time was set to 8760 hours. Utilities costs (Turton, 2012) and chemicals costs (ICIS database) are reported in Table 3.

Table 3: OPEX, costs of utilities and chemicals

Utility/Consumable	Description	Value
Steam for boilers	Latent heat only,	14.83 \$ GJ <sup>-1</sup>
	Medium pressure (10 barg, 184°C)	
Cooling water	Water at 20°C	0.354 \$ GJ <sup>-1</sup>
n-Ethyl Acetate	-	0.59 \$ lb <sup>-1</sup>
n-Propil Acetate	-	0.69 \$ lb <sup>-1</sup>
n-Butil Acetate	-	0.85 \$ lb <sup>-1</sup>

## Results and discussion

All the main results for the four different scenarios considered are reported in Table 4.

The configuration which shows the lowest TAC is the one of SIM 3, i.e. the one in which propyl acetate was used as entrainer. Considering only the azeotropic composition of the mixture water-propyl acetate and water-butyl acetate (water percentage of 0.54 and 0.73 respectively), the latter is preferable, since the amount required is lower. However, butyl acetate requires higher condenser duty (azeotrope boils at a higher temperature) and it is more expensive compared to propyl acetate. Ethyl acetate, needs to be added in a larger quantity, as stressed by the distillate flowrate, although its boiling point is lower compared to propyl acetate. PX has the advantage to be already present in situ, since it is the reagent for the phthalic acid synthesis. However, the separation is more difficult and expensive due to its high boiling point, in fact a 42 stages column is needed to achieve the separation. Another interesting advantage of the use of propyl acetate relies in the good immiscibility gap with water. The solubility of water increases along the series PX<BA<PA<EA, which is coherent with the molar fraction of the entrainer in the WW (Table 3). The quality of the bottom stream, however, is lower with PX. The contribution to the CAPEX and OPEX of heat exchangers

used to pre-heat the streams entering the column is negligible. The high pressure steam feeding the column reboiler constitutes the majority of the operating expenses.

More in general, the use of PX is interesting because no traces of an external component are added, but it is a less advantageous choice compared to propyl acetate considering only the TAC. On the other side, the use of PA affects the terephthalic acid synthesis due to its presence in the stream of AA recycled.

Table 4: Simulation results for all the four scenarios

Parameter	Unit of measure	SIM 1	SIM 2	SIM 3	SIM 4
Entrainer	-	p-xylene	methyl acetate	propyl acetate	butyl acetate
Entrainer make up flowrate	Kmol h <sup>-1</sup>	22.74	1.26	1.23	1.25
W/AA flowrate (x <sub>AAc</sub> =0.5)	Kmol h <sup>-1</sup>	100	100	100	100
Distillate flowrate (D)	Kmol h <sup>-1</sup>	48.56	174.25	97.18	74.80
Bottom flowrate (B)	Kmol h <sup>-1</sup>	74.18	50.39	51.78	49.19
X <sub>WW,AA</sub>	-	0.002	0.013	0.005	0.056
X <sub>WW,entrainer</sub>	-	0	0.019	0.004	0.002
X <sub>B,W</sub>	-	0.112	0.020	0.019	0.020
X <sub>B,entrainer</sub>	-	0.262	0.0002	0.020	0.023
Column reflux ratio (RR)	-	5.7	3.5	3.5	3.5
Number of stages	-	42	13	13	15
Entrainer feed tray	-	1	4	4	6
W/AA feed tray	-	42	9	6	7
Total annual cost (TAC)	M\$ y <sup>-1</sup>	4.40	5.45	3.98	4.43

## Conclusion

The selection of an entrainer for an azeotropic distillation is a compromise between the separation efficiency and the cost. We compared various solutions proposed in the literature for the recovery of acetic acid by distillation. We simulated the distillation of the mixture water and acetic acid and confirmed that the use of p-xylene is comparable to butyl acetate considering the cost. The best entrainer is propyl acetate, with a total annual cost (TAC) of 3.98 M\$ and a good quality of residue stream (concentration of acetic acid of 96.1%mol) is obtained.

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