

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

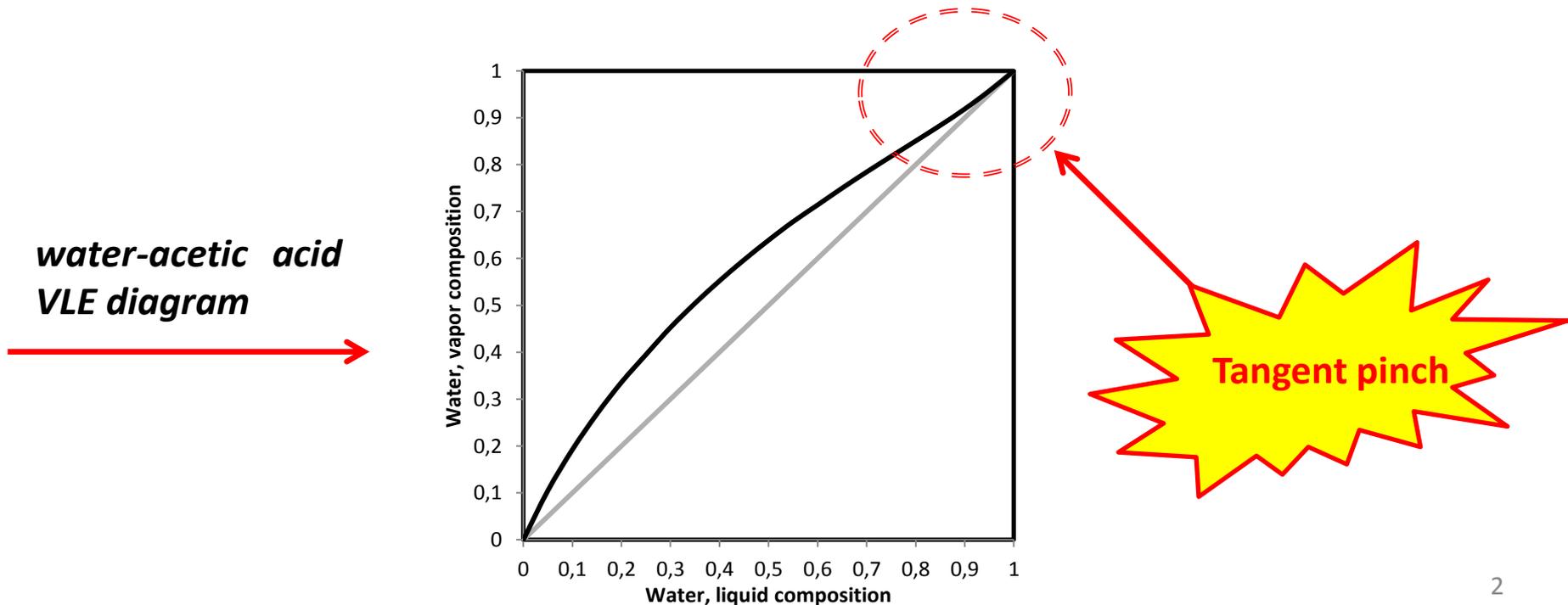


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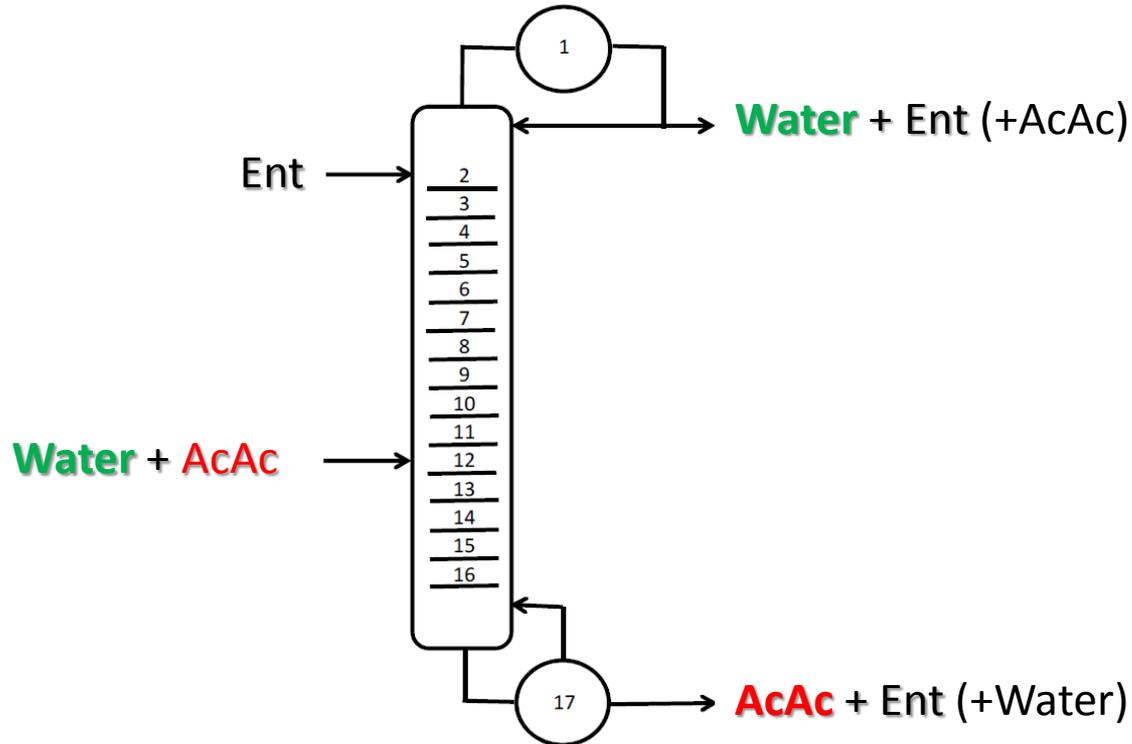
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The recovery of acetic acid from aqueous solutions is an important operation particularly in the cellulose acetate industry and in the terephthalic and isophthalic acid production process.

Acetic acid and water system does not form azeotrope at atmospheric pressure but shows a tangent pinch on the pure water end making **inconvenient their separation by direct distillation.**

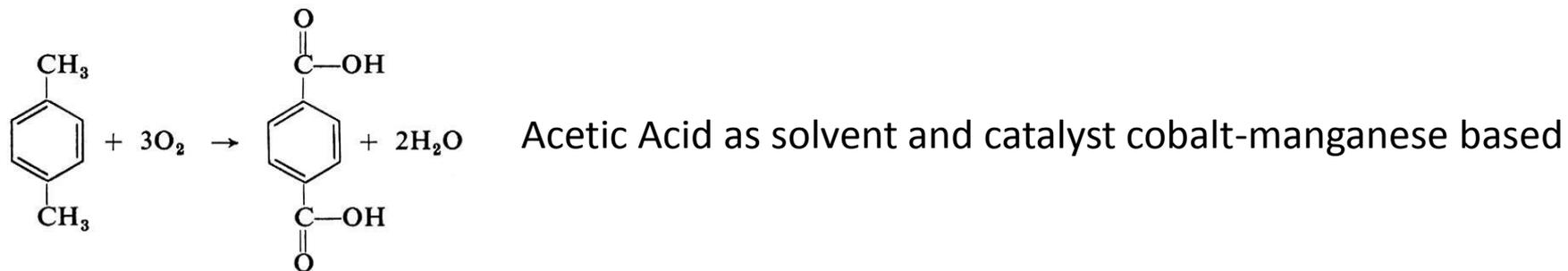


The addition of a third component generally immiscible with water permits to separate water and acetic acid by **heterogeneous extractive distillation**



Different kind of entrainers were proposed: ethyl acetate, n-butyl acetate, vinyl acetate or iso-butyl acetate. They work very well for recovering acetic acid from water but are potential contaminants when the separation is part of a more complex production process.

## Terephthalic acid production



**Water-acetic acid separation in this industrial process is a crucial point.**

Our proposal: p-xylene can work as water's entrainer and be directly recyclable with acetic acid without any further purification because it is the principal raw material of the terephthalic acid production



No need for a further purification of the mixture acetic acid/p-xylene



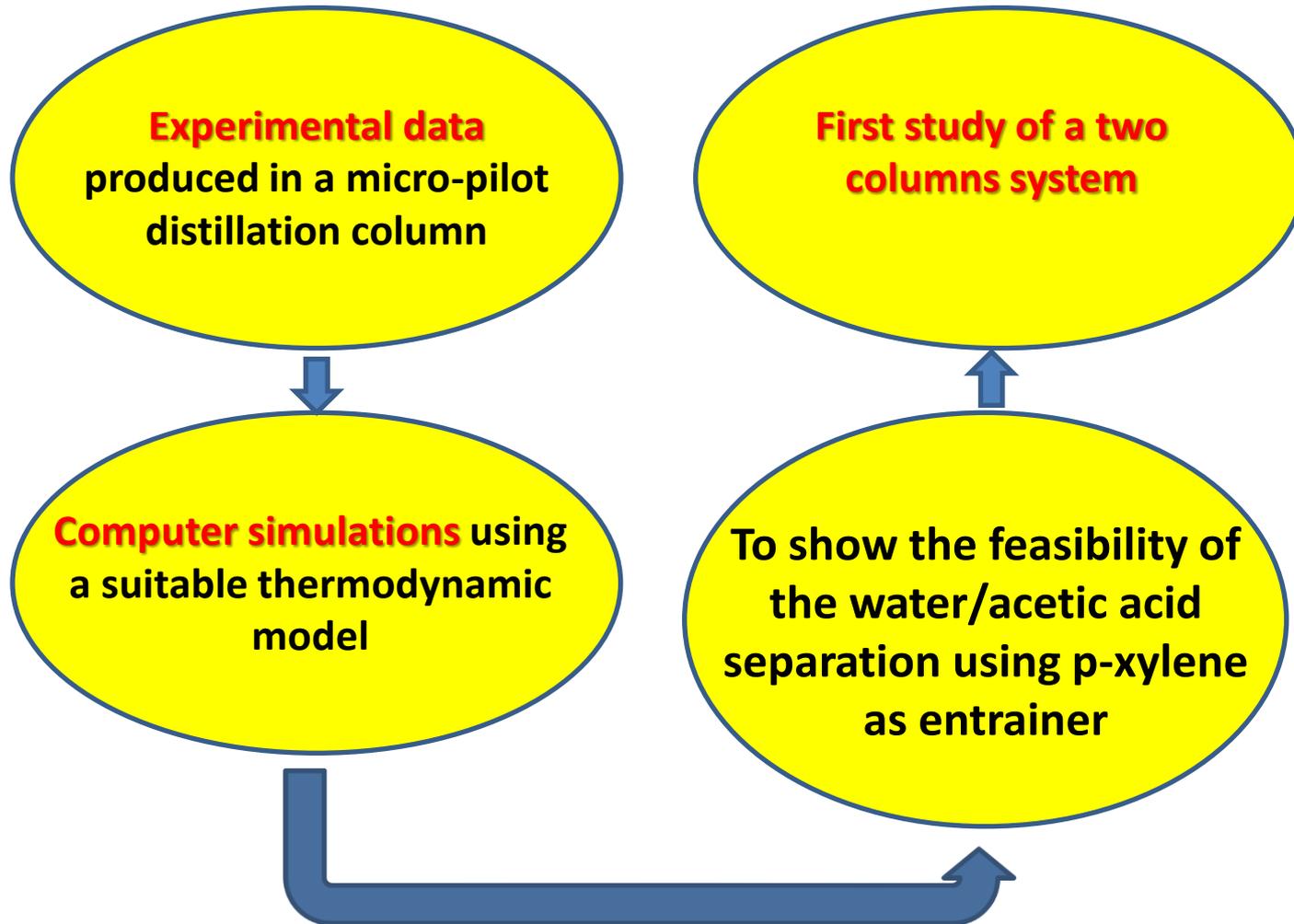
No introduction of a component not involved, but potentially disturbing the terephthalic production process.

## Water/Acetic Acid/p-xylene system

Component	Azeotropic composition (% <sub>mol</sub> )	Normal Boiling point (°C)
water	---	100
acetic Acid	---	118
p-xylene	---	138
water/p-xylene*	74,5/25,5 (LLV)	92
acetic acid/p-xylene*	82/18 (LV)	115,3

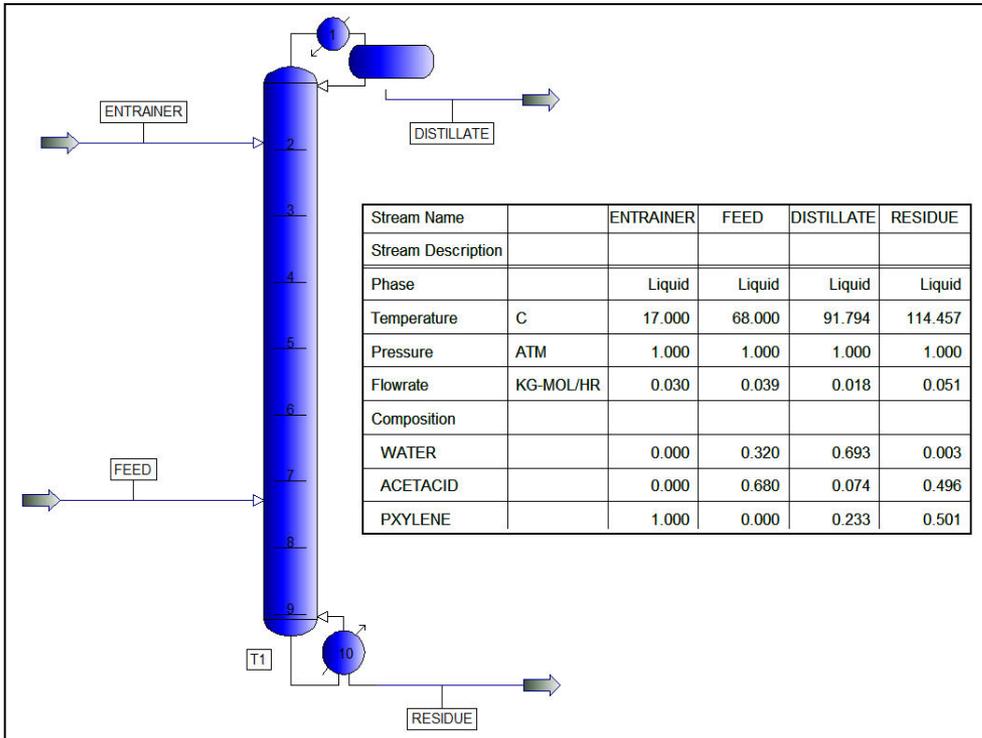
\* Wang et al. *J. Process Control* 18(2008)45-60.

# Our aim:



# Simulation

The simulations were carried out using **PRO II Version 8.3 by SimSci Simulator**



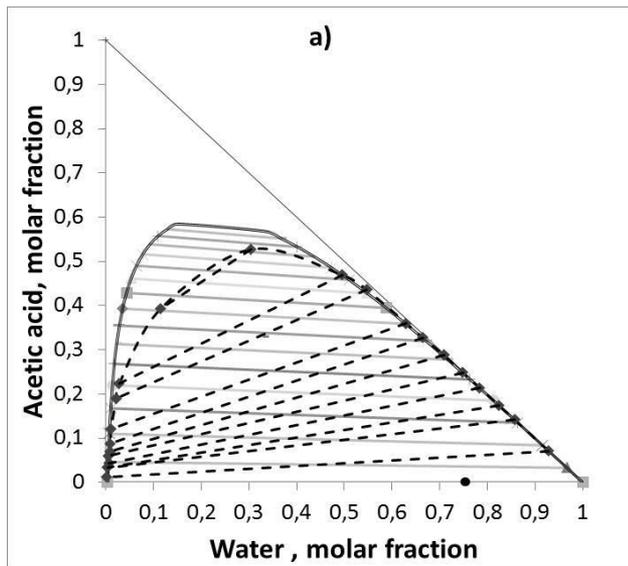
The vapor pressures of water, acetic acid and p-xylene were calculated using the equation and the parameters of the PRO II database

The computer program used for the micro-pilot simulations was based on the CHEMDIST algorithm of PRO II.

# Thermodynamic aspects: LLE

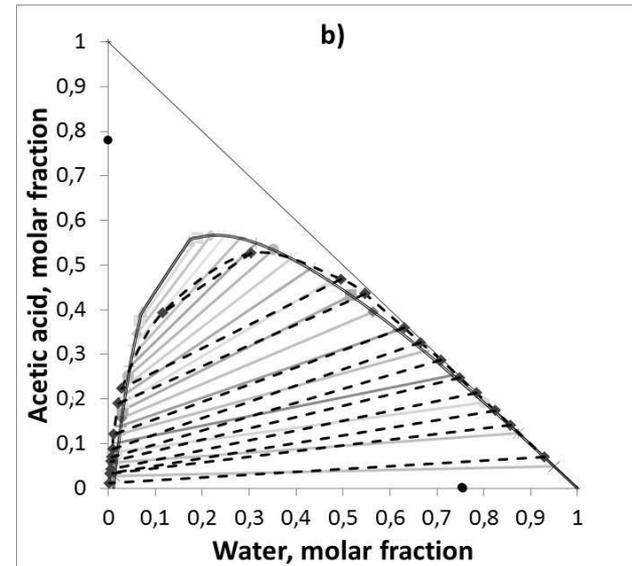
Liquid-liquid equilibrium (LLE) experimental data of the ternary system were published by Murogova et al. [R. A. Murogova et al. , Zh. Prikl. Khim. (Leningrad) 46 (1971) 2464-2466 ] and simulated using UNIFAC or Modified UNIFAC (Temperature dependent).

----- Experimental  
———— Simulated



**UNIFAC**

A. Fredenslund, R. L. Jones, J. M. Prausnitz, Group-contribution estimation of activity coefficients in nonideal liquid mixtures, A.I.Ch.E. J. 21(6) (1975) 1086-1099.

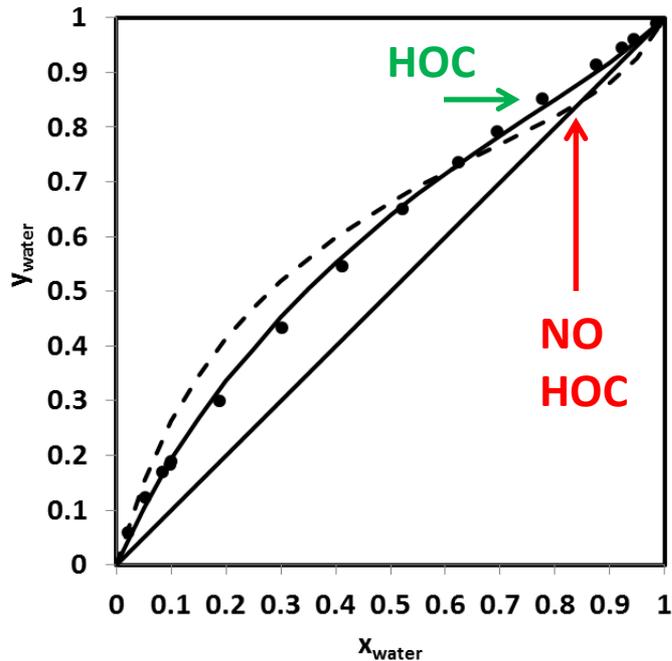


**Modified UNIFAC (Temperature dependent)**

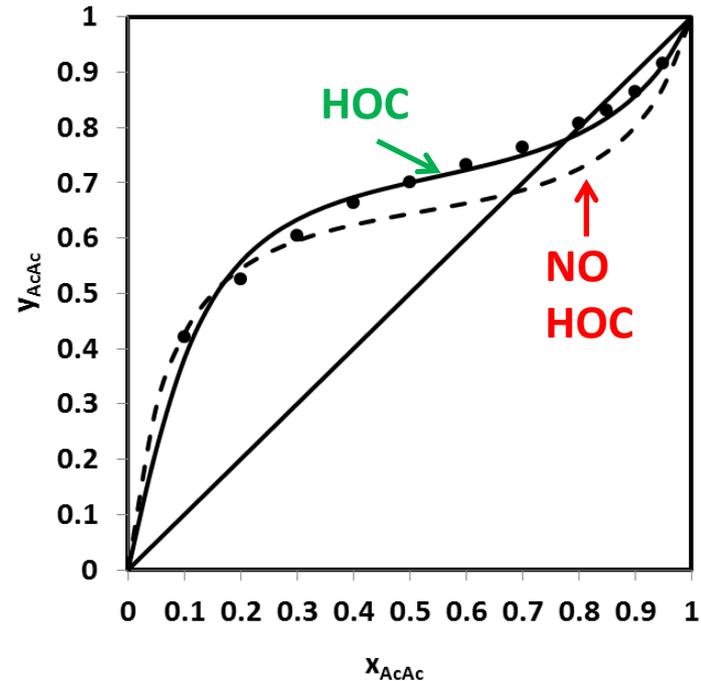
B. L. Larsen, P. Rasmussen, A. Fredenslund, A modified UNIFAC group contribution model for prediction on phase equilibria and heats of mixing, Ind. Eng.Chem. Res. 26(11) (1987) 2274-2286.

# Thermodynamic aspects: VLE

Binary vapor-liquid equilibria (VLE) water/acetic acid and acetic acid/p-xylene were simulated using modified UNIFAC for the activity coefficients calculations. A better reproducibility of the experimental data is obtained adopting the **Hayden-O'Connell (HOC) second virial coefficient model for taking into account the acetic acid association in vapor phase.**



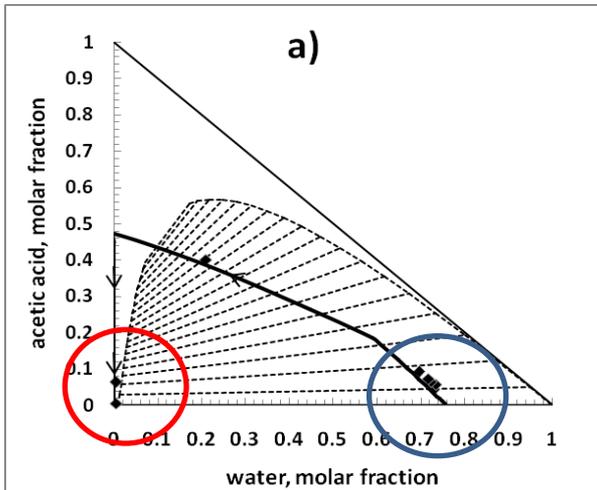
**water/acetic acid**



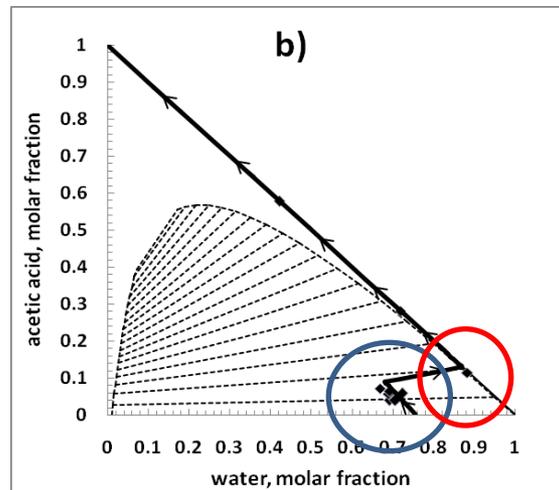
**acetic acid/p-xylene**

# Open evaporation runs

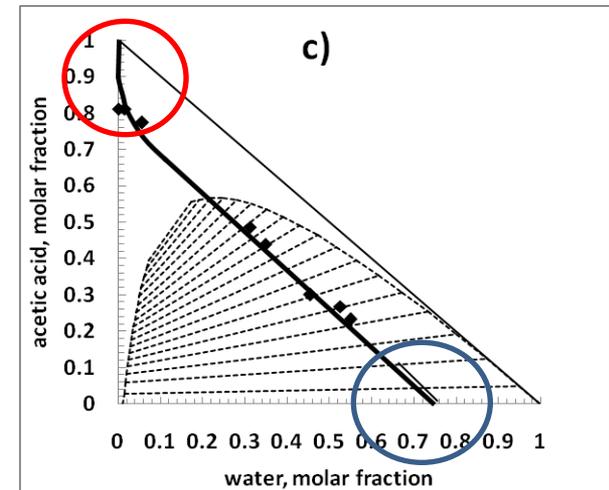
In a batch distillator with a reboiler of 100 ml three different mixtures were evaporated (reflux ratio = 0). The condensed vapors were sampled regularly obtaining three different distillation curves.



$$x_w = 0.60, x_{AcAc} = 0.10; x_{p-xyI} = 0.30$$



$$x_w = 0.73, x_{AcAc} = 0.18, x_{p-xyI} = 0.09$$



$$x_w = 0.40, x_{AcAc} = 0.40, x_{p-xyI} = 0.20$$

The good fit confirms the right thermodynamic choices

## Distillation Runs: $R = \infty$

### Estimation of the total trays efficiency

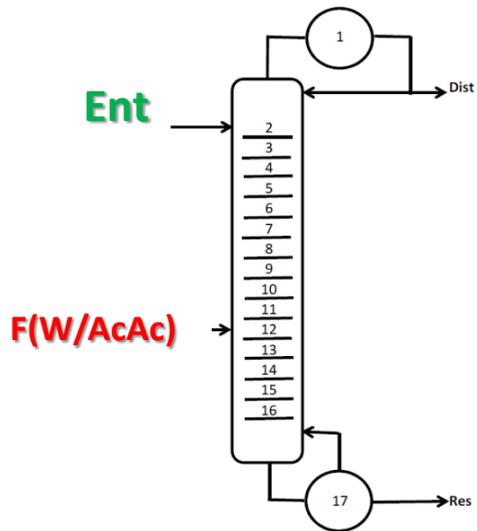
Two Runs, performed at  $R = \infty$ , have been used to estimate the global efficiency of the column, using two different loading of the reboiler ( $F = W = D = 0$ ).

	Run 1	Run 2
$x_{F,AcAc}$	0.10	0.80
$x_{F,W}$	0.10	0.10
$x_{F,p-xyl}$	0.80	0.10
$x_{dist,AcAc}$	<0.001	0.0237
$x_{dist,W}$	0.7557	0.7361
$x_{dist,p-xyl}$	0.2438	0.2402
$x_{res,AcAc}$	0.1012	0.805
$x_{resW}$	0.0919	0.095
$x_{res,p-xyl}$	0.8068	0.100
$y_{12}^{th}{}_{tray,AcAc}$	0.021	0.109
$y_{12}^{th}{}_{tray,W}$	0.739	0.682
$y_{12}^{th}{}_{tray,p-xyl}$	0.240	0.209
$T_{dist} [^{\circ}C]$	92	93
$T_{res} [^{\circ}C]$	95	108

The number of trays that minimize the difference between experimental and simulated data was determined to be equal to **eight**, corresponding to a mean **trays efficiency of 0.53**, consistent with the presence of a double liquid phase on some trays.

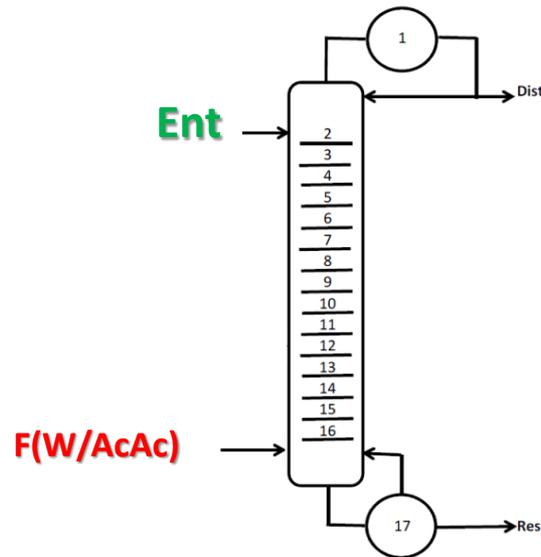
# Continuous Distillation Runs

Runs 3-4



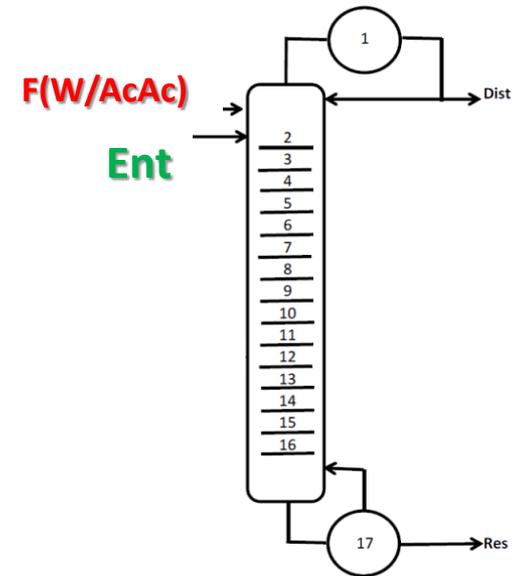
Total column

Run 5



Rectification part

Run 6



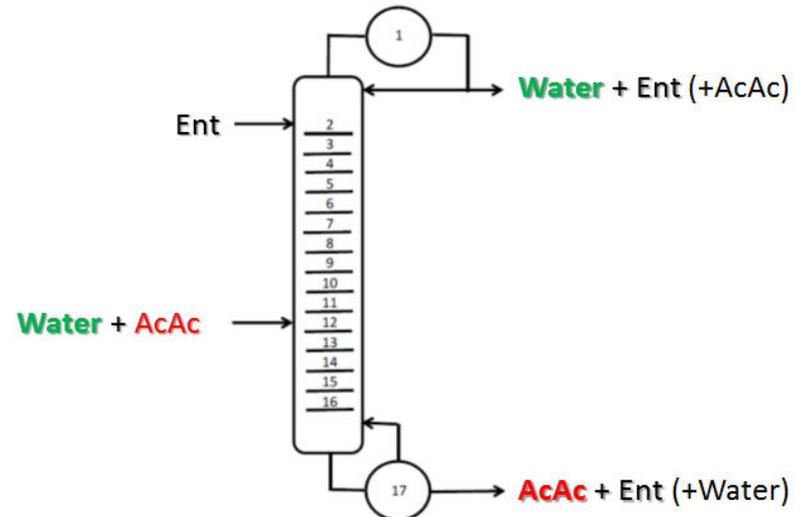
Stripping part

## Continuous Distillation Runs

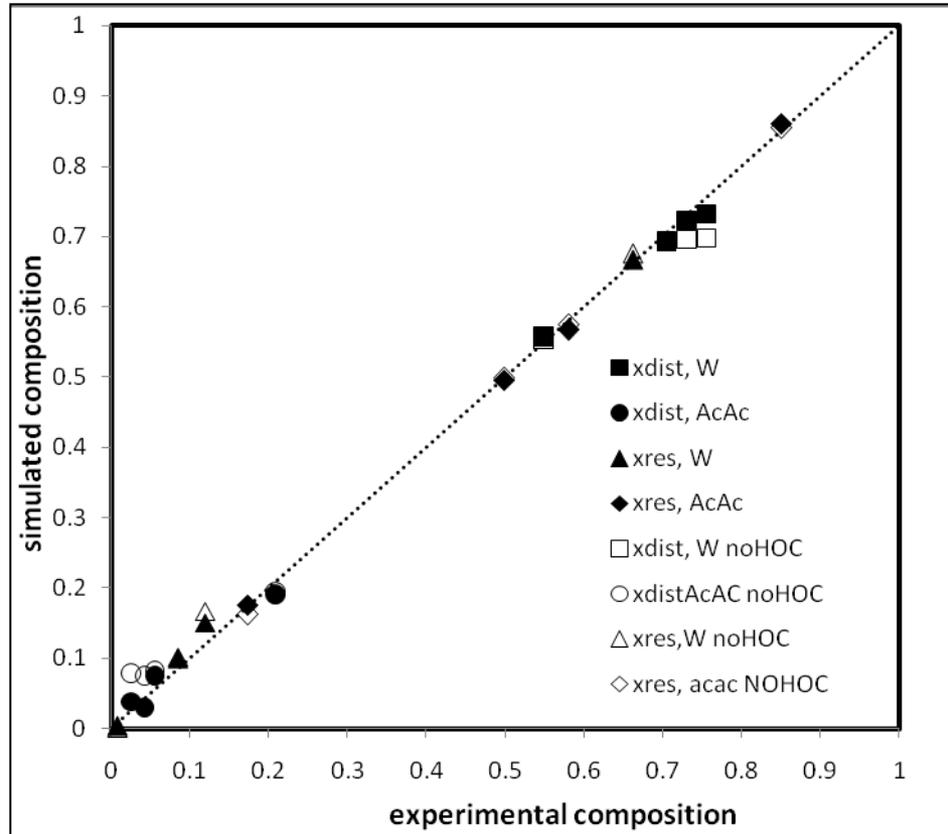
### Experimental results

	Run 3 (Total)	Run 4 (Total)	Run 5 (Rect.)	Run 6 (Strip.)
<b>R</b>	<b>0.5</b>	<b>1.0</b>	<b>0,5</b>	<b>0,5</b>
$x_{F,AcAc}$	<b>0.57</b>	<b>0.68</b>	<b>0.17</b>	<b>0.61</b>
<b>F/Ent (l/l)</b>	<b>0,88</b>	<b>0,47</b>	<b>0,88</b>	<b>1,90</b>
$x_{dist,AcAc}$	<b>0.042</b>	<b>0.055</b>	<b>0.026</b>	<b>0.21</b>
$x_{dist,W}$	<b>0.755</b>	<b>0.704</b>	<b>0.731</b>	<b>0.55</b>
$x_{dist,p-xyl}$	<b>0.203</b>	<b>0.241</b>	<b>0.243</b>	<b>0.24</b>
$x_{res,AcAc}$	<b>0.58</b>	<b>0.498</b>	<b>0.173</b>	<b>0.850</b>
$x_{res,W}$	<b>0.12</b>	<b>0.008</b>	<b>0.663</b>	<b>0.085</b>
$x_{res,p-xyl}$	<b>0.30</b>	<b>0.494</b>	<b>0.164</b>	<b>0.065</b>
$T_{dist}$ [°C]	<b>92</b>	<b>94</b>	<b>96</b>	<b>92</b>
$T_{res}$ [°C]	<b>103</b>	<b>119</b>	<b>116</b>	<b>95</b>

- The number of trays for our column is not sufficient to obtain low amount of AcAc in the distillate and low amount of water in the residue.
- This aim has been obtained increasing the ratio F/E or splitting the column for the separate study of the rectification and stripping part

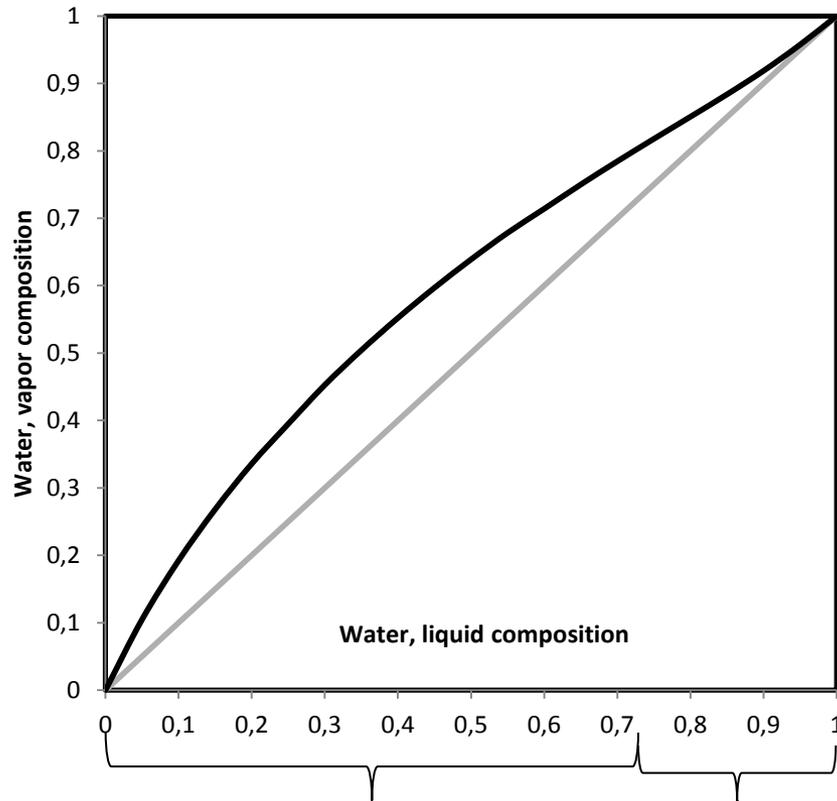


## Continuous Distillation Runs Simulation results



The simulated composition of all streams in all the experimental runs (performed in different operative condition and using different experimental parameters) are close to the experimental data, which means that these system simulations were accurate.

# Process optimization



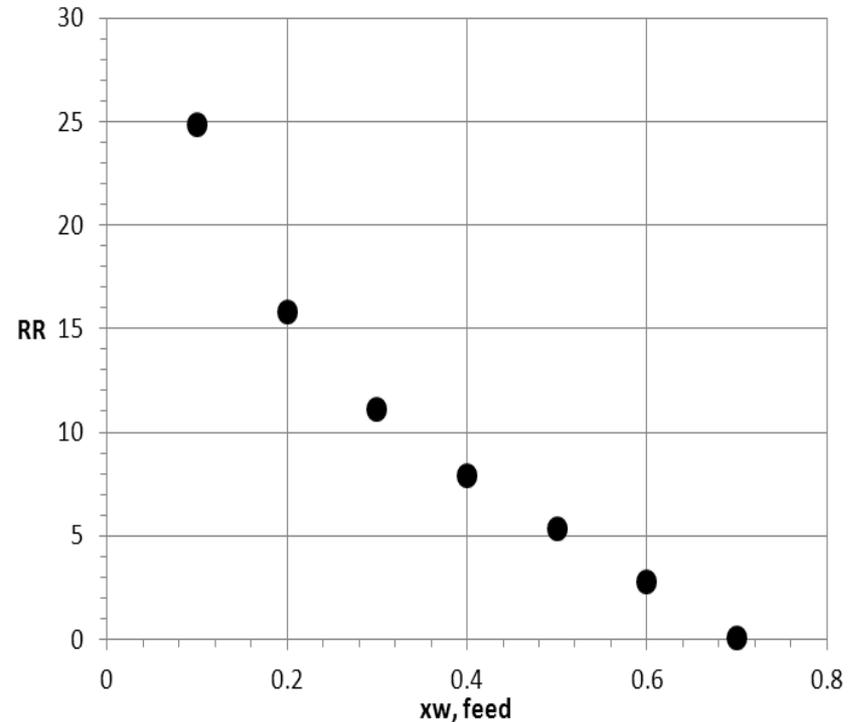
**Two  
columns  
system**



# Two columns system

## First column study

- 7 ideal stages column
- Feed stream:  $26.62 \text{ kmol h}^{-1}$  (equivalent to  $1000 \text{ l h}^{-1}$ )
- 7 different compositions, characterized by a molar fraction of water from 0.1 to 0.7
- Specifications of simulation: composition of water in the distillate equal to 0.74 and equal to 0.02 in the residue.
- Calculated parameter: reflux ratio required to achieve such separation and distillate flow



## Two columns system

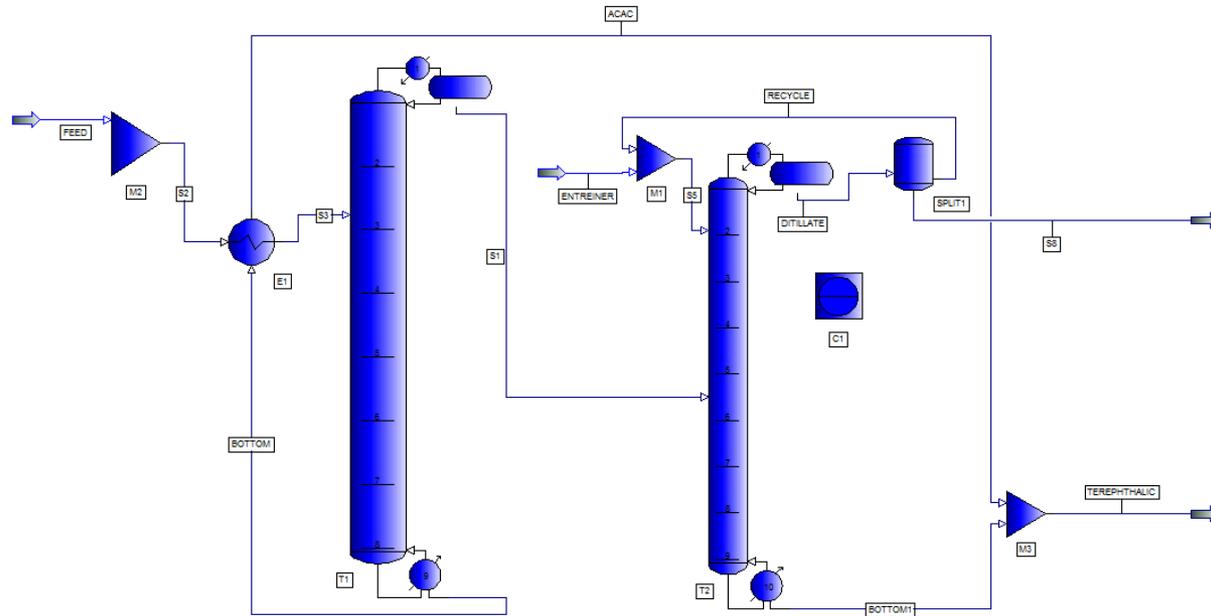
- Feed:  $26.62 \text{ kmol h}^{-1}$ , equimolar water and acetic acid
- Entrainer feed:  $6.6 \text{ kmol h}^{-1}$  of p-xylene
- Direct distillation columns: trays number: 7, molar reflux ratio: 5,7
- Extractive distillation columns: trays number: 8, molar reflux ratio: 8

*Simulated results of the two columns separation plant*

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

1. Column 2: fed with a quantity of p-xyl corresponding to 26% molar of the total, 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.
2. p-xyl feed in the column is obtained by mixing a small fresh stream ( $2.3 \text{ kmol h}^{-1}$ ) and a recycled one ( $4.31 \text{ kmol h}^{-1}$ ,  $x_{\text{p-xyl}}=0.984$ ) coming from the top of the column.

# Two columns system

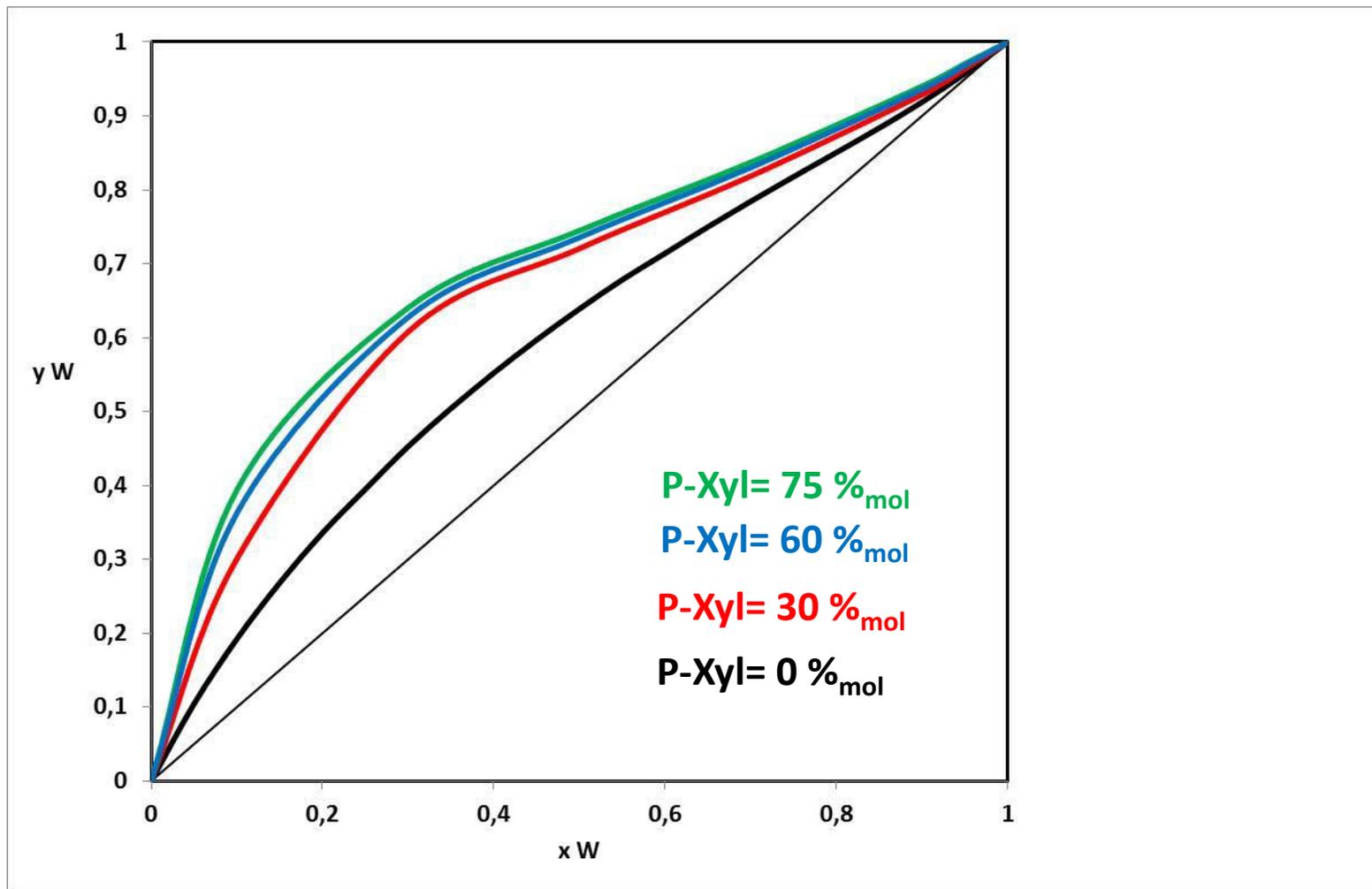


Summarizing, in this two columns based separation plant, for  $13.31 \text{ kmol h}^{-1}$  of acetic acid incoming,  $0.458 \text{ kmol h}^{-1}$  is lost with the outward flow of water (<3%), while the rest is successfully recovered.

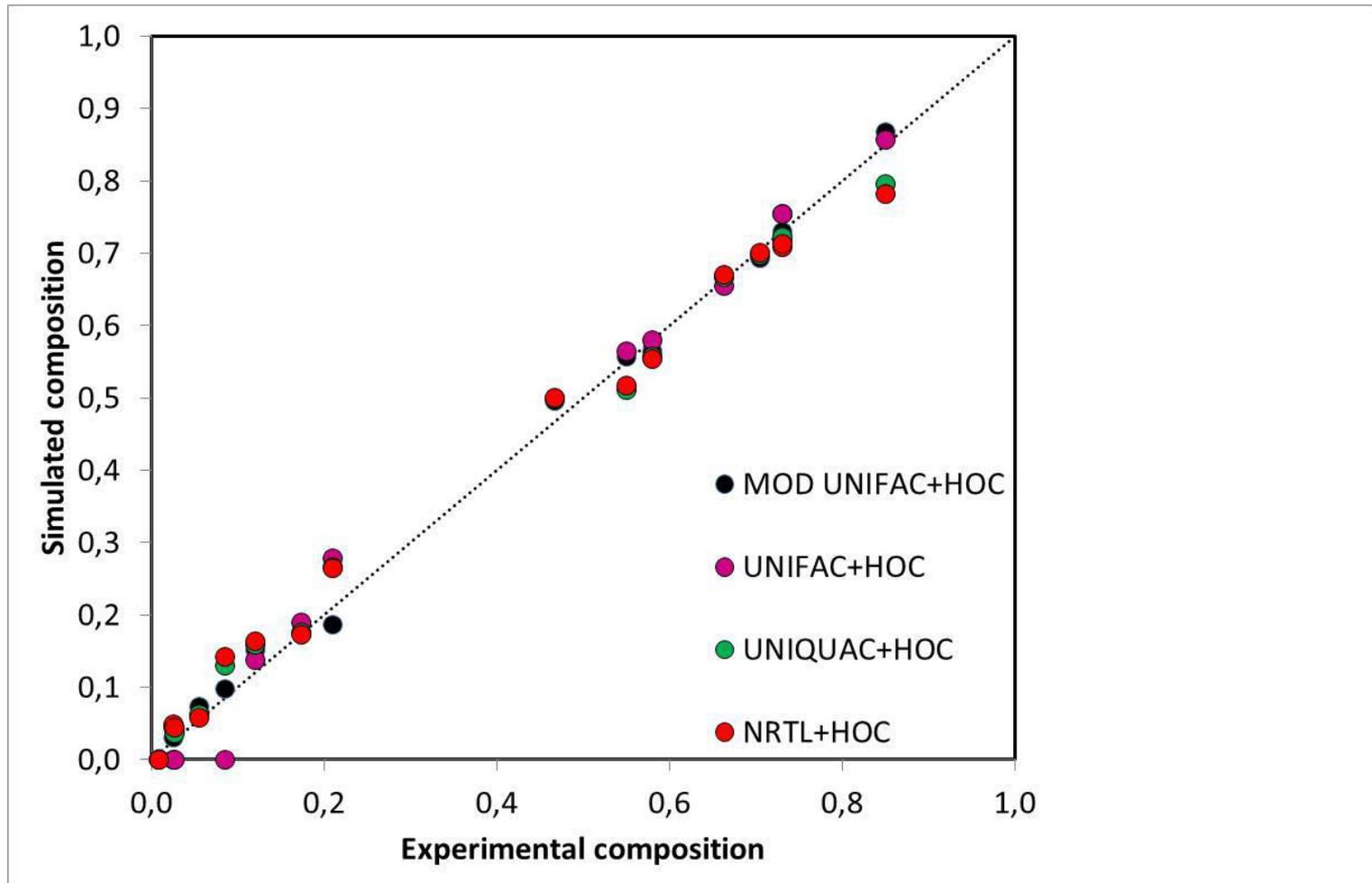
# Conclusion

- 1) The possibility of using p-xylene as entrainer for the water/acetic acid separation by extractive heterogeneous distillation was investigated and verified.**
- 2) An excellent description of the ternary VLLE was obtained using the Lyngby modified UNIFAC equation for calculating the activity coefficients and the Hayden-O'Connell correlation for taking into account the acetic acid association.**
- 3) The rectifying and stripping sections were studied separately showing that it's possible to reach very low concentrations of acetic acid in the top of the column and of water in the bottom and, therefore, to recycle directly the acetic acid/p-xylene mixture to the terephthalic acid production saving the energy of such a separation.**
- 4) The separation process could be optimized by joining a first direct distillation column and a second extractive distillation column.**

## Study of relative volatility water-AcAc in presence of entrainer

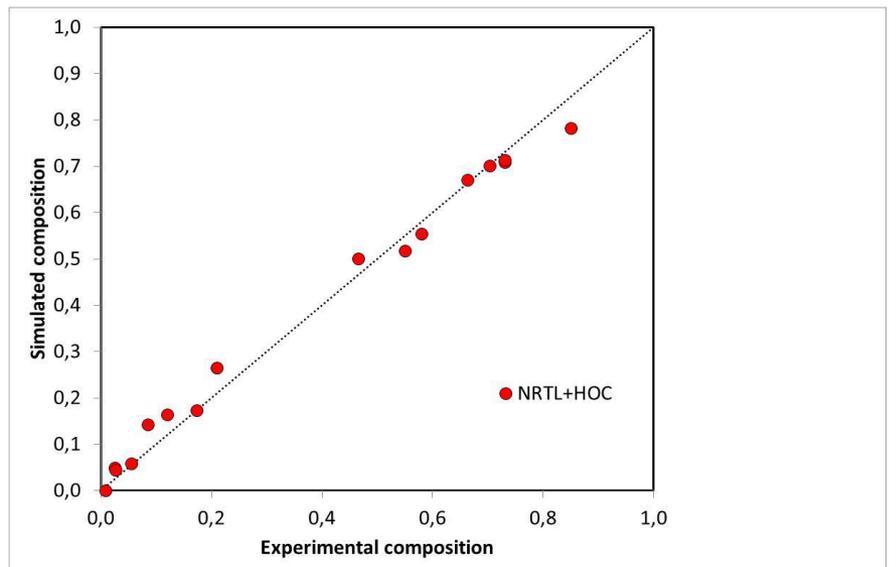
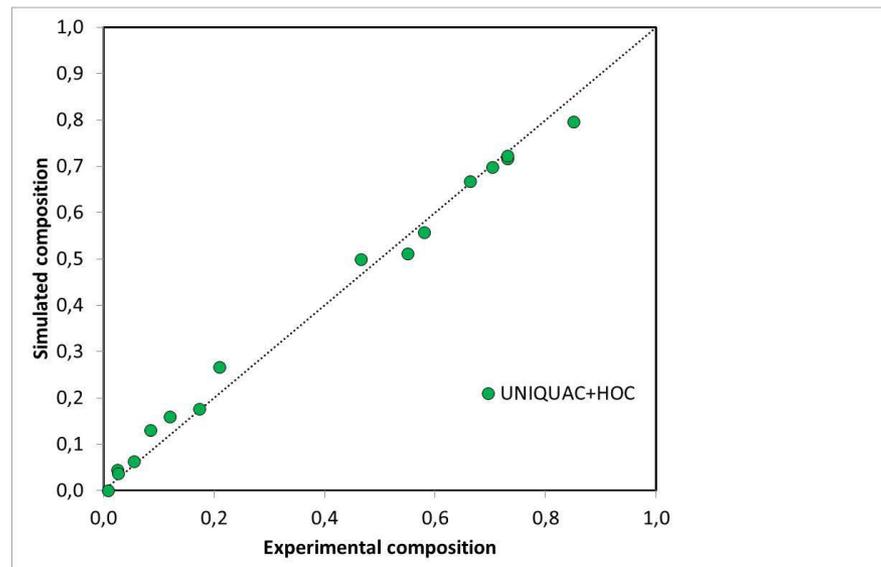
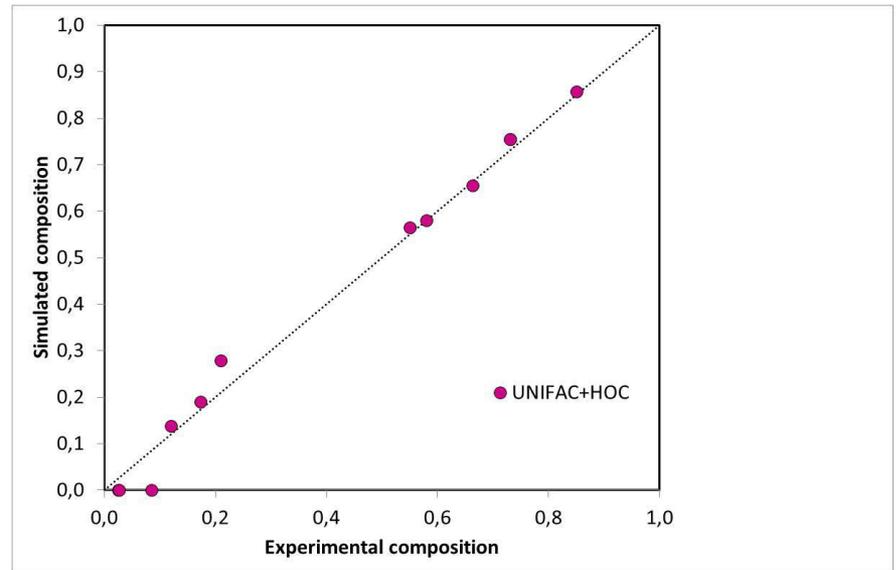
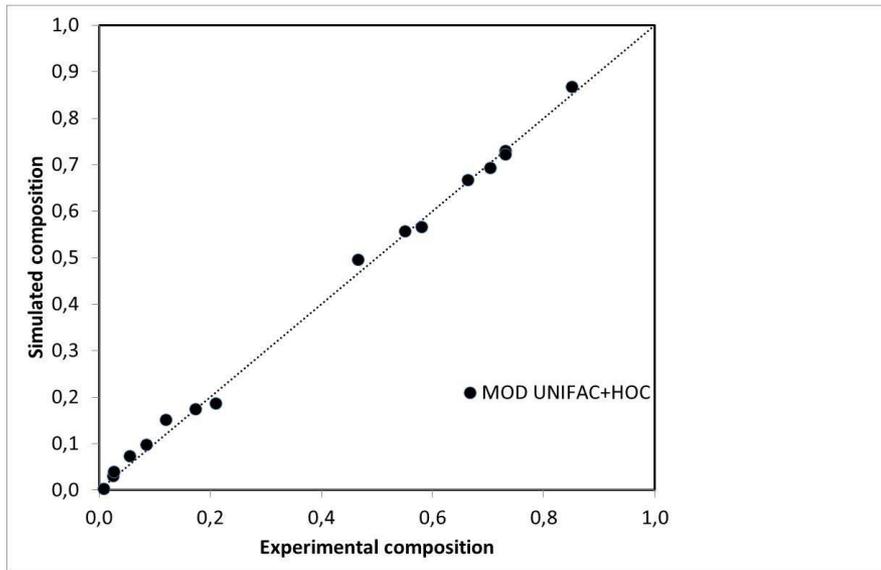


## Continuous Distillation Runs: comparison using different model for the calculation of activity coefficients



Among all the considered models, the previsionsal modified UNIFAC one seems to be the most suitable

# Continuous Distillation Runs: comparison using different model for the calculation of activity coefficients



$$\ln p_v = C1 + \frac{C2}{T} + C3 \ln T + C4 x T^{C5}$$

Component	C1	C2	C3	C4	C5
W	73.6	-7258.2	-7.3	4.2E-06	2.0
AcAc	53.3	-6304.5	-4.3	8.9E-18	6.0
p-xyl	85.5	-7595.8	-9.4	5.7E-06	2.0

**Heterogeneous Distillation of the System Water-  
Acetic Acid- p-Xylene:  
PART II: new thermodynamic approach and  
economic column scale up**

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In the first part, with the aim to use a predictive model, UNIFAC together with the Hayden O'Connell correlation was adopted to model this ternary system.

The fugacity coefficient was accounted (acetic acid association in vapor phase) because the UNIFAC model alone was unable to correctly predict the fluid phase equilibria of the ternary mixture.

In this second part, differently, the **UNIQUAC activity model** was adopted for the calculation of the activity coefficients and the **acetic acid association was considered negligible, due to both the temperature inside the column and to the acetic acid dilution in the mixture**, as detailed in the next slides.

In this work, **UNIQUAC binary parameters were regressed using the robust optimizer belonging to the BzzMath** library starting from these considerations and taking into account different experimental equilibrium data available in literature. These data concern both the ternary system and the binary mixtures involved.

## Thermodynamic Aspects

An important aspect of the studied system concerns the association of AcAc molecules to give dimers and tetramers in the vapor phase;

In the present study the proposed thermodynamic interpretation is based on the following considerations:

1) UNIQUAC activity model can represent conveniently this system but a robust regression of the parameters is necessary due to the complexity of the mixture involved in the distillation column;

2) the fugacity coefficient can be supposed to be equal to 1 considering both the low pressure (atmospheric) used in this work and the hypothesis of very low AcAc association in the vapour phase at the experimental temperatures

# Explanation

The formation of the dimer molecules is not considered because the temperatures at which the column was operating are in the range **92-138 °C** and this means that the association constant ( $k_D$ , that depends exponentially on temperature) is very low. In fact, by the Marek and Standart equation\*, increasing the temperature, for example from 20 °C till 120°C, results in decreasing the  $k_D$  value of about 2500 times.

Another important consideration is that the critical point for the separation of the W/AcAc system is the zone in which AcAc molecules are very diluted in water and then the actual contribution of acetic acid associated molecules should be neglected.

*\*Marek, J.; Standart, G. Vapor-Liquid Equilibria in mixtures containing an associating substance. I. Equilibrium relationship for system with an associating component. Collect. Czech. Chem. Commun. **1954**, 19, 1074*

## Thermodynamic Aspects

This thermodynamic approach, very rigorous for the liquid activity calculation but simplified for what concerns the acetic acid association, can be very useful in order to obtain a fast simulation of the system, limiting the computational cost.

This last statement is particularly meaningful in a plant real-time analysis, where if the simulation convergence is reached faster, a better dynamic control could be possible.

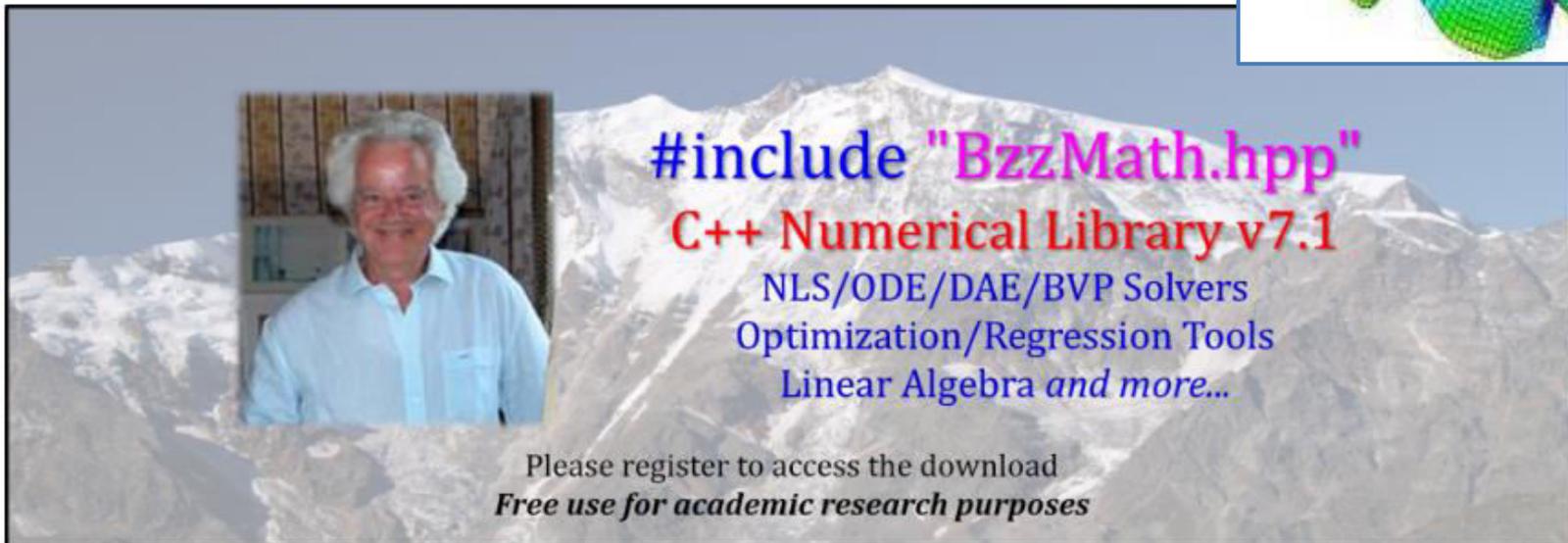
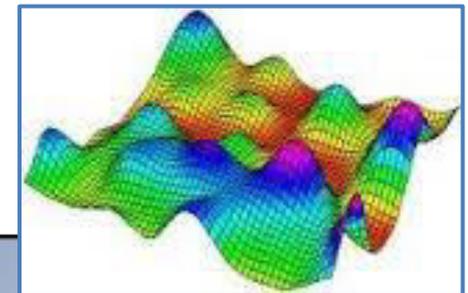
In any case, the hypothesis here discussed required the experimental validation

**UNIQUAC regression** of the model parameters was performed by means of the set of robust optimizers belonging to the BzzMath library\*.

Such optimizers are based on the object-oriented programming and parallel computing so as to reduce the computational time. This library possesses numerical methods able to simultaneously handle the so-called narrow-valley problem, which typically arise in the estimation of kinetic and thermodynamic parameters, the possible multi-collinearities which could be due to coupled chemical-physical phenomena and the possible presence of bad-quality measures with the identification of outliers

\*<http://super.chem.polimi.it/>

BzzMath v7.1 Released



**#include "BzzMath.hpp"**  
**C++ Numerical Library v7.1**  
NLS/ODE/DAE/BVP Solvers  
Optimization/Regression Tools  
Linear Algebra *and more...*

Please register to access the download  
*Free use for academic research purposes*

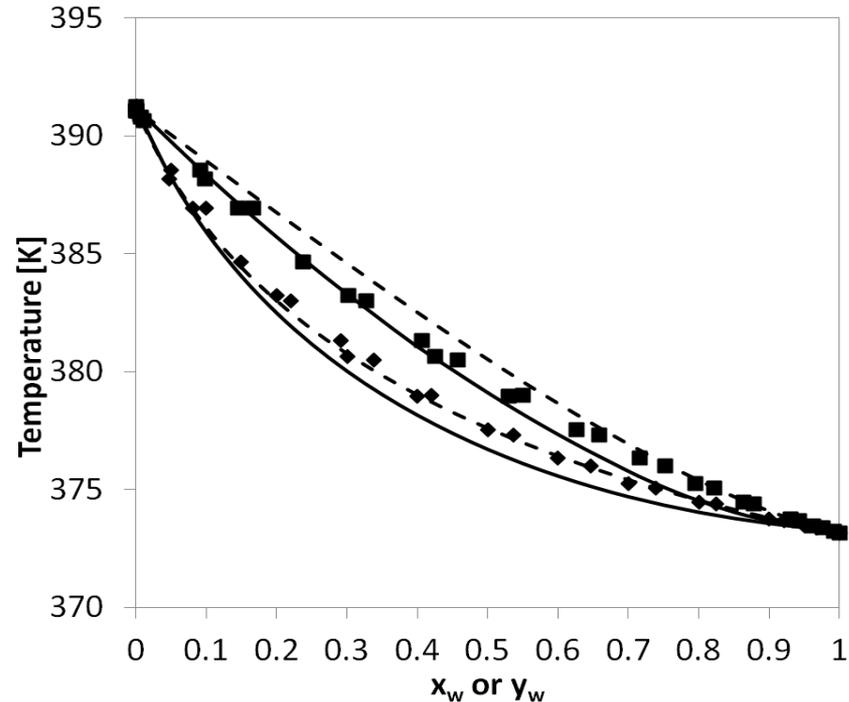
# Thermodynamic Aspects

Optimized UNIQUAC parameters using the rigorous C++BzzMath library. VLE are the parameters for the calculation of the vapour-liquid equilibria while VLLE are the parameters for the calculation of the ternary vapour-liquid-liquid equilibrium

(i/j)	VLE				VLLE			
	$a_{ij}$ [K]	$a_{ji}$ [K]	$b_{ij}$ []	$b_{ij}$ []	$a_{ij}$ [K]	$a_{ji}$ [K]	$b_{ij}$ []	$b_{ij}$ []
Water/Acetic Acid	-120.12	-2224.8	0.52	5.594	101.54	-127.45	0	0
Acetic Acid/p-xylene	83.682	79.613	0	0	-73.85	335.94	0	0
Water/p-xylene	219.34	4649.5	0	0	219.34	4649.5	0	0

# Thermodynamic Aspects

*Comparison between experimental (points) and simulated data by UNIQUAC of water/acetic acid system Dotted line: Robust parameters Solid line: least square method (LSA) parameters*



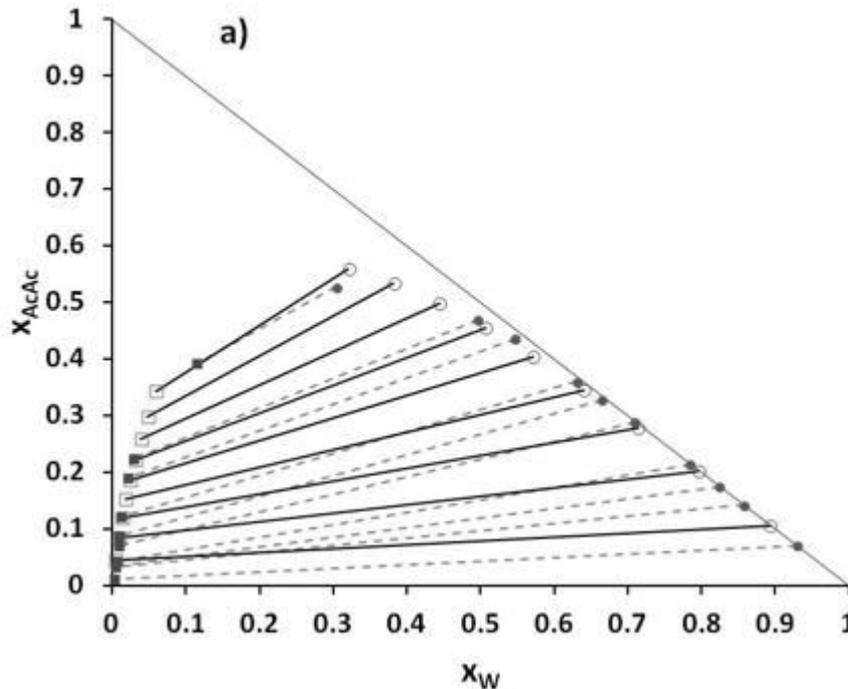
Although the fitting of the vapor composition is not excellent in the acetic acid rich mixture part of the phase diagram, the accuracy of this model for what concern the pinch point temperatures and compositions is very satisfactory, confirming the thermodynamic approach.

This general result allows making a suitable interpretation of our azeotropic distillation column that requires high precision in the critical pure water region rather than a good average fitting in the whole composition of the liquid-vapor diagram

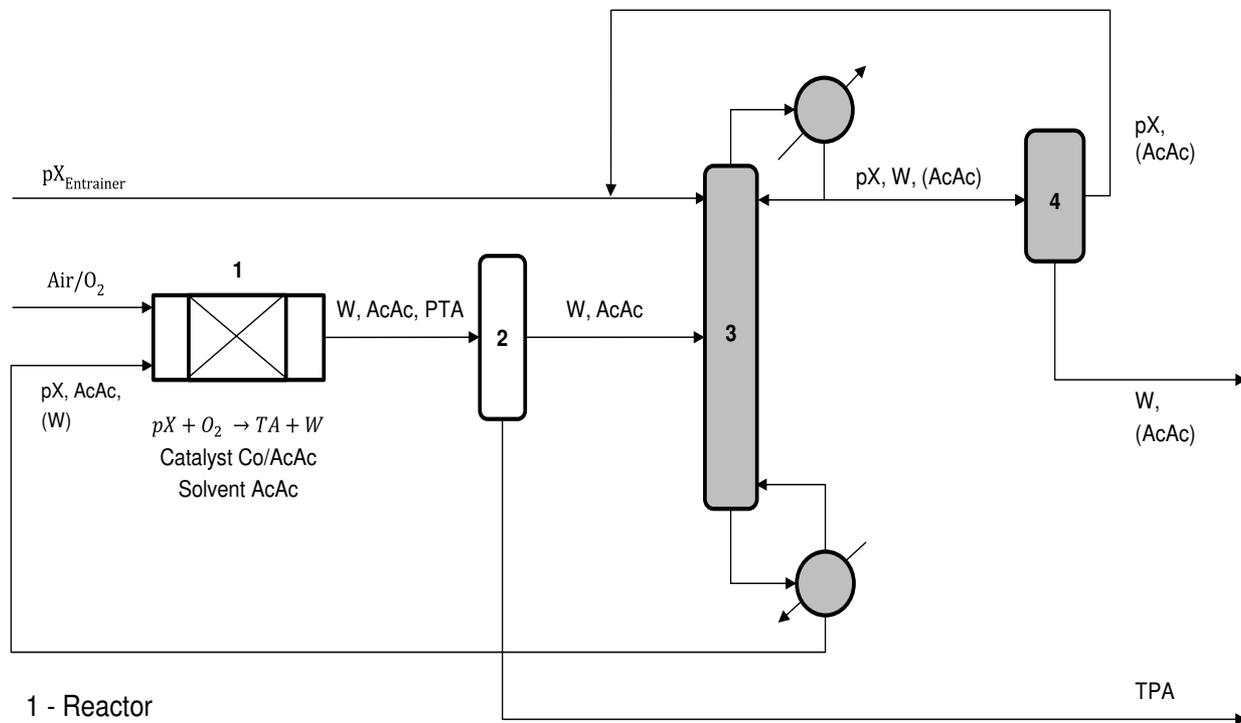
# Thermodynamic Aspects

Mean absolute deviation between VLLE experimental data and the same calculated with the UNIQUAC model using robust, non robust and database parameter.

Regression Algorithm	Aqueous phase			Organic phase			Vapour phase		
	W	p-xyl	AcAc	W	p-xyl	AcAc	W	p-xyl	AcAc
Robust (BzzMath)	0.029	0.005	0.028	0.007	0.029	0.021	0.010	0.021	0.020
PRO/II (LSA)	0.159	0.019	0.140	0.012	0.072	0.060	0.057	0.033	0.090
PRO/II (database)	0.319	0.044	0.275	0.037	0.226	0.187	0.222	0.062	0.143







- 1 - Reactor
- 2 - TPA Separator
- 3 - Heteroextractive Distillation
- 4 - Decanter

The miscibility gap between W and pX is exploited to separate the distillate stream in a decanter where an aqueous and an organic phase are obtained. The organic phase is composed of nearly pure pX that is recycled back to the top section of the column, while the aqueous stream with traces of AcAc is withdrawn and sent to wastewater treatment. From the bottom of the heteroextractive column, a stream composed by AcAc and the excess of the extractive entrainer is conveniently recycled back to the catalytic reactor where pX is converted to TPA and W with oxygen (eventually from air), using a Co/Mn based catalyst and AcAc as solvent.

**Two different optimizers** are compared in the following: the one available within the SimSci PRO/II commercial software and the BzzMath robust optimizer belonging to the homonymous C++ numerical library



# Process optimization



The process optimization/scale up has been performed at different levels.

- 1) At first, the **single heteroextractive column configuration** for the separation of W / AcAc mixtures is considered, in order to have a base-case for the comparison between the two optimizers.
- 2) In a second stage, the abovementioned downstream operation is tailored to the **PTA production process**, for which specific economical and operational considerations could be attained. In this case, the **double column configuration** is assessed, in which the first column is a conventional distillation column that operates a first cut between W and AcAc in the region not interested by the tangent pinch, whereas the second heteroextractive column refines the cut up to the target product specification.
- 3) Finally, **the overall process** is taken into consideration by adding the PTA catalytic reactor section to the downstream section with suitable recycles, in order to derive **global material balances and global performances** of the overall process.

In order to find the best plant configuration **an economic-based optimization must be solved.**

We define:

- the capital required for the purchase and construction of the plant: **CAPEX, i.e. CAPital EXpensive**
- the money needed to run the plant, ie. The annual operative costs: **OPEX, i.e. OPerative EXpensive**

the CAPEX are only one cost, that is only at the beginning of the life of the plant, which has as its unit of measure \$, while OPEX are an expense that is presented annually for the entire life of the plant and thus will have as unit of measure \$ / year.

$$Total\ Annual\ Cost = TAC = \frac{CAPEX}{AA} + OPEX$$

- Operating costs include entrainer and duties costs
- Column investment costs include trays, column, condenser and reboiler installation and purchase costs, which depend on the value of the optimization variables.

$$TAC(\mathbf{x}) = \frac{C_{inv}}{\text{payback time}} + C_{op} = \left( \frac{C_{col} + C_{trays} + C_{reb} + C_{cond}}{\text{payback time}} \right) + C_{steam} + C_{cw} + C_{pX}$$

The **Guthrie Equations** (Guthrie 1969) allow, through the aid of cost indexes, to correlate the price of individual devices of a process to the operational and geometric features of the same devices.

The generic structure of these formulas can be summarized as follows

$$Cost_o = a \frac{M \& S}{280} L_1^b L_2^c F_p F_M$$



- M&S represents the index of the cost of Marshall and Swift
- 280 is the value of M&S in 1969 (the year in which these relations have been proposed);
- $L_1$  and  $L_2$  represent the characteristic size of the equipment in question (not always both are present);
- $F_p$  and  $F_M$  are factors which take account of the pressure and the material of the equipment. For this reason they are often defined pressure factor and material factor.
- $a$  is an economic variable adaptive which calculates the cost of the equipment in the year that have been proposed these equations (1969).

**Marshall & Swift Equipment Cost Index** was created to make comparisons between two former quarters or years. Index comparisons are developed by dividing the index for the date for which a cost is desired by the index for the date of the known cost and multiplying the resulting factor by the known cost. The **Marshall & Swift Equipment Cost Indexes** are based on a national average for 47 different industries. A cost index is made up of a market basket of equipment and indicates the general direction in which equipment costs are moving. They represent an estimate of the trends in installed equipment costs from 1914 to date.

### Marshall and Swift Equipment Cost Index

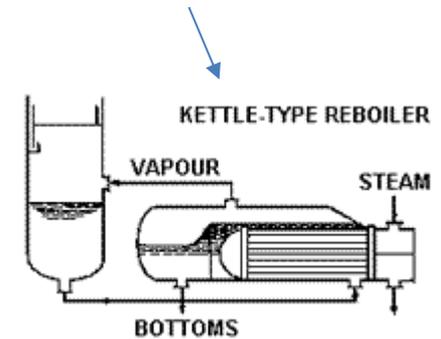
Year	All Industries	Process Industry
1995	1027.5	1029.0
1996	1039.2	1048.5
1997	1056.8	1063.7
1998	1061.9	1077.1
1999	1068.3	1081.9
2000	1089.0	1097.7
2001	1093.9	1106.9
2002	1104.2	1116.9
2003	1123.6	

in order to actualize a cost can be used, in general, the indices of cost according to the relation:

$$Costo_{attuale} = Costo_{anno\_rif.} \left( \frac{M \& S_{attuale}}{M \& S_{anno\_rif.}} \right)$$

## DISTILLATION COLUMN: CAPEX

APEX costs are mainly due to the materials necessary to the construction of the equipment, namely that for the vessel of the tower, for trays, for the reboiler Kettle and the head condenser



**1) The cost of the vessel** is a function of the height (H) and diameter (D) of the tower

$$Costo_{Vessel} [\$] = \left( \frac{M \& S}{280} \right) 101.9 D^{1.066} H^{0.82} (2.18 + F_C)$$

$F_C$  is the factor that takes into account the operating conditions and is defined as:

$$F_C = F_M F_P$$

Because of the presence of acetic acid in the system the use of Carbon Steel is not possible due to the corrosion problems. For which it will be necessary to use, at least, Stainless Steel which corresponds to a value equal  $F_M$  2,25.

The column works at atmospheric pressure, then  $F_P=1$ .

The height  $H$  of the column will be a function of the number of stages used to carry out the distillation

$$H_{col} = 0.6096(N_{Piatti} - 1) + 4.6$$

## 2) The cost of the tray

The plates are spaced by a distance ( $s$ ) equal to about 2 feet (about 60 centimeters) in a manner that allows the maintenance manual inside the tower. The unit cost will be a function of the area and therefore of the diameter of the column.

$$Costo_{Piatto} [\text{\$}] = \left( \frac{M \ \& \ S}{280} \right) 4.7 D^{1.55} s F_C$$

The diameter,  $D$ , must be entered in ft. Multiplying this value by the total number of plates the total cost is obtained

$F_C$  in this case will be a function of the type of tray ( $F_R$ ), of the material ( $F_M$ ) and the spacing between one another ( $F_d$ ).

$$F_C = F_R + F_d + F_M$$

Considering a distance,  $s$ , equal to 2 ft, from tables of literature (Douglas 1988), the factor  $F_d$  will be unitary. It is assumed to use perforated plates in standard Stainless Steel which corresponds to a value of  $F_R$  equal to zero and  $F_M$  equal to 1.7.

### 3) The cost of the heat exchanger

As for the heat exchangers their characteristic parameter is their exchange area (A, in the following formula expressed in ft<sup>2</sup>) or the power (Q, expressed in kcal / h) in them exchanged, if you consider a fluid service in conditions of phase transition.

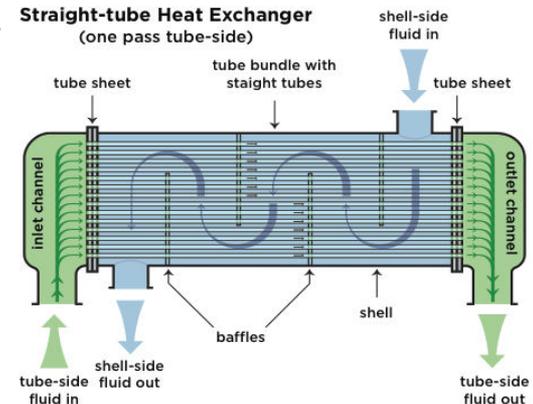
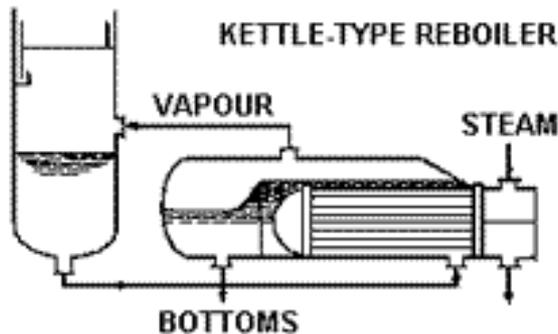
$$Costo_{Scambiatore} [\text{\$}] = \left( \frac{M \ \& \ S}{280} \right) 101.3 A^{0.65} (2.29 + F_C)$$

The factor  $F_C$  will be a function of the type of the heat exchanger, the material of construction and the operating pressure according to the relation

$$F_C = (F_d + F_P) F_M$$

The construction material will once again Stainless Steel ( $F_M$  equal to 2.81). The operating pressure is equal to one atmosphere ( $F_P$  equal to zero).

The bottom reboiler is of Kettle type, which corresponds to a  $F_d$  equal to 1.35, while the head condenser is a heat exchanger with fixed tube ( $F_M$  equal to 0.8).



Once all the parameters presented above were calculated, it is possible to evaluate the investment capital of the azeotropic distillation column with the equation:

$$CAPEX[\$] = Costo_{Vessel} + Costo_{piatti} + Costo_{Kettle} + Costo_{Condensatore}$$

## DISTILLATION COLUMN: OPEX

OPEX includes all the costs of the facility, i.e the cost of utilities, the cooling water for the condenser, the low pressure steam to the reboiler and the cost of entrainer. All these parameters were taken from the devoted literature (Turton, Bailie et al. 2009).

Price of the main utilities used in the chemical industry

Utility	Description	Cost \$/GJ	Cost \$/Common Unit
Air Supply	Pressurized and dried air (add 20% for instrument air) a. 6 barg (90 psig) b. 3.3 barg (50 psig)		\$0.49/100 std m <sup>3</sup> * \$0.35/100 std m <sup>3</sup> *
Steam from Boilers	Process steam: latent heat only a. Low pressure (5 barg, 160°C) from HP steam With credit for power Without credit for power b. Medium pressure (10 barg, 184°C) from HP steam With credit for power Without credit for power c. High pressure (41 barg, 254°C)	13.28 14.05 14.19 14.83 17.70	\$27.70/1000 kg \$29.29/1000 kg \$28.31/1000 kg \$29.59/1000 kg \$29.97/1000 kg
Steam Generated from Process	Estimate savings as avoided cost of burning natural gas in boiler	12.33	
Cooling Tower Water	Processes cooling water: 30°C to 40°C or 45°C	0.354	\$14.8/1000 m <sup>3</sup> †
Other Water	High-purity water for a. Process use b. Boiler feed water (available at 115°C)‡ c. Potable (drinking) d. Deionized water		\$0.067/1000 kg \$2.45/1000 kg \$0.26/1000 kg \$1.00/1000 kg
Electrical Substation	Electric Distribution a. 110 V b. 220 V c. 440 V	16.8	\$0.06/kWh
Fuels	a. Fuel oil (no. 2) b. Natural gas c. Coal (f.o.b. mine mouth)	14.2 11.1 <sup>§</sup> 1.72	\$549/m <sup>3</sup> \$0.42/std m <sup>3</sup> * \$41.4/tonne
Refrigeration	a. Moderately low temperature Refrigerated water in at T = 5°C and returned at 15°C b. Low temperature Refrigerant available at T = -20°C c. Very low temperature Refrigerant available at T = -50°C	4.43 7.89 13.11	\$0.185/1000kg Based on process cooling duty

Table 2: Utilities and entrainer costs (Turton et al., 2008).

	<b>Cost</b>	
p-xylene	1400	\$/ton
Steam	7.78e-6	\$/kJ
Cooling water	3.54e-7	\$/kJ

## Entrainer (p-xylene) cost

From the same source earlier you can get a price of p-xylene equal to \$ 1,135 / kg for the year 2000.

In order to have a more updated value applies the previous relation going to evaluate this parameter to 2011 being Note the respective indices of Marshall & Swift (respectively from 1103 to 2000 and 1536.5 to 2011). The updated price is thus equal to \$ 1.5812 / kg.

In order to calculate the value of the OPEX is necessary annualize the feedback of such costs by using the following relations

$$Costo_{Acqua} \left[ \frac{\$}{y} \right] = P_{acqua} h_{marcia} (Q_{cond})$$

$$Costo_{Vapore} \left[ \frac{\$}{y} \right] = P_{Vapore} h_{marcia} (Q_{Reb})$$

$$Costo_{pX} \left[ \frac{\$}{y} \right] = P_{pX} h_{marcia} (F_{pX})$$

- $P_i$  is the price or per unit of power supplied (in the case of water and steam) or per unit mass (in the case of entrainer);
- $H_{marcia}$  indicates the hours of operation of the plant in a year (in the present case it is assumed that the plant works throughout the year for a total of 8760 h=24h/d\*365d).
- $F_{pX}$  represents the mass flow rate of p-xylene make - up of the plant.

For which the operating costs will be given by the sum of these three contributions

$$OPEX \left[ \frac{\$}{y} \right] = Costo_{Vapore} + Costo_{Acqua} + Costo_{pX}$$

## Minimization of a objective function (TAC)

The minimization of the objective function (Total Annual Cost) is subject to MESH equations of the distillation column, purity specification constraints and optimization variables bounds reported in the following Tables.

Purity specifications.

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### Purity specification

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AcAc in the aqueous stream	$\leq 5000$ ppm
W in the bottom	$< 3$ % w/w

---

First guess and lower and upper bound of the optimization variables.

⊕

<b>x</b>	<b>Optimization variable</b>	<b>Lower bound</b>	<b>First guess</b>	<b>Upper bound</b>
x <sub>1</sub>	Total entrainer flowrate [kmol/h]	30	150	500
x <sub>2</sub>	Reflux Ratio	0.2	2.2	6.5
x <sub>3</sub>	Entrainer inlet stage	1	1	2
x <sub>4</sub>	Number of stages	2	27	100
x <sub>5</sub>	Feed inlet stage	4	15	100
x <sub>6</sub>	Feed temperature [K]	298	363	363
x <sub>7</sub>	Entrainer temperature [K]	298	353	393

**MESH** is an acronym referring to the different types of equation that are used in the model:

**M** stands for material balances

**E** stands for equilibrium relationships (to express the assumption that the streams leaving the stage are in equilibrium with each other)

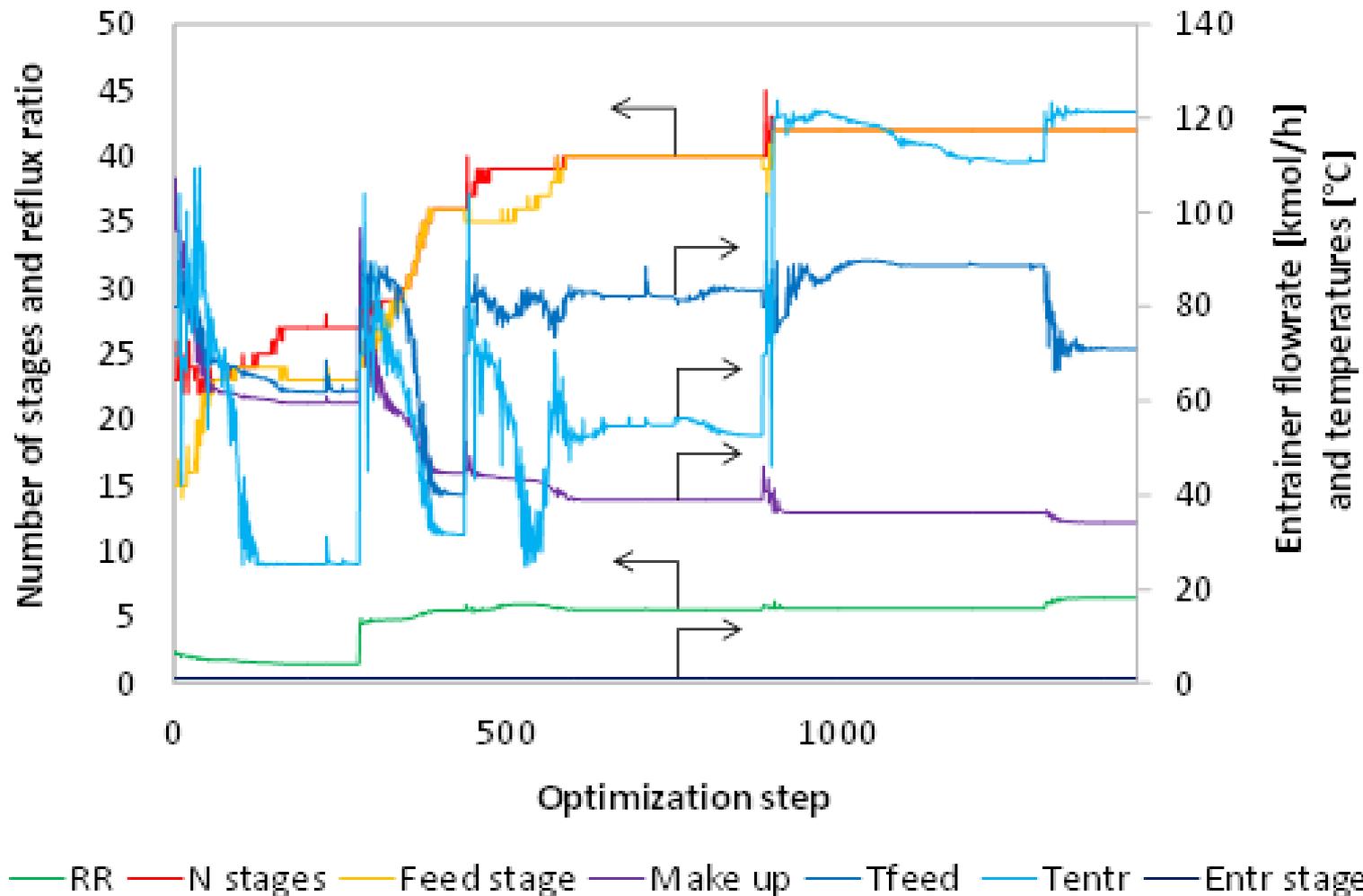
**S** stands for summation equations (mole fractions)

**H** stands for heat or enthalpy balances (processes conserve energy, as well as mass).

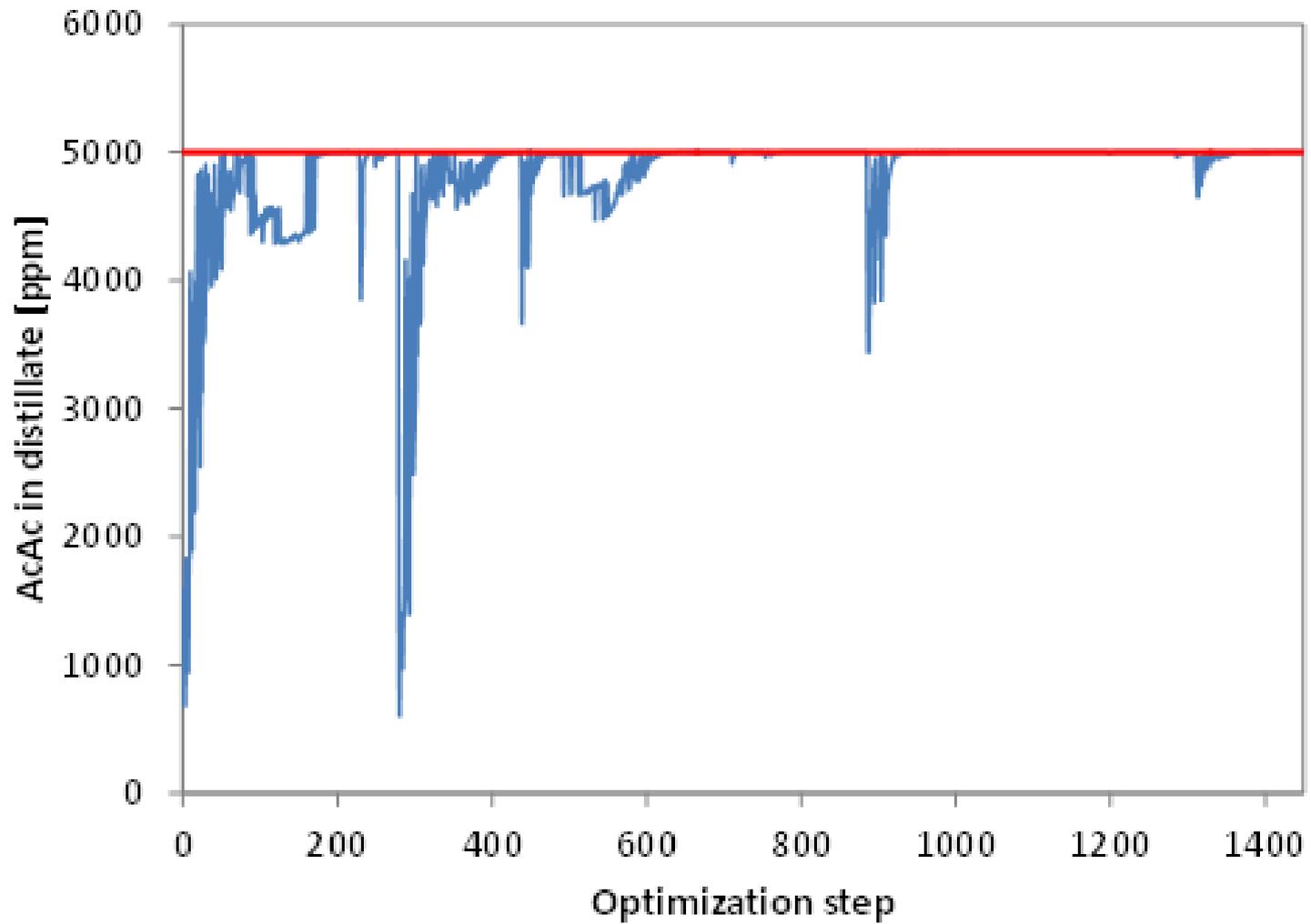


Cost and optimization variables evolution along the optimization steps are shown in the following four Figures:

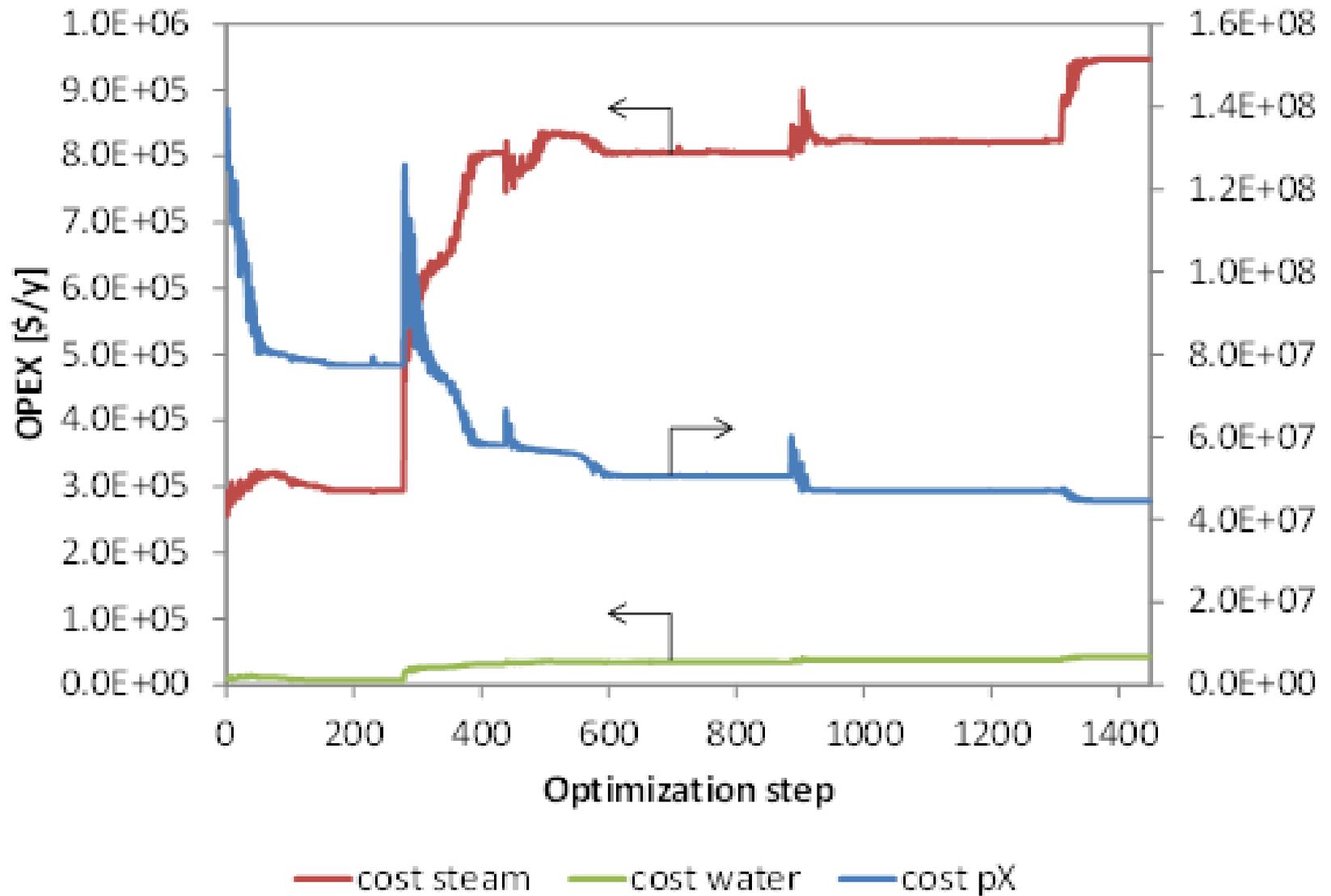
**Optimization variables**



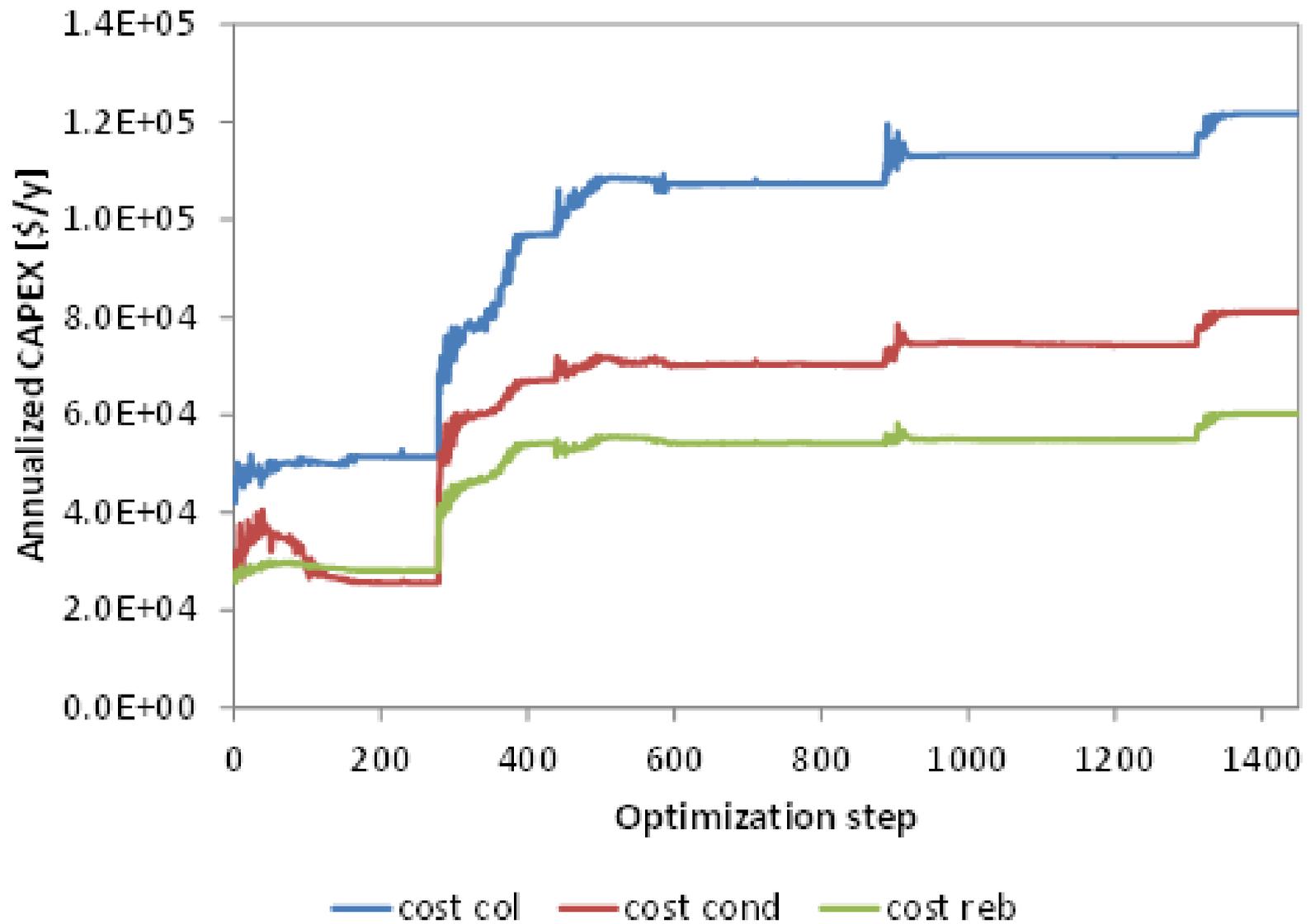
## Purity specification



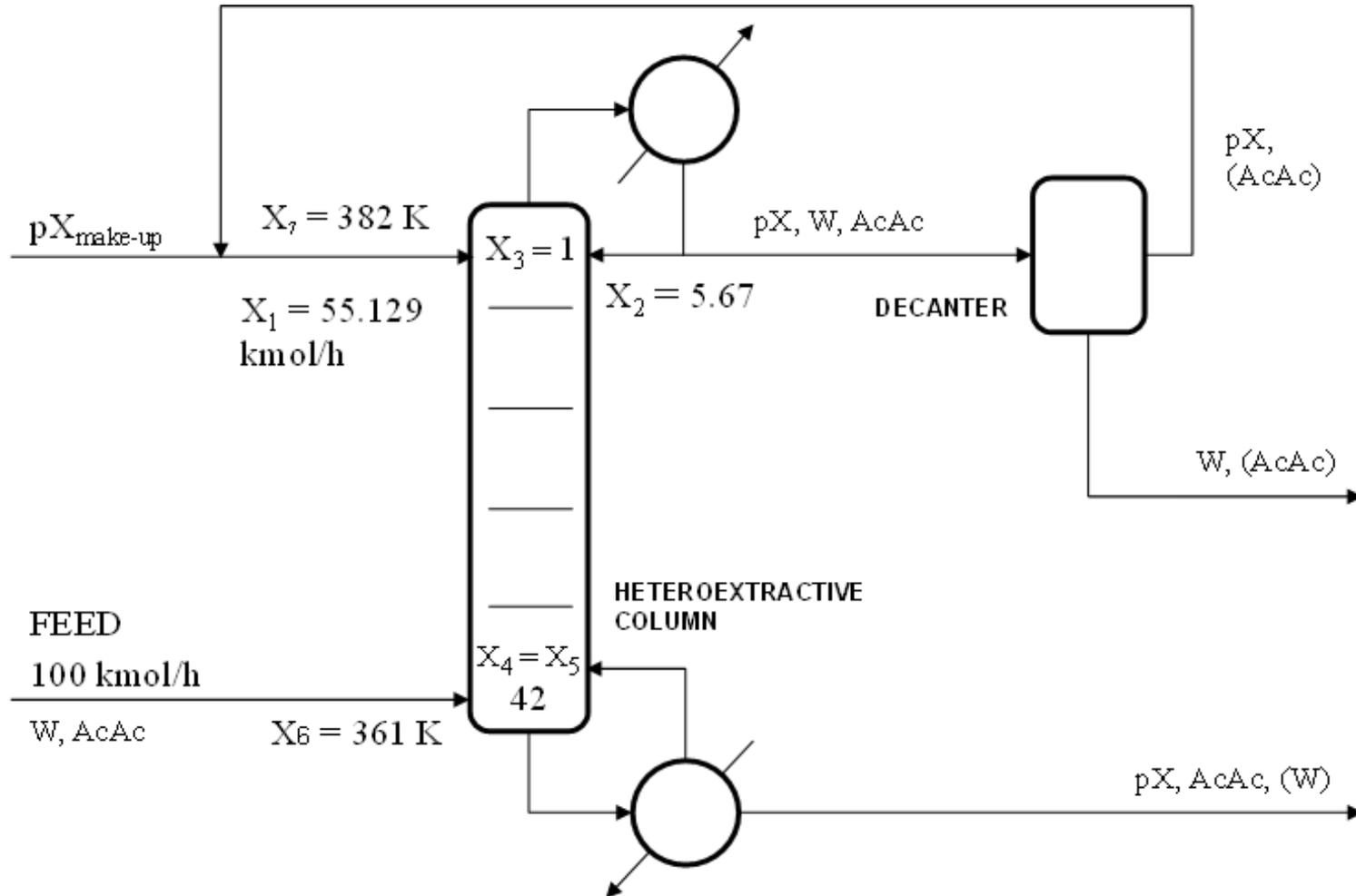
# OPEX



# CAPEX



Optimized configuration of the single heteroextractive column (BzzMath optimizer).  $X_1$  is the total pX flowrate,  $X_2$  is the reflux ratio,  $X_3$  is the entrainer stage,  $X_4$  is the number of stages,  $X_5$  is the feed stage,  $X_6$  is the feed temperature and  $X_7$  is the entrainer temperature



## Results discussion:

Optimization results immediately show that the Total Annual Cost of the column is **deeply dependent from the cost of the entrainer make-up.**

For this reason the optimizer increases the number of stages in order to have a lower pX flowrate required to achieve the specifications.

In fact, the cost of the column grows from the first guess up to the end of the optimization but its weight on the total cost is much lower than the entrainer one.

Moreover, the purity constraint is always fulfilled.

## Optimization of the single column by PRO II

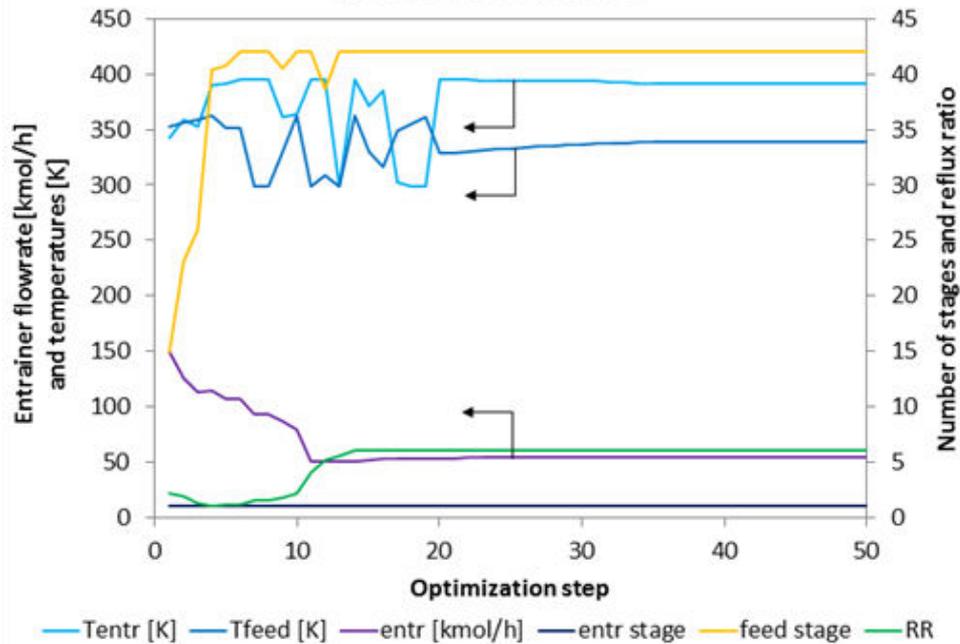
Unfortunately, the commercial optimizer does not allow selecting the number of stages as an optimization variable.

Consequently, in order to have a reasonable comparison, two different optimizations are proposed:

- the first one with the same starting point for both the BzzMath and PRO/II optimizers (PRO/II A),
- the second one with the optimal number of stages obtained from the BzzMath economic optimization (PRO/II B).

The *PRO/II Calculator* has been adopted for the evaluation of the costs, while the *PRO/II Optimizer* has been adopted for the optimization

### Optimization variables

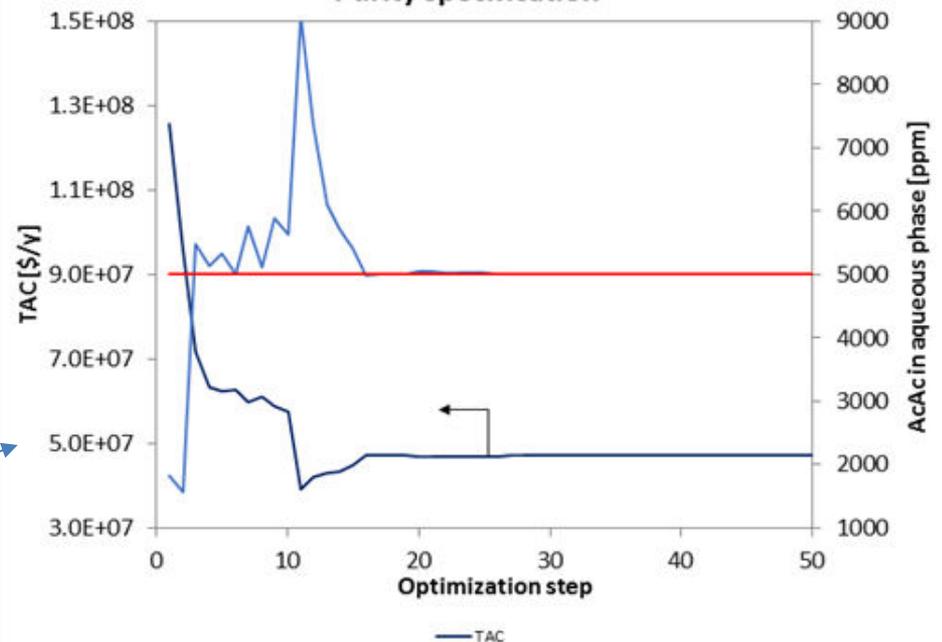


*Trends of the manipulated variables and TAC and purity specification during the optimization with PRO/II (case B).*

the reflux ratio is progressively increased to satisfy the purity specification with less amounts of entrainer, which is reduced due to its corresponding high OPEX

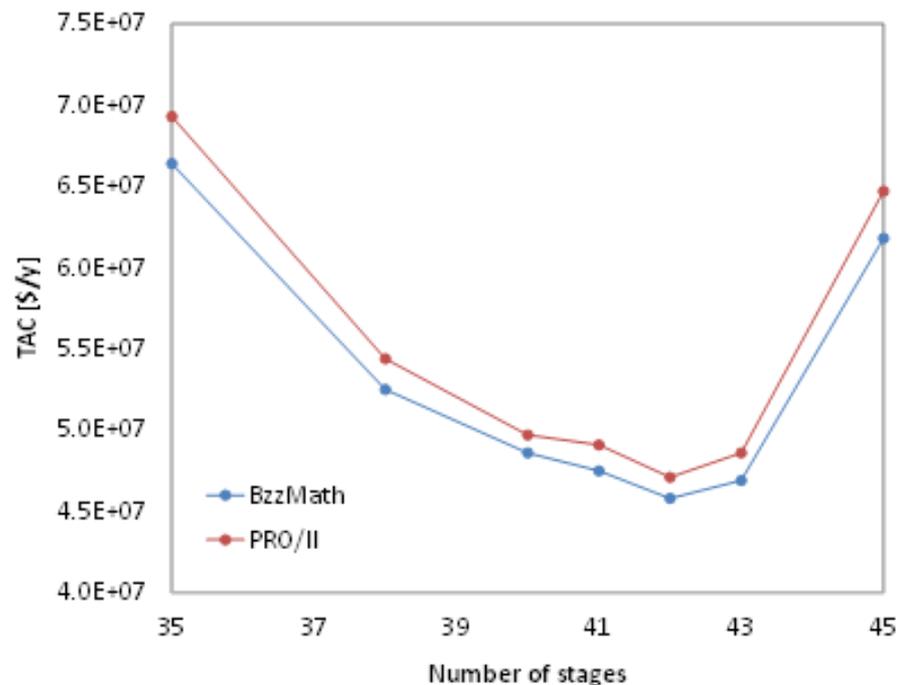
PRO/II optimizer violates the bound in the first 20 iteration steps, reaching lower values of TAC. At the end, to satisfy the purity constraint a higher value of TAC is obtained with respect to the BzzMath robust optimizer

### Purity specification



## Summary of the results of the three optimization studies

	Entrainer RR [kmol/h]	Entrainer N stage	Entrainer N stages	Feed stage	T feed [K]	T entr [K]	TAC [\$/y]
<i>Results considering the cost of make-up pX</i>							
First guess	150	2.2	1	23	15	353	1.25E+08
BzzMath	55.129	5.67	1	42	42	361	4.58E+07
PRO/II A	136.8	1.1	1	23	23	346	7.67E+07
PRO/II B	56.8	5.9	1	42	42	338	4.71E+07

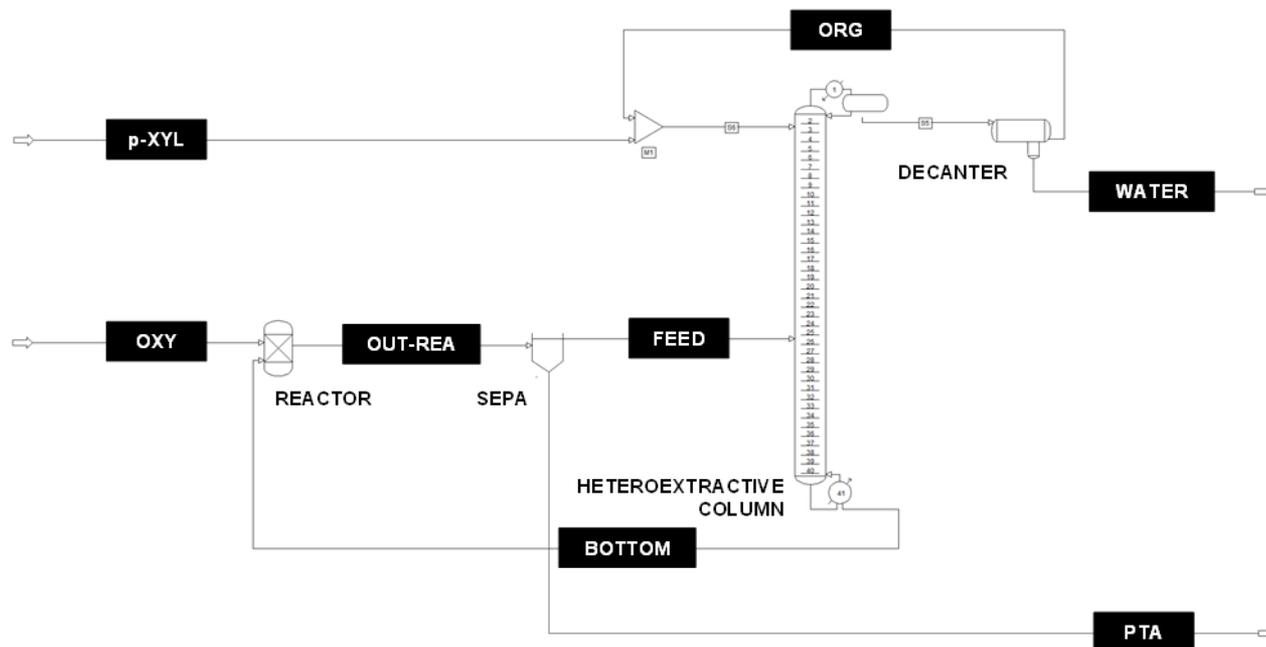


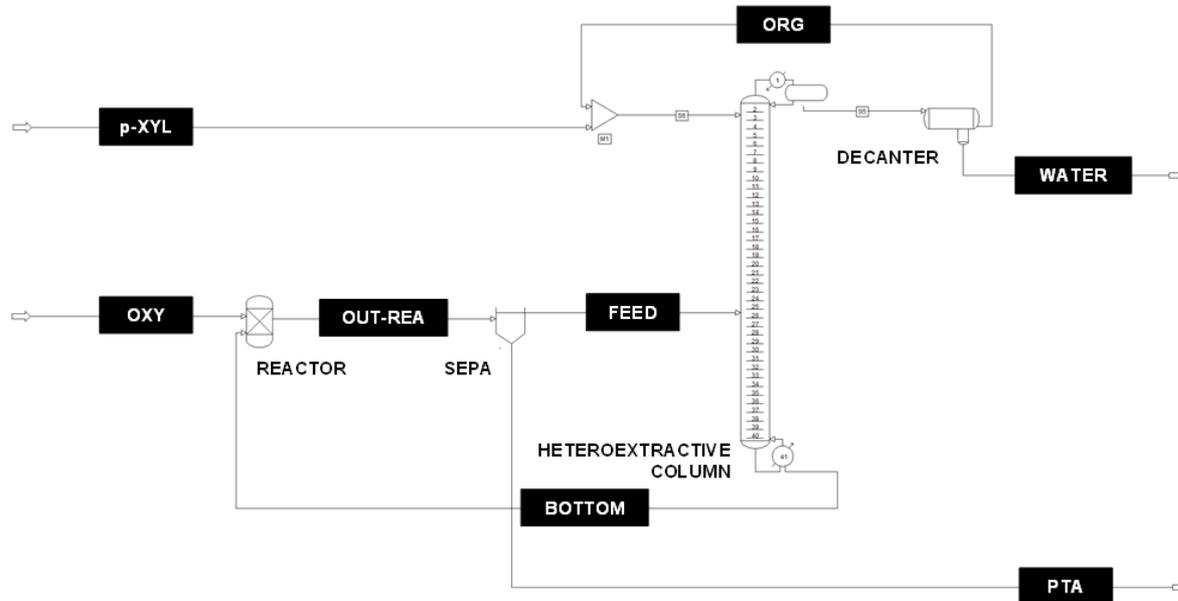
An average economical saving of about 3.5 % is realized with the robust optimizer

## Robust optimization of the PTA downstream section

In the previous part the optimization of a single heteroextractive column has been presented focusing on the comparison between the performance of the two optimizers, whereas in this part the integration of the technology within the PTA production process is addressed.

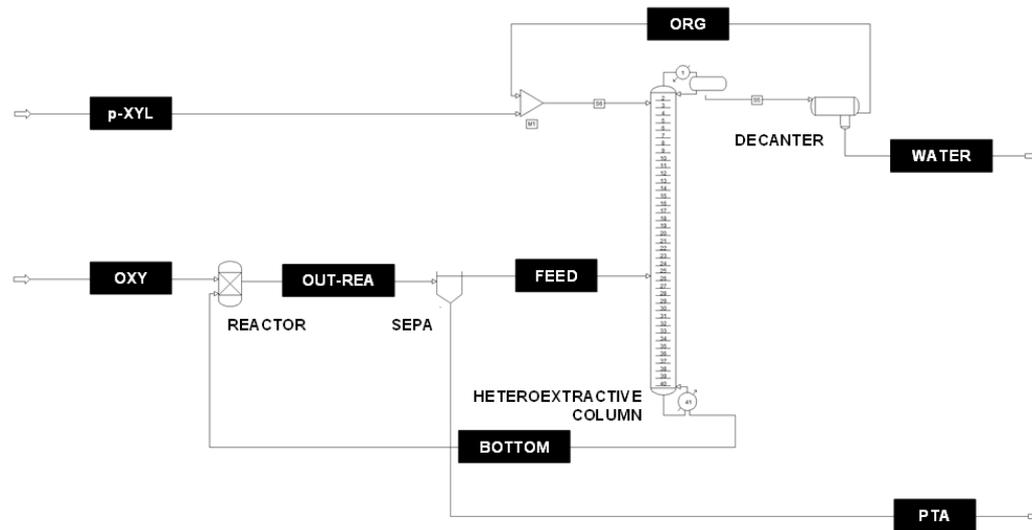
**Two different process configurations are considered: the single column and the double column configurations.** For both of the proposed solutions, a robust optimization with the BzzMath optimizer has been performed





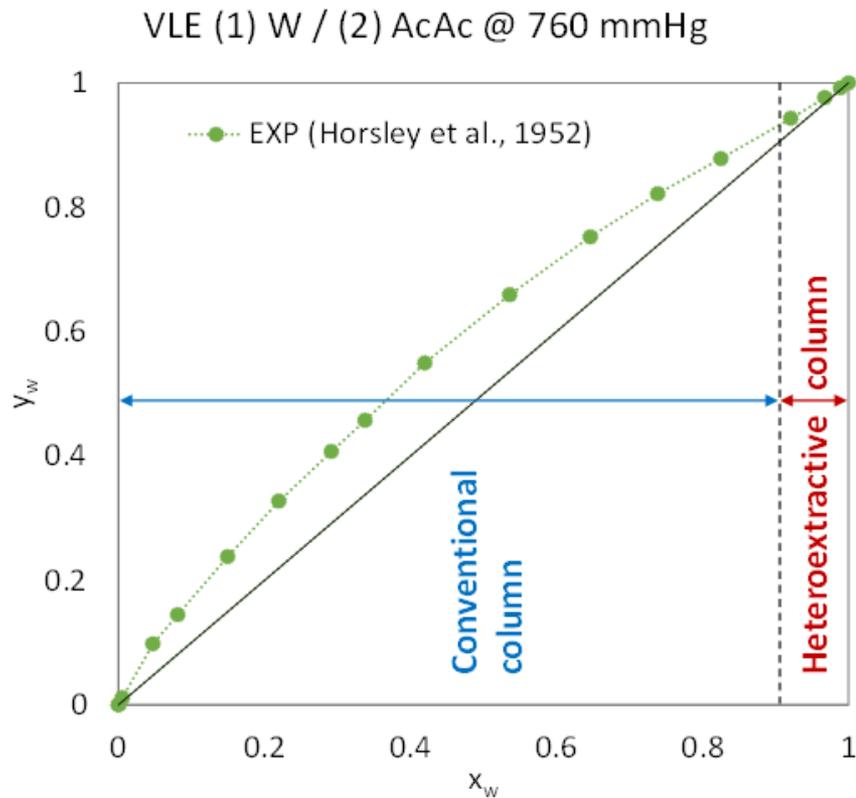
pX is the raw material for the catalytic synthesis and it is already purchased as the main reactant fed to the reactor. Moreover, the bottom of the heteroextractive column is composed of a mixture of AcAc and pX, which are the solvent and the reagent respectively, ready to be sent to the reactor. For this reason, in the case of TPA production process, pX cost is not related to downstream operation and it should not be considered in the economical objective function.

In this case, the increase of the make-up entrainer flowrate does not imply an extra OPEX, but simply results in a distillation column with a higher diameter and a smaller number of stages required to reach product purity specifications. In other words, the trade-off becomes between column height and column diameter.



With this last assumption, the optimization of the single heteroextractive column is performed without considering the cost of pX, and assigning a value of make-up entrainer (pX) flowrate coherent with the flowrate of water fed to the downstream section, which is produced in the PTA synthesis (molar ratio  $W:pX = 2:1$ ). This upper bound on the make-up pX is imposed in order to limit the amount of pX withdrawn from the bottom of the column and to avoid the use of an additional expensive recovery distillation column to recycle extra pure pX to the heteroextractive column.

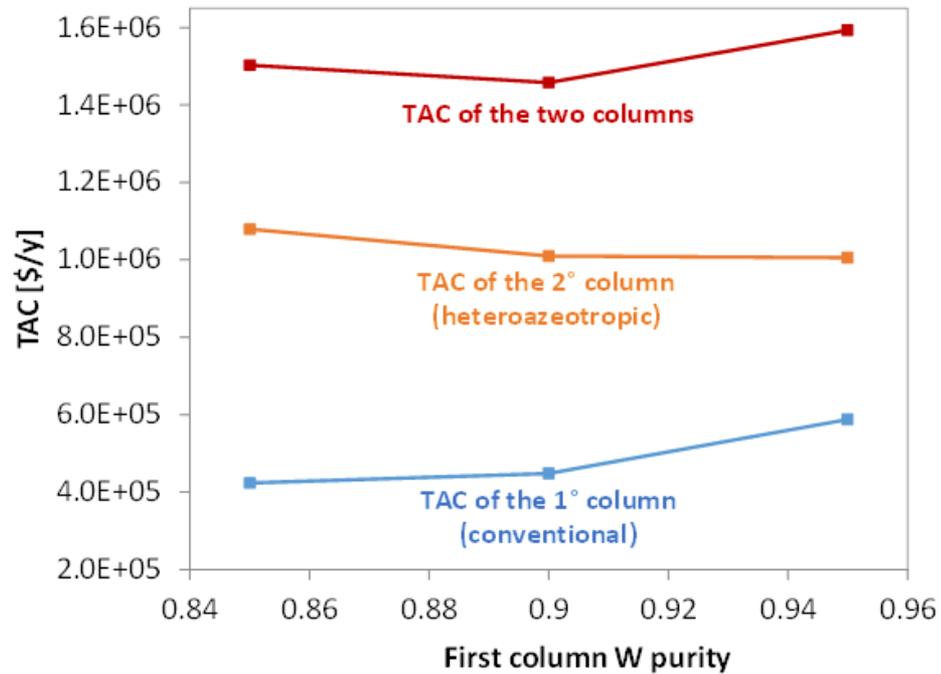
**The double column configuration is addressed and compared with the single column configuration** in order to study the trade-off between the extra CAPEX of the additional conventional column and the reduced OPEX and CAPEX of the second heteroextractive column. According to this process solution, the first conventional distillation column operates a preliminary cut between W and AcAc without the addition of pX. The separation is realized in the VLE region not interest by the tangent pinch on the water pure end



The optimization is carried out sequentially, by optimizing at first the conventional distillation column with three possible water compositions in the distillate (molar fractions of 0.85, 0.90 and 0.95). Distillate composition, temperature and flowrate are then used to feed the second heteroextractive distillation column, which is optimized as well.

	<b>TAC I column</b> [\$/y]	<b>TAC II column</b> [\$/y]	<b>TAC (global)</b> [\$/y]
<i>Results without considering the cost of <u>pX</u> make-up</i>			
Single column	-	-	1.08E+06
Double columns 0.85	4.24E+05	1.08E+06	1.50E+06
Double columns 0.90	4.48E+05	1.01E+06	1.45E+06
Double columns 0.95	5.87E+05	1.01E+06	1.59E+06

**The single column configuration results in a lower TAC with respect to the double column configuration, because the extra CAPEX of the first distillation column is greater than the reduction of OPEX (less entrainer and thus smaller duties) and CAPEX (smaller column) of the heteroextractive column.**



Total Annual Cost of the double column configuration as a function of the distillation cut between the two columns (i.e. W distillate purity of the first column).

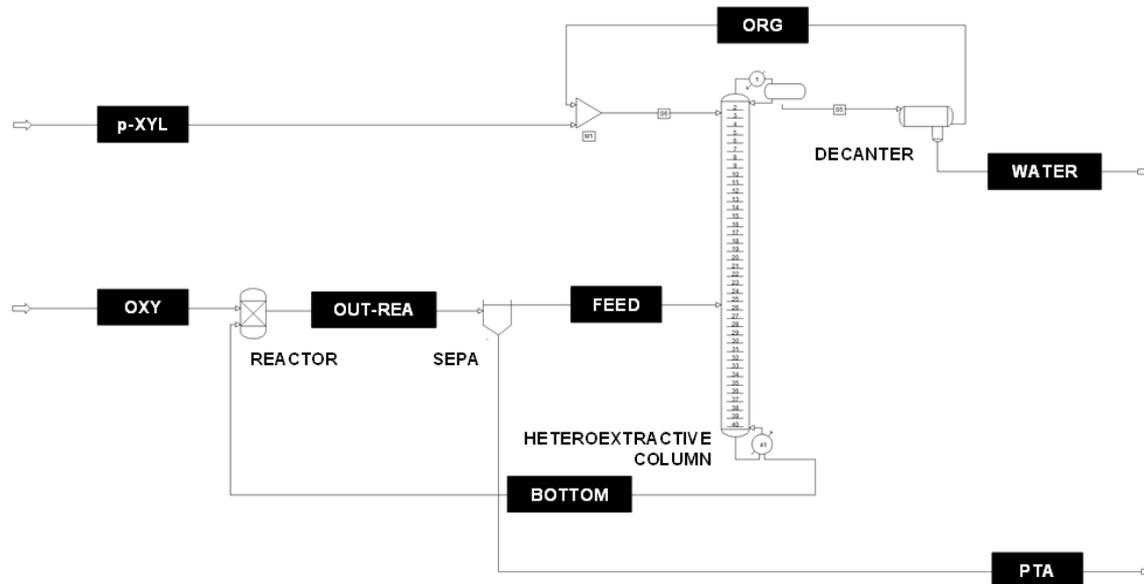
## Economical comparison with others entrainer proposed in literature

The economics and operability of this heterogeneous extractive distillation becomes appealing in particular considering the TPA production process, also in comparisons with different configurations proposed in literature

<b>Entrainer</b>	<b>TAC [\$/y]</b>	<b>TAC/FEED [\$/y]</b>
pX	1.08E+06	1.08E+04
ethyl-acetate	1.64E+05	1.28E+04
i-buthyl acetate	1.03E+05	8.04E+03
n-buthyl acetate	1.73E+05	1.35E+04

i-buthyl acetate allows to reach a lower TAC than pX, which, in turn, is more economically sustainable than ethyl-avcetate and n-buthyl acetate. Moreover, **using pX, no contamination of products with additional chemicals occurs.**

# Final process optimization



The synthesis reactor is simulated with a conversion reactor and PTA is recovered from the reactor outlet stream composed by a PTA / W / AcAc mixture with an ideal separator (SEPA). Make-up pX, mixed with the recycle pX from the decanter, is fed to the top of the heteroextractive column, which is required to separate the AcAc / W mixture. Water is withdrawn from the decanter, while the AcAc / pX mixture is recycled back to the reactor along with the oxidizer (OXY).

	<b>pXYL</b>	<b>OXY</b>	<b>OUT-REAPTA</b>	<b>FEED</b>	<b>ENTR</b>	<b>DIST</b>	<b>WATER</b>	<b>ORG</b>	<b>BOTT</b>	
Flowrate [kg/h]	2410.4	21.83.0	8034.5	3774.8	4259.6	4171.1	2582.4	823.9	1760.7	5855.6
Flowrate [kmol/h]	22.74	68.22	132.39	22.74	109.65	39.35	62.17	45.56	16.61	86.95
XAcAc	0	0	0.410	0	0.496	0	0.001	0.002	0	0.626
XpXYL	1	0	0	0	0	1	0.267	0	1	0.262
XW	0	0	0.420	0	0.504	0	0.732	0.998	0	0.112
XO2	0	1	0	0	0	0	0	0	0	0
XPTA	0	0	0.170	1	0	0	0	0	0	0



# List of Symbols

Symbol	UOM	Description
TAC	[\$/year]	Total annual cost
<u>C<sub>inv</sub></u>	[\$]	Investment costs (CAPEX)
C <sub>op</sub>	[\$/year]	Annual operational costs (OPEX)
<u>C<sub>col</sub></u>	[\$]	Column investment cost
<u>C<sub>trays</sub></u>	[\$]	Trays investment cost
<u>C<sub>reb</sub></u>	[\$]	Reboiler investment cost
<u>C<sub>cond</sub></u>	[\$]	Condenser investment cost
<u>C<sub>steam</sub></u>	[\$/year]	Steam annual cost
<u>C<sub>cw</sub></u>	[\$/year]	Cooling water annual cost
<u>C<sub>pX</sub></u>	[\$/year]	pX annual cost
M&S	[-]	<u>Marshall&amp;Swift</u> Index
D	[ft]	Column diameter
H	[ft]	Column height
F <sub>c</sub>	[-]	Correction factor (Douglas et al., 1988)
s	[ft]	Tray spacing
<u>Q<sub>cond</sub></u>	[kcal/h]	Condenser duty
<u>Q<sub>reb</sub></u>	[kcal/h]	Reboiler duty
<u>N<sub>stages</sub></u>	[-]	Number of stages
F	[ <u>kmol/h</u> ]	Molar flowrate
<i>Subscripts</i>		
TPA		Terephthalic acid
W		Water
AcAc		Acetic acid
<u>pX</u>		p-xylene

