
Dr. Jordi Bonet i Ruiz
Departament Enginyeria Química

Dr. Alexandra Elena Bonet Ruiz
Departament Enginyeria Química



Treball Final de Grau

Simulation of the acetic acid dehydration collected from terephthalic acid production

Simulació de la deshidratació de l'àcid acètic provinent de la producció d'àcid tereftàlic

Daniel Ortuño Boter

June 2015



Dos campus d'excel·lència internacional

B:KC Barcelona Knowledge Campus

HUB Health Universitat de Barcelona Campus

Aquesta obra esta subjecta a la llicència de:
Reconeixement–NoComercial–SenseObraDerivada



<http://creativecommons.org/licenses/by-nc-nd/3.0/es/>

REPORT

CONTENTS

1. SUMMARY	3
2. RESUM	5
3. INTRODUCTION	7
3.1. TEREHPHTHALIC ACID	7
3.1.1. Manufacturing process and solvent recover	7
3.2. AZEOTROPIC DISTILLATION	8
3.2.1. Heterogeneous Azeotropic Distillation	9
3.2.1.1. <i>Organic acids dehydration</i>	11
3.2.1.2. <i>State of the art</i>	12
3.2.2. Fundamentals	13
3.2.2.1. <i>Residue curves maps</i>	14
3.2.2.1.1. <i>Mathematical model for residue curves</i>	16
3.2.2.2. <i>Topology of the residue curve maps and distillation regions</i>	17
4. OBJECTIVES	21
5. METHODOLOGY	22
5.1. SOFTWARE TOOLS	22
5.2. SYSTEM CHARACTERISTICS	22
5.3. THERMODYNAMIC MODEL	23
5.4. METHODOLOGY	24
6. RESULTS	28
6.1. THERMODYNAMICS	28
6.2. METHODOLOGY RESULTS	38
6.2.1. Fix the desired purity of HAc	38

6.2.2. Formulate the overall mass balance considering two assumptions:	38
6.2.3. Select the tie line (liquid-liquid equilibrium) of the decanter system MA/water/PX that fulfils the overall mass balance	42
6.2.4. Formulate the decanter mass balance taking into account the organic and aqueous purge and recirculation currents.	44
6.2.5. Find the optimal relation between feed stage and the decanter input stream flow rate.	49
6.3. COMPARISON OF RESULTS	53
7. CONCLUSIONS	54
8. REFERENCES AND NOTES	55
9. ACRONYMS	57
APPENDICES	59
APPENDIX 1: TIE LINES VALUES	62
APPENDIX 2: IMULATION WANG AND HUANG (2012)	63
APPENDIX 3: SIMULATION WANG AND WONG (2013)	66

1. SUMMARY

Terephthalic acid is an important raw material for the production of polyethylene terephthalate (PET). It is obtained by the catalytic oxidation of p-xylene in air, in the presence of acetic acid (HAc) as solvent. Once the synthesis is done, the solvent is to be recycled and reused back to the chemical reaction media. In the reactor output residual stream, the solvent is mixed with other reaction products (great amount of water, traces of methyl acetate) and unreacted p-xylene. High investment and operating costs are required if conventional distillation is used in the HAc dehydration unit (solvent purification) due to a tangent pinch on the pure-water end in the HAc-water system. An entrainer is often introduced into the unit in order to make the separation easier by using a heterogeneous azeotropic distillation (HAD) column. Given the non-idealities, the phase splitting, the distillation boundaries present, and the possible existence of multiple steady states in such a system, such columns can be extremely difficult to simulate and to operate. This work proposes a simple methodology to simulate the described process of acetic acid recovery using a heterogeneous azeotropic distillation column. A preliminary study of the thermodynamic properties of the mixture is performed in order to understand the system behaviour and to predict possible results.

Keywords: heterogeneous azeotropic distillation, terephthalic acid production, rigorous simulation.

2. RESUM

L'àcid tereftàlic és una matèria primera important per a la producció del polietilè tereftalat (PET). S'obté de l'oxidació catalítica del p-xilè (PX) amb aire en un reactor en presència d'àcid acètic (HAc) com a dissolvent. Un cop realitzada la síntesi, el dissolvent es vol reciclar i reutilitzar al medi de reacció, però aquest surt del reactor barrejat amb altres productes de reacció: principalment aigua, i una mica de metil acetat (MA), que és un subproducte, i el p-xilè que no ha reaccionat. Es requereixen alts costos d'inversió i d'operació si s'utilitza una destil·lació convencional per a la deshidratació de l'àcid acètic degut a que existeix una zona de pinçament entre la mescla d'aigua i HAc situat a l'extrem de l'aigua pura. Un "entrainer" sovint s'introdueix a la unitat a fi de facilitar la separació mitjançant una columna de destil·lació azeotròpica heterogènia (HAD). Donades les no idealitats, la separació de fases, els límits de destil·lació presents, i la possible existència de múltiples estats estacionaris en el sistema, les columnes d'aquest tipus poden ser extremadament difícils de simular i operar. L'objectiu d'aquest treball és proposar una metodologia simple per a simular el procés descrit. Un estudi preliminar de les propietats termodinàmiques de la mescla es realitza per tal d'entendre el comportament del sistema i per predir els possibles resultats.

Paraules clau: destil·lació azeotròpica heterogènia, producció de l'àcid tereftàlic, simulació rigorosa.

3. INTRODUCTION

In this section, the motivation of the present study is described, together with basic fundamentals to support the provided information.

3.1. TEREPHTHALIC ACID

Terephthalic acid is an important raw material for the production of polyethylene terephthalate (PET). The global market for PET is around 32 million tons a year. More than 60 % of the world's PET production is for synthetic fibres (polyester), and about 13 million tons of PET are used as raw material for packages. PET is a high quality plastic that is identified with the number one or acronym PET, surrounded by three arrows on the bottom of packages made from this material, as SPI identification system (Cano, 2014).

3.1.1. Manufacturing process and solvent recover

In the process of manufacturing terephthalic acid, p-xylene (PX) is catalytically oxidized with air in a reactor in the presence of acetic acid (HAc) as solvent. The products from the condensed liquid stream of the oxidation reactor and other dilute HAc streams, comprising mostly of the oxidation by-products (methyl acetate (MA) and water) and a small part of unreacted p-xylene, are fed to a dehydration unit to recover high-purity HAc and to remove the oxidation by-products. The recovered HAc is recycled back to the oxidation reactor for reuse as the solvent, while water and MA are sent to a wastewater treatment process. (Wang and Wong, 2013) In Figure 1, the typical process of manufacturing terephthalic acid is shown, and the red dotted square indicates the scope of our study inside the global process.

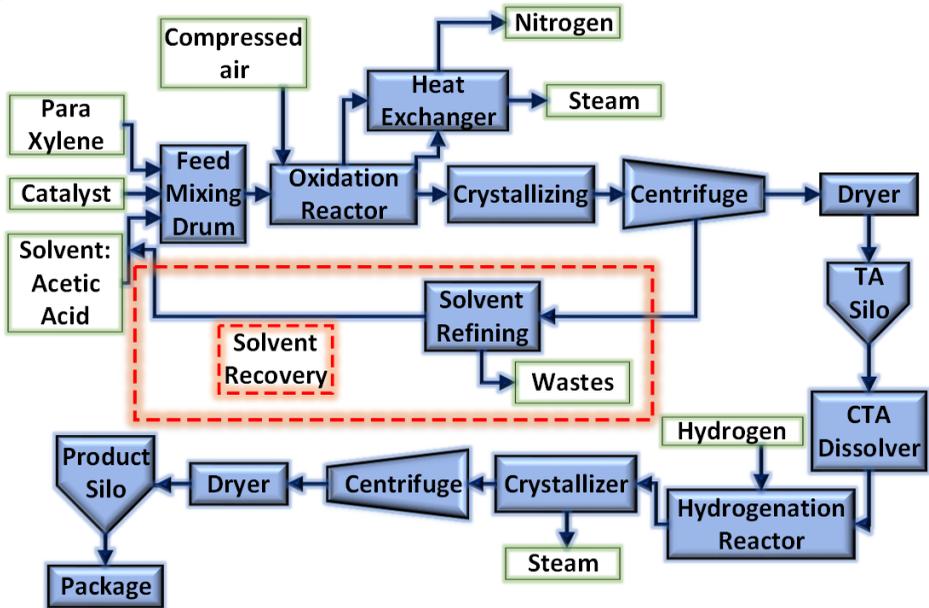


Figure 1. Typical Terephthalic Acid manufacturing process.

High investment and operating costs are required if conventional distillation is used in the HAC dehydration unit due to a tangent pinch on the pure-water end in the HAC/water system (Edge HAC/H₂O binary diagram of Figure 12).

3.2. AZEOTROPIC DISTILLATION

For narrow-boiling or even azeotropic systems, the purification is hardly or even not possible. In such a case, three well-established methods for modifying the equilibrium to allow obtaining pure products are considered first: (1) varying the pressure between two columns (pressure swing distillation), (2) adding an additional compound to influence the activity coefficients (extractive distillation), or (3) forming a better-suited multicomponent azeotropic point (azeotropic distillation) (Górak and Olujic, 2014).

In this case, pressure swing distillation was rejected due to the fact that, even increasing the pressure of the process, the tangent pinch on the pure-water end in the HAC/water system does not disappear. Extractive distillation was rejected too because, to perform this kind of distillation a minimum of two columns are needed, one to purify the desired product, and one to purify the extractive agent in order to reuse it. In literature, that the most used process to dehydrate HAC

currently is the azeotropic distillation which can be performed using only one column (Wang and Huang, 2012; Wang and Wong, 2013). For these reasons, this work is focused on the study of azeotropic distillation configuration.

By azeotropic distillation, even complex mixtures with ternary azeotropes and with demixing behaviour into a heteroazeotrope can be handled. The added compound (entrainer) produces a more suitable (at least ternary) azeotrope. As a reference, a binary azeotrope is used. A "suitable" azeotrope is one that (Górak and Olujic, 2014):

1. Shows the lowest (minimum azeotrope) or highest (maximum azeotrope) boiling point in the ternary mixture.
2. Contains a higher concentration of one of the components of the original feed mixture than any binary azeotrope.

In this study, in the ternary mixture of HAc/H₂O/PX (Figure 12), p-xylene forms a binary azeotrope with water that is located in an immiscible area and shows the lowest boiling point in the mixture. It is classified as a minimum heteroazeotrope. This azeotrope could carry the water to the top of the column leaving the HAc pure at the bottom of the column, and later the PX/water azeotrope could be broken in the decanter with a liquid phase splitting, reaching high purities of each product. This process is called heterogeneous azeotropic distillation.

3.2.1. Heterogeneous Azeotropic Distillation

Heterogeneous azeotropic distillation exploits differences in volatility and liquid-liquid phase split by linking a distillation column and a decanter. Therefore, it may also be interpreted as a hybrid separation process. Liquid phase splitting in the decanter facilitates breaking of the azeotrope to reach high purity products. Heteroazeotropic distillation is therefore used for the separation of heterogeneous azeotropic mixtures; it also offers a favourable option for the separation of homogeneous azeotropic mixtures if an entrainer is added to induce a liquid-liquid phase split.

For ternary mixtures, the feasibility of heteroazeotropic distillation can be directly assessed by an analysis of the corresponding residue curve map (RCM). Similar to homogeneous systems, the residue curves cannot cross the boundary line. However, if a point on an residue curve inside the heterogeneous region results in two separate liquid phases with equilibrium concentrations x^I and x^{II} in two different distillation regions, liquid-liquid phase separation can be exploited to cross the boundary line. The tie-lines connect the equilibrium concentrations of the separated liquid

phases of a point that is situated inside an immiscible region. An example for such a process is illustrated in Figure 2.

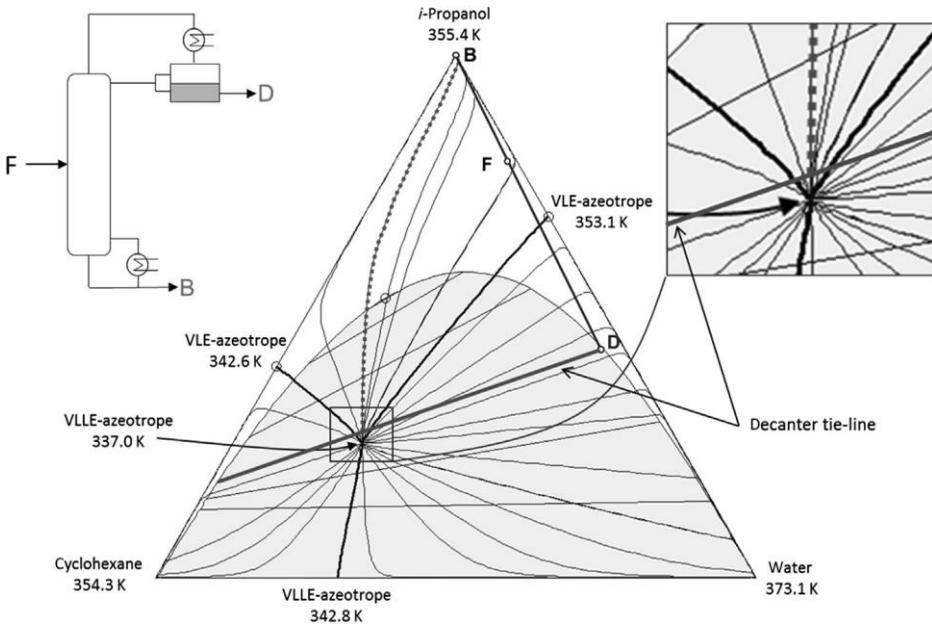


Figure 2. Residue curve map of the heterogeneous mixture of isopropanol, water, and cyclohexane at 1.013·10⁵ Pa. VLE, vapor-liquid equilibrium; VLE, vapor-liquid-liquid equilibrium

(Górak and Sorensen, 2014).

Due to the combination of a column and a decanter, the design of a heteroazeotropic distillation column offers additional degrees of freedom and reveals different requirements for feasible separations. In the standard configuration of a heteroazeotropic distillation column, the decanter separates the condensed liquid at the top of the column. For a feasible separation, a continuous concentration profile needs to connect the bottom product and the decanter tie-line, where the top product is situated. Therefore, the top vapor composition must be in the same distillation region as the bottom product. An exemplary specification is shown in Figure 2, where the dotted residue curve represents a feasible column profile. Other configurations are also possible to exploit the topology of the phase diagram. The design of such processes relies on a creative use of RCM analysis to identify a suitable configuration for the separation of the

azeotropic mixture into desired products. The differences of split feasibility at total and finite reflux also need to be considered for simple heteroazeotropic distillation columns (Górák and Sorensen, 2014).

3.2.1.1. Organic acids dehydration

In the dehydration of organic acids, heteroazeotropic distillation is very common. This technique involves separating close boiling components, water and the organic acid, by adding a third component, the entrainer, to form a minimum boiling azeotrope which carries the water overhead and leaves dry acid in the bottom. The overhead is condensed to two liquid phases; the organic, "entrainer rich" phase being refluxed while the aqueous phase is decanted. Given the non-idealities, the phase splitting, the distillation boundaries present, and the possible existence of multiple steady states in such a system, columns like these can be extremely difficult to simulate and to operate, (*ChemStation*[®], 2015). Figure 3 shows a current representation of the dehydration process using a heterogeneous azeotropic distillation column.

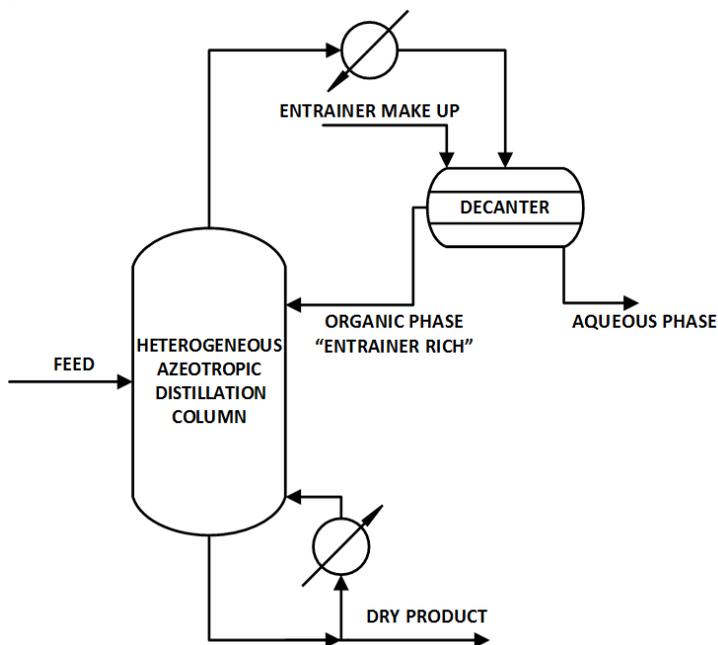


Figure 3. Representation of dehydration process using a heterogeneous azeotropic distillation column.

3.2.1.2. State of the art

The entrainer used before 1932 was ethylene dichloride. Nowadays, entrainers most frequently used are acetic esters, such as ethyl acetate (EA), n-butyl acetate (NBA), isobutyl acetate (IBA), and n-propyl acetate (NPA). Sirola (1995) used EA as an entrainer to design a complete HAc dehydration process with multiple-effect azeotropic distillation. Wasylikiewicz et al. (2000) used a geometric method to optimize the design of a HAc dehydration column with NBA as an entrainer. Kurooka et al. (2000) proposed a nonlinear control system for a HAc dehydration column also with NBA as an entrainer. Parten and Ure (1999) described a HAD column using IBA or NPA as an entrainer to separate water from HAc. Chien et al. (2004) studied the design and control of a HAc dehydration column using three candidate entrainers (EA, NBA, and IBA). A suitable entrainer of IBA was selected by total annual cost analysis. Later, Chien et al. (2005) investigated the influence of PX feed impurity on the design and operation of an industrial HAc dehydration column. In normal operation, PX does not leave the column from top or bottom product; it is accumulated in the decanter and in the upper section of the column. Huang et al. (2007) and Lee et al. (2008) also addressed the design and control of a HAc dehydration column with PX or m-xylene feed impurity. Wang et al. (2008) proposed the energy-saving plantwide design and control of a HAc dehydration process via HAD and divided wall distillation. MA is recovered from the column top of the divided wall distillation and can be recycled to a PX oxidation reactor to inhibit MA formation by the undesired decomposition reaction of HAc in the production of terephthalic acid. The product containing entrainer and water is withdrawn from the side stream of the divided wall distillation column and recycled back to the decanter to compensate for entrainer loss. In these studies, IBA was used as an entrainer.

Recently, Li (2011) performed the dynamic simulation and analysis of an industrial purified terephthalic acid solvent dehydration process using NBA as an entrainer to separate HAc and water. Li and Huang (2011) presented a study of multiple steady states for HAc dehydration via heterogeneous azeotropic distillation with NBA as an entrainer. However, there are some drawbacks for the HAD column using IBA or NBA, a foreign chemical in the process of producing terephthalic acid, as the entrainer. Small amount of IBA (or NBA) lost to the streams of recovered HAc and MA will be recycled back to a PX oxidation reactor and then decomposed to methanol, propanol, isobutanol (or n-butanol), and carbon oxides (Lee et al., 2007). These decomposition products can further react with organic radicals in the oxidation reactor and produce a number of impurities, which contaminate process streams and terephthalic acid product. Unreacted alcohol

compounds enter into the HAD column together with dilute HAc streams. They significantly influence the performance of the HAD column and cause poor separation and higher utility consumption.

PX is a feedstock used for the production of terephthalic acid. It can form a minimum-boiling heterogeneous azeotrope with water and is more advantageous as an entrainer than IBA because of its higher amount of water entrained in the azeotrope. Consequently, less energy is required for the separation of HAc and water.

Wang and Huang (2012) investigated the possibility of using PX component in the feed stream of the HAD column as the entrainer to separate HAc and water. They demonstrated that not only the drawbacks of the HAD column with IBA as the entrainer could be overcome but also less energy was used for the column with PX as the entrainer if PX accumulated in the column was withdrawn from the side stream.

Wang and Wong (2013) proposed two strategies to implement a dynamic transition of the HAD column from the current process employing IBA as the entrainer into the HAD column that uses p-xylene as the entrainer, without the need of shutdown and start-up.

Huang et al. (2013) analysed the distillation behaviour of the system in the industrial HAc dehydration process using NPA as entrainer. Then the mechanism model of heterogeneous azeotropic distillation was developed, and the simulation of the industrial HAc dehydration process was performed, including dehydration column, PX purification column, and NPA recovery column. Based on the process model, the sensitivity analysis of the bottom water content, reflux flow, two side-draws, and two heat feeds are carried out, and operation optimization suggestions were proposed.

3.2.2. Fundamentals

This section shortly introduces the necessary fundamentals for understanding the thermodynamics, the process setup for azeotropic distillation and, the most important, to check the basic physical feasibility of the distillation system. First, residue curve maps are presented. Then, distillation regions and singular points are distinguished. Based on that, possible products of the distillation process can be deduced.

3.2.2.1. Residue curves maps

The increasing processing power provided by the computers allows nowadays performing calculations faster, more efficiently and with lower errors. Complex systems of equations can be converged sometimes with success and obtain solutions that fulfil the mass and energy balances. More rigorous is the model, more parameters are required to define exactly the system behaviour. Despite this fact, when the problem is approached, only the main chemical components and its basic thermodynamic data are known. At this early stage, an overall view and understanding of the system behaviour is desired instead of a wide list of parameters. For this reason, the residue curve maps that will be introduced in this chapter are the first approach to face a distillation system because they only depend on basic thermodynamic data. The residue curve maps are for the chemical engineer what are the streets maps for a taxi driver. It is possible to go without maps but without a very good knowledge and previous experience there, more turns around will be performed before reaching the goal.

The representation and graphical visualization of the chemical components in the composition space is a powerful tool for the analysis and interpretation of systems behaviour. The topological analysis of the thermodynamics is based on the classical works of Schreinemakers (1901) and Ostwald (1902) that linked the vapour liquid equilibrium of a ternary mixture with the behaviour of the residue curves. Some years later, Wade and Merriman (1911) introduced the definition of maximum and minimum boiling azeotropes. The residue curve (Doherty et al., 1979) is defined as a set of the liquid compositions followed by the residue in the still of a Rayleigh distillation as the evaporation advances in time. The Rayleigh distillation is an open simple batch distillation with a single theoretical stage (Rayleigh, 1902) (Figure 4). An initial amount of a liquid mixture with a specified initial composition is brought to its boiling point at a given pressure by heating. By further heating, the liquid is vaporized and the more volatile components removed from the system. The output vapour is assumed to be in equilibrium with the liquid phase. Because the vapour is enriched with the more volatile species, the least volatile species are enriched in the residue. (Bonet-Ruiz, 2012)

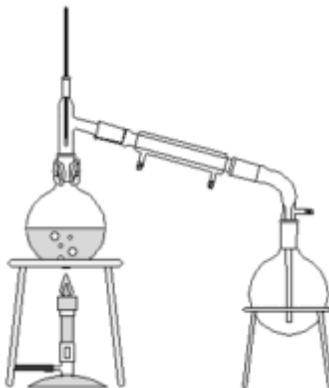


Figure 4. Rayleigh distillation scheme.

For a ternary mixture, the evolution of the residue composition is then plotted on a Gibbs diagram and a curve is drawn through the composition points taken, giving a residue curve. When several residue curves are plotted together, they form a Residue Curve Map. In the Gibbs triangle, each vertex represents a pure component. The edges of the triangle correspond to binary mixtures and each point inside the triangle stands for a certain ternary composition. The compositions can be expressed in mass or mole fractions. By definition, residue curves do not intersect. Therefore, there are no closed cycles. Figure 5 shows the residue curve map for a ternary system as illustrative example of their aspect (Bonet-Ruiz, 2012)

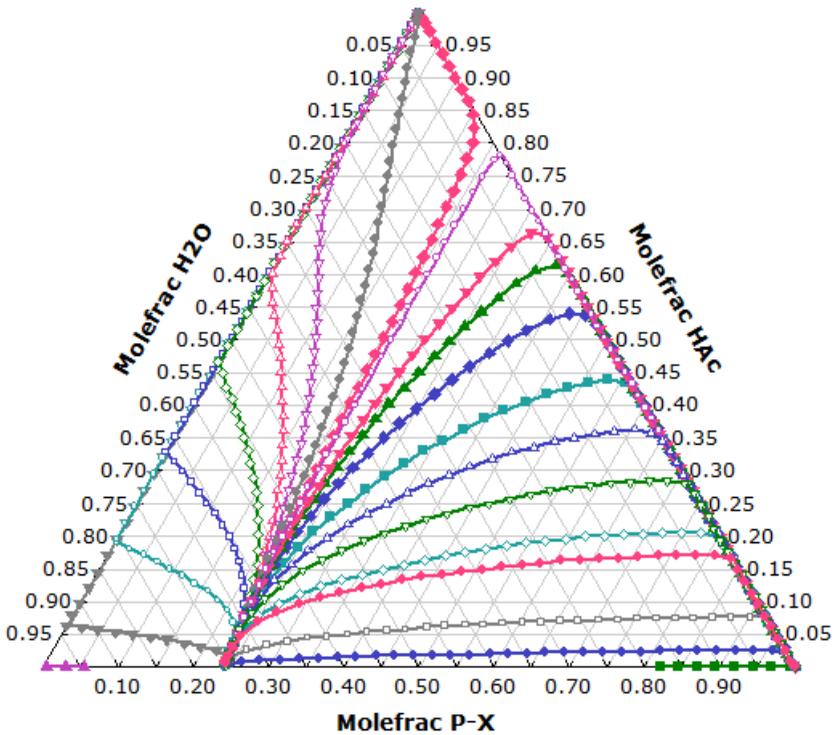


Figure 5. Residue curve map example.(HAc/H2O/MA P=1 atm from our study).

3.2.2.1.1. Mathematical model for residue curves

It is traditional for chemical engineers to model packed columns through the concept of transfer units (NTU) according to the dimensionless expression (Taylor and Krishna, 1993):

$$\frac{dy}{dz} = NTU \cdot (y^* - y) \quad (1)$$

where y^* is the vapour composition in equilibrium with the bulk liquid (x) and y is the vapour composition in contact with the bulk liquid (x). The difference between y^* and y is the driving force for the components transfer from the liquid phase (x) to the vapour phase (y), $\zeta=z/H$ is a dimensionless height ratio where H represents the overall height of packing. When the reflux is infinite then:

$$x = y \quad (2)$$

And the expression (1) becomes, in the case of infinite reflux (2), the following equation:

$$\frac{dy}{d\zeta} = NTU \cdot (y^* - x) \quad (3)$$

The similitude of equation (3) with the residue curve map expression (4) is obvious:

$$\frac{dy}{d\tau} = (x - y^*) \quad (4)$$

The coincidence of the residue curve profile with the profile of a packed column with infinite reflux was demonstrated by several authors (Van Dongen and Doherty, 1985; Laroche et al, 1992). The value of τ is directly related to the height of the column. From the equations (3) and (4), the variable related with the time can be linked with the NTU. Integrating for the total height of a column, the NTUs are calculated from the next equation:

$$\int_{\tau}^{\tau-0} d\tau = NTU \cdot \int_{\zeta=0}^{\zeta=1} d\zeta = NTU = \int_{x0}^x \frac{dx}{y^*-x} \quad (5)$$

The NTU depends only on the composition column profile and it does not depend on the characteristics and performance of the packin.(Bonet-Ruiz et al, 2010)

3.2.2.2. Topology of the residue curve maps and distillation regions

Matsuyama and Nishimura (1977) investigated and classified all feasible topologies of residue curve maps. In order to introduce the reader, some definitions about the topology of the residue curve maps are introduced in this paragraph. Doherty and Perkins (1978) proved that the residue curve on each point is unique if it is not a singular point, consequently, residue lines cannot cross each other. In addition, there are some points from which diverge or converge families of residue curves. These are some of the so-called singular points. The points from where diverge some of the residue curves are called unstable nodes and the points to where converge some of the residue curves are called stable nodes. There is a third kind of singular point where some of the residue curves converge and some others diverge; these are called saddle points.

The singular points correspond to compositions for which although a higher volume of vapour is retrieved from the system, the liquid composition remains the same. This happens for the pure

components and for the azeotropic compositions in non-reactive systems because the liquid and vapour compositions are equal.

A more general definition of azeotrope given by Prigogine and Defay (1967) is more suitable: it is a state in which there is mass transfer at the interface, while the compositions of both phases remain constant. For the isobaric case, there are only isolated singular points. For a constant pressure, the temperature always increases along a residue curve, because the liquid phase depletes in the more volatile components. Therefore, the boiling temperature of the residue increases. If the boiling points are plotted over the composition space giving a temperature surface, the unstable nodes represent the local minimum of this surface while the stable nodes represent the local maximum of this surface. The globally lowest (highest) boiling point is always at an unstable (stable) node.

The set of residue curves that diverge from the same unstable node and converge to the same stable node defines a distillation region. If there are more than one node of the same kind (stable or unstable), there will be at least as many simple distillation regions as nodes. The residue curve that separates two simple distillation regions is called a boundary line. At least one of the ends of a residue curve boundary must be a saddle. Previously, a global vision of the residue curve maps and its topology is provided. The usefulness of the residue curves comes from the fact that the variation against time of the residue composition, in the still of a simple distillation, is matching the compositions along the length of a packed distillation column at infinite reflux flow rate. It is important to notice that it corresponds to an infinite reflux flow rate and not to an infinite reflux ratio or total reflux.

The consequence of this assumption is that the feed position has no influence on the column. The feed, as the distillate and bottoms flow rates, has a non-zero value infinitely smaller than the vapour and liquid flowrate inside the column so that the feed effect is negligible in the column profile. This allows a first plot of the residue curve map and, in a second step, an analysis considering the compositions of the input and output flows to and from the distillation column. Usually, when a column profile is represented graphically in a ternary diagram, a certain deviation of the column profile towards the feed composition is observed. Due to the infinite reflux flowrate assumption, the residue curves do not deviate to the feed and therefore they are a limit condition and not a real situation. As the reflux used in the column becomes higher, the column profile gets closer to the residue curve.

The main use of the residue curves is concerning the feasibility of a separation. If there is a residue curve running between two compositions in the residue curve map, it means that a distillation column that collects these compositions by the distillate and bottoms is feasible. The feed composition must fulfil the mass balance and graphically it means that the point corresponding to the feed must be over the straight line defined by the distillate and bottoms composition. The lever rule can be applied to determine the correspondent flow rates. The existence of the residue curve assures that this separation is feasible in a distillation column with an infinite reflux, or in a distillation column with a high enough reflux. One of the nowadays drawbacks of the residue curve maps is that they provide the feasibility of the separation but not the difficulty of the separation. From the residue curve map, the feasibility can be assured but not the technical feasibility because it could be feasible with a too high reflux or number of stages, which would be economically unviable.

According to the residue curves map feasibility, a separation is only feasible when both the distillate and bottoms are inside the same distillation region. The feed can be present in a different distillation region when the boundary is curved, having to fulfil the mass balance, but it must not be on the same residue curve with distillate or bottoms. However, the residue curve region boundaries can be crossed by a rectification as is pointed out by Doherty and Perkins (1978). It is because the tie lines are always tangent to the residue lines at the liquid point and the boundaries are usually curved. (Bonet-Ruiz, 2012) Figure 6 illustrates a study of the previous residue curve map example.

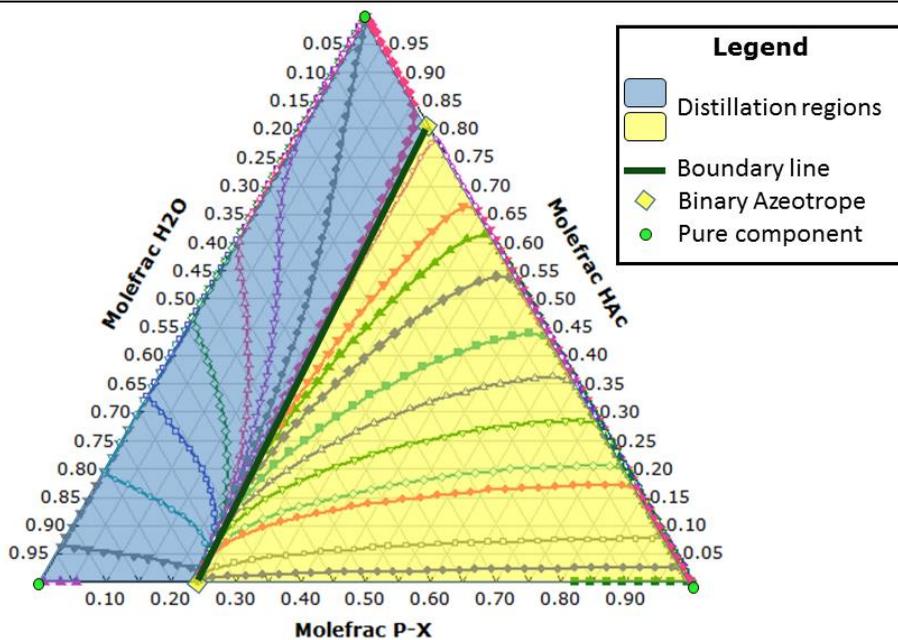


Figure 6. Residue curve map example study.(HAc/H₂O/MA P=1 atm from our study).

4. OBJECTIVES

The purification and recovery of acetic acid, the solvent, is an important step in the terephthalic acid manufacturing process. Heterogeneous azeotropic distillation is currently used to purify the organic acid. The methodology and simulation used in this kind of distillation is complex and difficult. The aim of this work is to:

- Study the behaviour of heterogeneous azeotropic distillation applying it in the case of the acetic acid dehydration.
- Determine the influence of impurities on the ease of separation of a mixture.
- Propose a new non-iterative methodology to design a heterogeneous azeotropic distillation (HAD) column, based on the thermodynamic properties of the system, mass balances and setting the values of the variables of interest: the HAc purity.
- Check results by rigorous simulation of the process.
- Compare the methodology and results with previous works: Wang and Huang (2012) and Wang and Wong (2013).

5. METHODOLOGY

This section describes the software tools used in this study for simulations and calculations, the components of the system, the thermodynamic model implemented and the methodology used.

5.1. SOFTWARE TOOLS

The separation system is simulated using Aspen Plus® V8.0 (Aspen Technology, Inc., 2015). It is a computer-aided software which uses the underlying physical relationships (e.g., material and energy balances, thermodynamic equilibrium, etc.) to predict process performance (e.g., stream properties, operating conditions, and equipment sizes).

Material balances are solved using Wolfram Mathematica® V10.0.1 (Wolfram Research Europe Ltd., 2015) and Xcas V1.1.4 (Institut Fourier, 2015). Wolfram Mathematica® is a computational software program used in many scientific, engineering, mathematical and computing fields, based on symbolic mathematics. Xcas is a free computer algebra system with an interface to perform computer algebra, function graphs, interactive geometry (2-D and 3-D), spreadsheet and statistics, programming.

Plotting is performed using MATLAB® V7.7.0.471 (R2008b) (The MathWorks, Inc., 2015). It is a multi-paradigm numerical computing environment and fourth-generation programming language.

5.2. SYSTEM CHARACTERISTICS

The compounds considered in the studied system are:

- Acetic Acid (HAc): It is the product of interest, since it is to be reused as solvent in the terephthalic acid production reactor with a high purity. Its boiling temperature is 118°C.
- Water (H₂O): It is a residue from the terephthalic acid synthesis. It must be removed from the product of the interest. Its boiling temperature is 100°C.

- Methyl Acetate (MA): It is a by-product from the terephthalic acid synthesis. It is to be used as entrainer on the distillation process. Its boiling temperature is 57°C.
- Para-Xylene (PX): It is the unreacted part of the reagent from the terephthalic acid synthesis. It is wanted to be used as entrainer on the distillation process. Its boiling temperature is 138.4°C.

The distillation process feed flow rate and composition were selected from previous works of Wang and Wong (2013) and Wang and Huang (2012), because these specifications were considered to be similar to an industrial case (Wang and Wong, 2013) and in order to compare the results of this study with their previous works. Table 1 indicates the feed values.

Table 1. Feed flow rate and composition.

Component	Molar flow [kmol/h]	Molar fraction
HAc	1000	0.49254
H ₂ O	1000	0.49254
MA	30	0.01478
PX	0.29	0.00014
TOTAL	2030.29	1

The column number of stages was selected from previous works of Wang and Wong (2013) and Wang and Huang (2012), because these specifications were considered to be similar to an industrial case (Wang and Wong, 2013) and in order to compare the results of this study with their previous works. Tale 2 shows the selected number of stages.

Table 2. Column number of stages.

Column n° of stages	45
---------------------	----

5.3. THERMODYNAMIC MODEL

Non-Random Two-Liquid (NRTL) activity coefficient model was used for the vapor–liquid–liquid equilibrium of this system accompanied with Hayden-O’Connell (1975) second virial coefficient model, which is used to account for the dimerization of HAc in vapour phase. The AspenPlus built-in association parameters were employed to compute fugacity coefficients. NRTL

parameters for the system are retrieved from Wang et al. (2008) who selected them from Chien et al. (2004), Gau (2005) and Wang (2004). Table 3 indicates the NRTL parameter values used.

Table 3. Parameter values for NRTL model.

Component i	Component j	A_{ij}	A_{ji}	$B_{ij}(K)$	$B_{ji}(K)$	Alpha
HAc	H ₂ O	0	0	-211.31	652.995	0.3
HAc	MA	0	0	-239.2462	415.2702	0.3
HAc	PX	0	0	466.217	215.826	0.3
H ₂ O	MA	0	0	860.256	442.401	0.383
H ₂ O	PX	5.91818	-6.03013	784.86	2909.308	0.162808
MA	PX	0	0	1353.844	-439.0727	0.3

5.4. METHODOLOGY

In this section, the methodology used in the study is explained and compared to the current methodology used in the design of such columns, taking as example the one used in the study of Wang and Huang (2012).

The simulation of this process via software is complex and difficult due to the fact that there is a column, a decanter and a recirculation stream coming from the decanter, which entails a recycling of information. In terms of process simulation, it involves much computation effort and a low probability of system convergence. Specifically, the simulator has to solve about 650 equations for each iteration.

The current methodology to solve this kind of columns is based on an iterative system where part of the independent variables are guessed, without any criteria, and part are changed until desired specifications are met. Then, previously guessed independent variables are changed in order to optimize the system. A clear example of this current methodology is employed in the study of Wang and Huang (2012). The methodology is illustrated with a graphical representation of their process. The design steps for reaching the optimal condition to operate the column used in the study of Wang and Huang (2012) are:

- (1) Guess distillate flow rate of organic-phase liquid.
- (2) Guess aqueous reflux ratio.

- (3) Change reboiler duty and PX makeup flow rate until two HAC specifications can be met.
- (4) Go back to step 2 and repeat step 3 until reboiler duty is minimized.
- (5) Go back to step 1 and repeat steps 2 and 3 until reboiler duty is minimized.

Figure 7 illustrates the graphical representation of Wang and Huang (2012) process methodology.

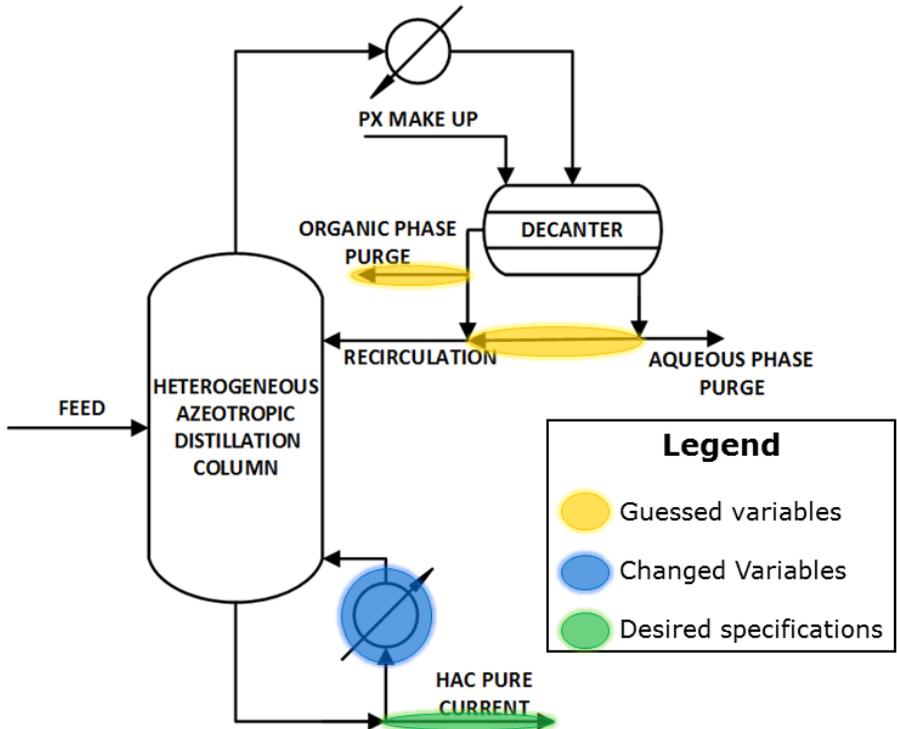


Figure 7. Graphical representation of Wang and Huang process methodology.

Being an iterative system and having no option to fix the desired specification, in this case the HAC purity, this methodology is not very efficient and it may last longer time to reach convergence and desired results; but it does not mean that it is wrong. As it can be seen, this system does not take into account the feed plate and the number of stages, which are fixed.

For this reason, this study proposes a new methodology based on a non-iterative algorithm, where the main specification, in this case the purity of the desired product, is fixed first. To convert the current methodology into this one, three changes have been applied:

- 1) **Cut the recirculation of information:** The recirculation of information is cut in order to eliminate the iteration problems and propose an easier system to converge in Aspen Plus® software. Consequently, in the rigorous simulation, composition and flow rate of streams involved in this cut, input and output, will have to be equal.
- 2) **Consider two assumptions:**
 1. HAc is only collected at the bottom of the column (See explanations at section 6.1).
 2. MA and PX are only collected at the top of the column. (See explanations at section 6.1).
- 3) **Remove PX make-up:** Since it is thought that this stream is not essential for the distillation feasibility, and it would take out the need to introduce external pure PX to the system.

The methodology proposed in this study is illustrated within the graphical representation of the process in Figure 8. Therefore, the design steps to determine the optimal operating conditions of the column proposed in this study are:

- (1) Fix the desired purity of HAc.
- (2) Formulate the overall mass balance considering two assumptions:
 - HAc is only collected at the bottom of the column. (See explanations at section 6.1).
 - MA and PX are only collected at the top of the column. (See explanations at section 6.1).
- (3) Select the tie line (liquid-liquid equilibrium) of the decanter system MA/water/PX that fulfils the overall mass balance.
- (4) Formulate the decanter mass balance taking into account the organic and aqueous purge and recycling streams.
- (5) Find the optimal relation between feed stage and the decanter input stream flow rate.

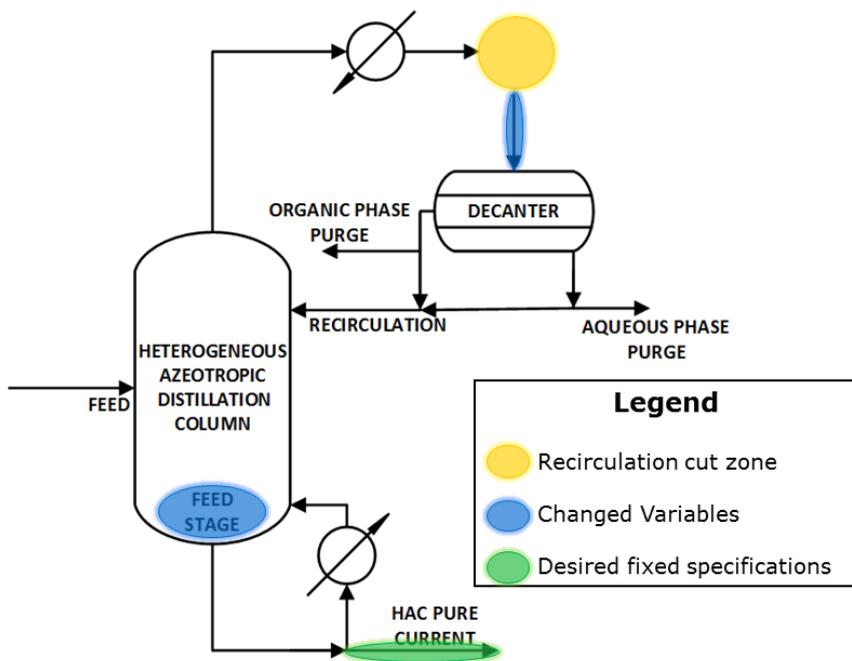


Figure 8. Graphical representation of the study process methodology.

6. RESULTS

In this section, thermodynamic results of the system, obtained with Aspen Plus® software and using the thermodynamic model explained at the previous section (section 5.4), are shown first. Then, the results of the study are shown in the order the methodology is proposed.

6.1. THERMODYNAMICS

Due to the fact that the system is formed by four components, graphical representations in 2-D are quite impossible to do. The only way of representing them is using 3-D technology, but Aspen Plus® does not have this tool.

Figure 9 illustrates an open tetrahedron where all four components are represented, made from ternary diagrams. If the tetrahedron is plotted in 3-D, like in Figure 10, the behaviour of the system is only represented accurately on its sides, the inside is an unknown approximated representation. That means that the real thermodynamic behaviour of the system is unknown, but in this study, it is approximated using the ternary diagrams where the main components (the most composition in the system, the desired ones, etc.) are found in.

The feed stream specifications (Table 1) provides data related to the two main components in the system: Acetic acid (HAc) and Water (H₂O), having greater difference from p-xylene (PX) and Methyl acetate (MA). For this reason, the overall ternary diagram of the system of this study should incorporate both components. Figure 11 provides the two ternary diagrams that incorporate HAc and H₂O.

In order to choose which of these two diagrams could represent more accurately the real behaviour of the overall system, each ternary diagram was studied and binary diagrams are included on its edges. An additional azeotrope search report is also provided, presenting specifications of azeotropes and singular points of each ternary system. Figures 12 – 17 illustrate the ternary diagram, residue curve map and azeotrope report of each ternary system, respectively.

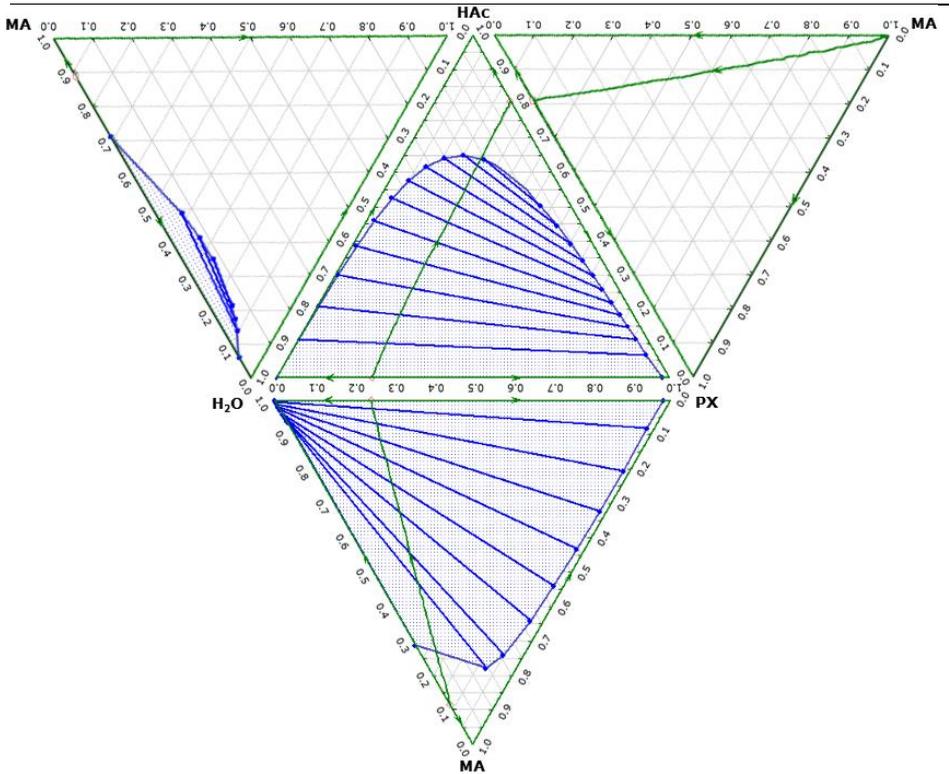


Figure 9. Open tetrahedron diagram of the system.

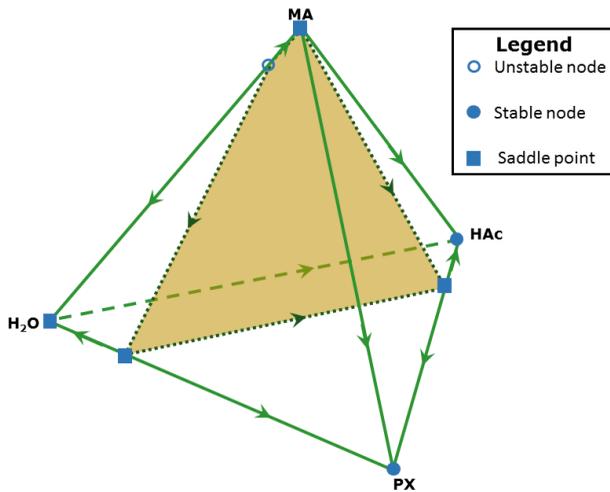


Figure 10. 3-D Approximation diagram of the system without phase split zone indication.

3-D approximation diagram (Figure 10) shows the singular points of the global system, including the four components. The shaded area represents the division of the system in two distillation regions. Its edges are the boundary lines of each ternary diagram, so the area could be called a “boundary wall”. The representation of the area is approximated, because the real behaviour inside the tetrahedron is unknown. The stable nodes of the system are pure HAc and pure PX, one in each distillation region. The only unstable node is found in the binary azeotrope between MA and H₂O. The other points are saddle points. It is important to mention that the singular points presented in the 3-D diagram can have a different interpretation from the singular points obtained with ternary diagrams, because the last ones do not consider the fourth component.

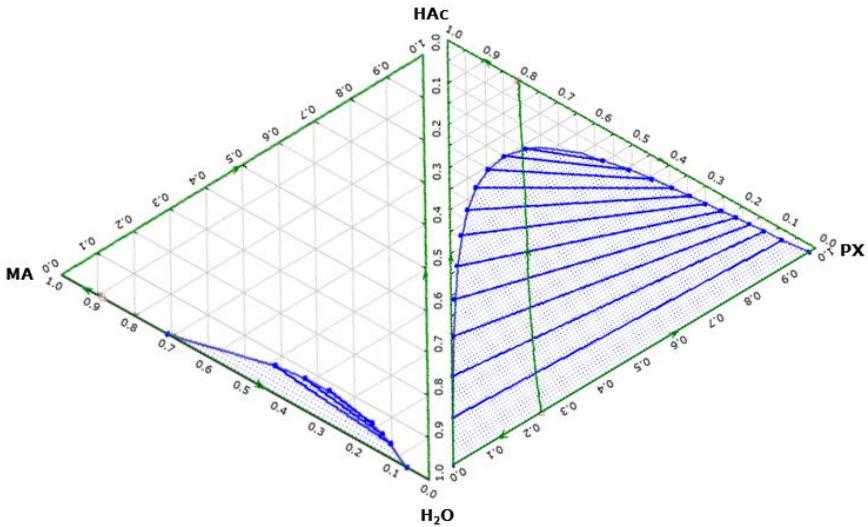


Figure 11. Ternary diagrams that incorporate HAc and H₂O.

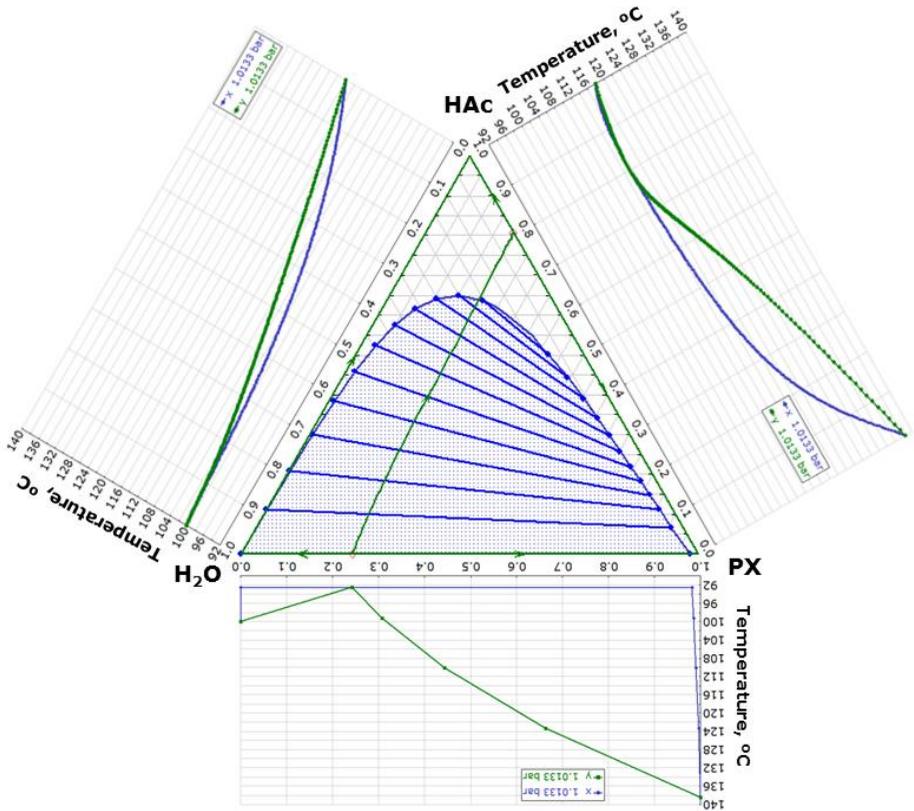


Figure 12. Column global ternary diagram (HAc/H₂O/PX) with the edge binaries.

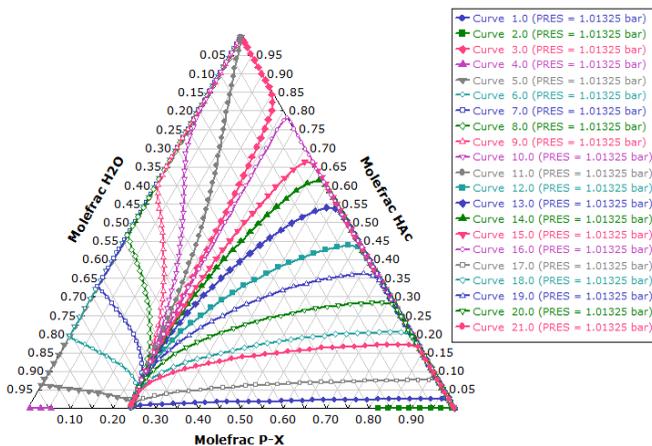


Figure 13. Residue curve map HAc/H₂O/PX.

AZEOTROPE SEARCH REPORT

Physical Property Model: NRTL-HOC **Valid Phase:** VAP-LIQ-LIQ

Mixture Investigated For Azeotropes At A Pressure Of 1 ATM

Comp ID	Component Name	Classification	Temperature
P-X	P-XYLENE	Stable node	138.37 C
HAC	ACETIC-ACID	Stable node	118.01 C
H2O	WATER	Saddle	100.02 C

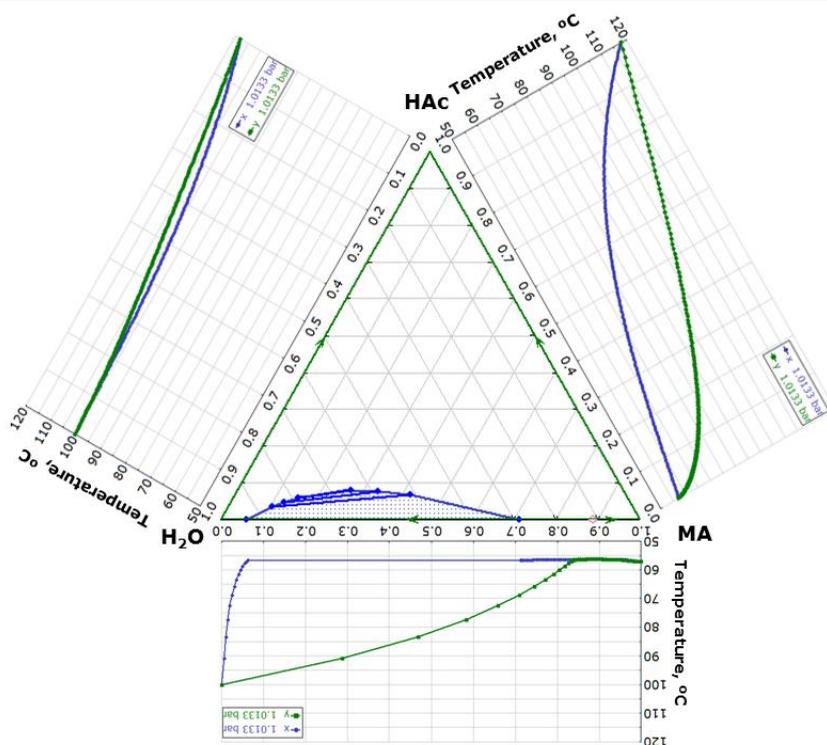
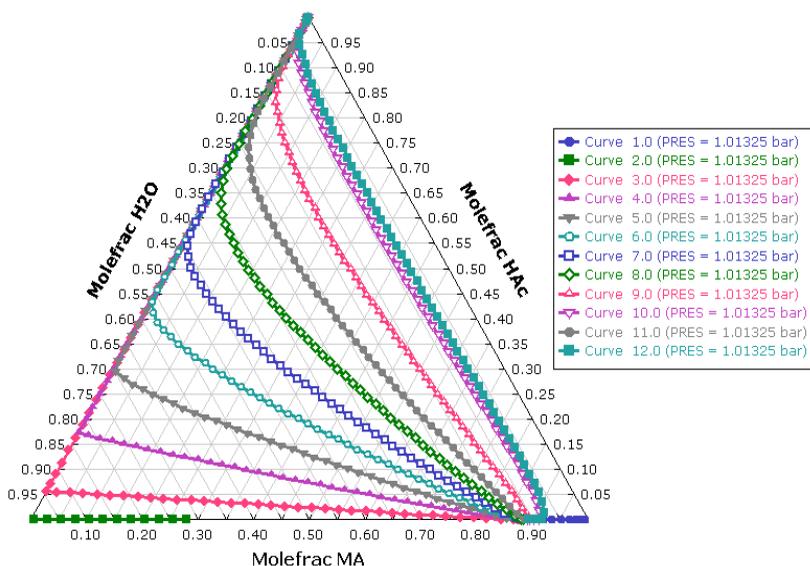
2 Azeotropes found

01	Number Of Components: 2		Temperature 115.22 C	
	Homogeneous		Classification: Saddle	
			MOLE BASIS	MASS BASIS
		P-X	0.1918	0.2955
	HAC	0.8082	0.7045	

02	Number Of Components: 2		Temperature 92.39 C	
	Heterogeneous		Classification: Unstable node	
			MOLE BASIS	MASS BASIS
		P-X	0.2425	0.6535
	H2O	0.7575	0.3465	

© 2011 Aspen Technology, Inc., 200 Wheeler Road, Burlington, Massachusetts 01803 USA Tel: + 1 888 996 7100

Figure 14. Aspen Plus® azeotrope search report and singular points of column global ternary system (HAc/H2O/PX).

Figure 15. Column global ternary diagram (HAc/H₂O/MA) with the edge binaries.Figure 16. Residue curve map HAC/H₂O/MA.

AZEOTROPE SEARCH REPORT

Physical Property Model: NRTL-HOC Valid Phase: VAP-LIQ-LIQ

Mixture Investigated For Azeotropes At A Pressure Of 1 ATM

Comp ID	Component Name	Classification	Temperature
MA	METHYL-ACETATE	Saddle	57.05 C
HAC	ACETIC-ACID	Stable node	118.01 C
H2O	WATER	Saddle	100.02 C

The Azeotrope

01	Number Of Components: 2		Temperature 56.15 C	
	Homogeneous		Classification: Unstable node	
			MOLE BASIS	MASS BASIS
		MA	0.8864	0.9698
	H2O	0.1136	0.0302	

© 2011 Aspen Technology, Inc., 200 Wheeler Road, Burlington, Massachusetts 01803 USA Tel: + 1 888 996 7100

Figure 17. Aspen Plus® azeotrope search report and singular points of column global ternary system (HAc/H₂O/MA).

The global ternary diagram of the system HAc/H₂O/MA (Figure 15) has only one distillation region and one azeotrope which is situated in a homogeneous zone. The phase split envelope is really small, which means that the posterior separation of the phases at the decanter would be restricted to a small specific range of decanter input compositions, and the split phases will have a really low purity of its main components. For these reasons, the chosen ternary diagram for the approximate representation of the global process behaviour will be the one formed by HAc/H₂O/PX.

Once the ternary diagram is selected, **two assumptions** are formulated in order to simplify the resolution and focus it to the desired operating conditions:

- **HAc is only collected at the bottom of the column:** Acetic acid is the product of interest in the process, it is required in a high purity and it is preferable not to lose it in other output streams of the process. In previous works of Wang and Wong (2013) and Wang and Huang (2012), the mass balance results show that acetic acid is leaving mainly by the column bottom stream, and in the other output streams of the process it is present as traces.
- **MA and PX are only collected at the top of the column:** Due to the fact that methyl acetate and its azeotrope with water have the lowest boiling temperature

values in the system, and considering the results of previous works of Wang and Wong (2013) and Wang and Huang (2012), where MA values at the bottom of the column are negligible, it is assumed that it is only collected at the top of the column. P-xylene, even having the highest boiling temperature of the system, it forms a minimum boiling azeotrope with water whose boiling temperature value is lower than the one of pure acetic acid. Therefore, having water in the system, PX will rather form an azeotrope. It is true that this assumptions restrict the operating conditions but the optimal conditions will remain.

The global ternary diagram of the system HAc/H₂O/PX (Figure 12) shows a boundary line that goes from the azeotrope of HAc/PX to the azeotrope of H₂O/PX, which is situated in a great phase split zone. This boundary line divides the diagram in two distillation regions. The representation scheme is described in Figure 18. The column bottom stream would be situated next to the pure HAc vertex. It means that the desired distillation region is situated on the left of the boundary line.

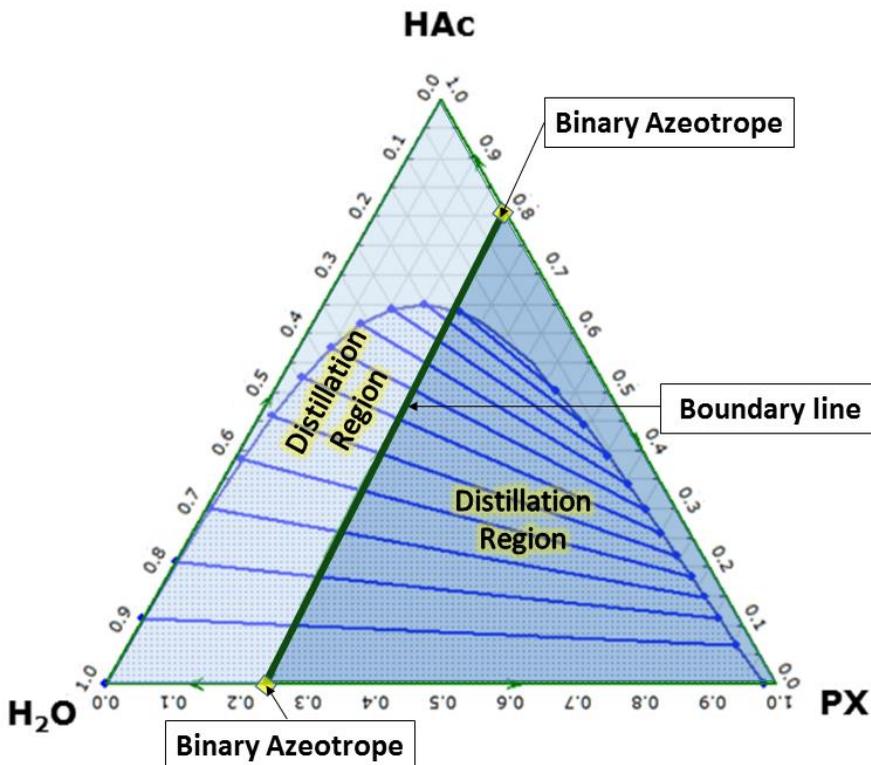


Figure 18. Column global ternary diagram (HAc/H₂O/PX) study.

Having taken the previous assumptions, all the streams that are collected at the top of the column contain MA, PX and water; and so the decanter system. It means that the behaviour of the system in the decanter is accurately represented with the ternary diagram of the system MA/H₂O/PX (Figure 19). Due to the fact that in the decanter the main action that takes place is the phase splitting, the singular points, azeotropes (Figure 21), distillation regions and boundary lines are not important for the study of the decanter. The important factors are the phase split region and its tie lines (Figure 20) (Appendix 1). It can be seen that although the concentration of MA is increased, the aqueous phase remains with a high purity of water. It means that most of the aqueous phase purge composition, which has a great flow rate value, will be water. It is an important fact if the purge is going to be classified as waste stream to be sent to a further wastewater treatment. MA concentration could be a problem in the decanter if its values were above 80% because the phase split region of the system would disappear.

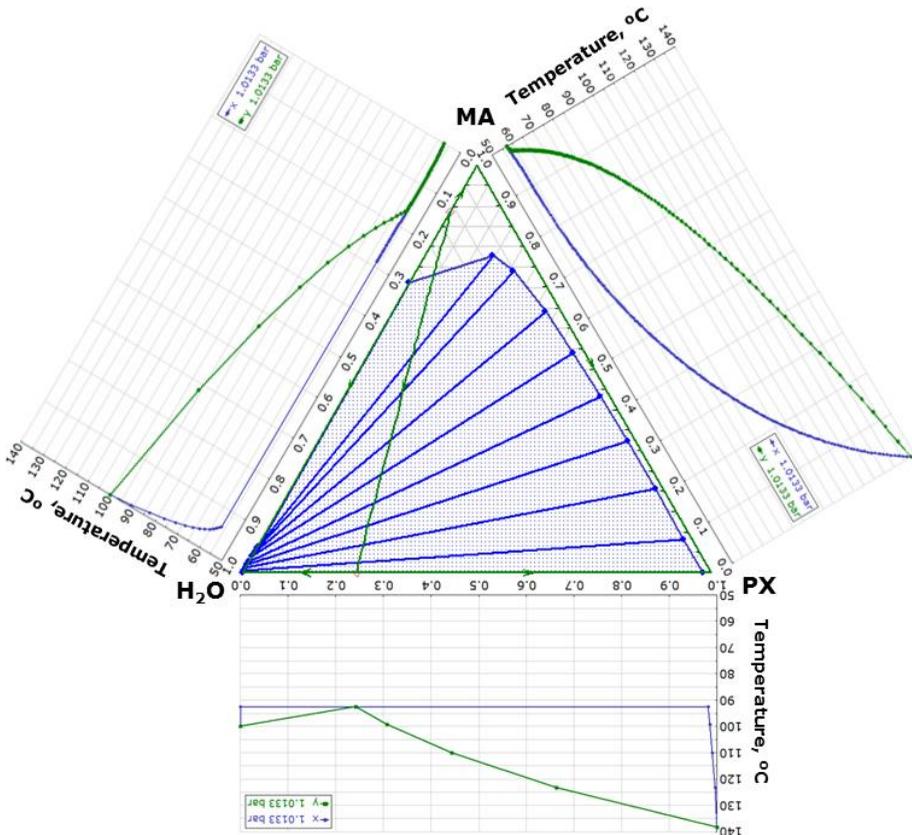


Figure 19. Decanter ternary diagram with the edge binaries.

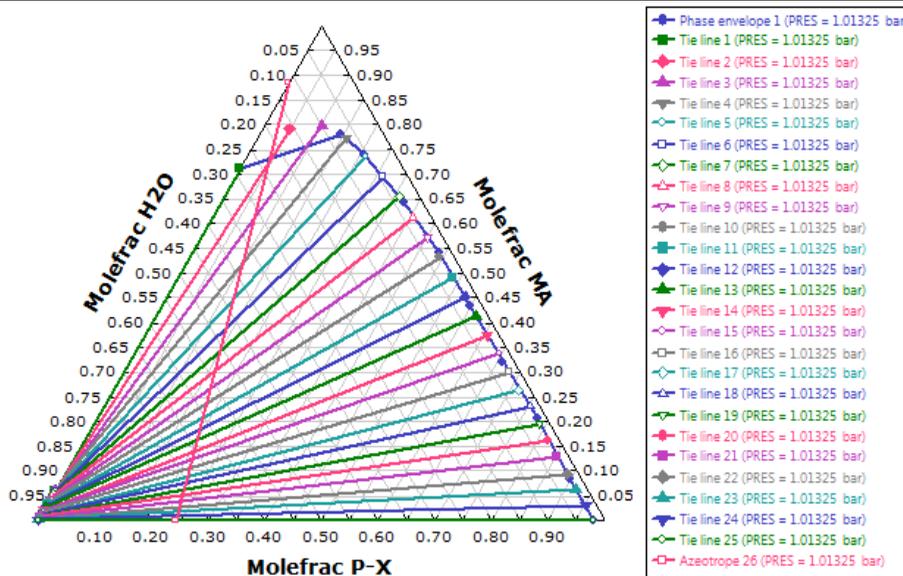


Figure 20. Ternary diagram decanter MA/H2O/PX with tie lines.

AZEOTROPE SEARCH REPORT

Physical Property Model: NRTL-HOC Valid Phase: VAP-LIQ-LIQ

Mixture Investigated For Azeotropes At A Pressure Of 1 ATM

Comp ID	Component Name	Classification	Temperature
P-X	P-XYLENE	Stable node	138.37 C
MA	METHYL-ACETATE	Saddle	57.05 C
H2O	WATER	Stable node	100.02 C

2 Azeotropes found

01	Number Of Components: 2	Temperature 92.39 C	
	Heterogeneous	Classification: Saddle	
		MOLE BASIS	MASS BASIS
	P-X	0.2425	0.6535
H2O	0.7575	0.3465	

02	Number Of Components: 2	Temperature 56.15 C	
	Homogeneous	Classification: Unstable node	
		MOLE BASIS	MASS BASIS
	MA	0.8864	0.9698
H2O	0.1136	0.0302	

© 2011 Aspen Technology, Inc., 200 Wheeler Road, Burlington, Massachusetts 01803 USA Tel: + 1 888 996 7100

Figure 21. AspenPlus® azeotrope search report and singular points of decanter ternary system (MA/H2O/PX).

6.2. METHODOLOGY RESULTS

This section shows the results obtained during the formulation and application of the proposed methodology. The results are shown in the order the methodology is carried out.

6.2.1. Fix the desired purity of HAc

In this study, the purity is fixed to the same value was previously proposed by Wang and Wong (2013) and Wang and Huang (2012)., This value is considered to fulfil the specifications needed for the recycling stream of terephthalic acid synthesis reactor (Wang and Wong, 2013), and in order to compare the results of this study with their previous works. However, this methodology can be used for different acetic acid purity values. Table 4 indicates the selected HAc purity.

Table 4. HAc purity of the study.

Component	Purity[%]
HAc	99.5

6.2.2. Formulate the overall mass balance considering two assumptions:

- **HAc is only collected at the bottom of the column. (See explanations at section 6.1).**
- **MA and PX are only collected at the top of the column. (See explanations at section 6.1).**

Considering the two assumptions, the overall mass balance becomes simpler and easier: all the HAc flow rate in the feed is collected only in the column bottom stream. PX and MA are leaving the system through the output streams at the top of the column: organic phase purge, organic phase recirculation and aqueous phase. . Water is leaving the system through all the output streams. However, fixing the purity of HAc in the column bottoms stream, the amount of water in this stream becomes fixed according to the sum of fractions to unity. Hence, the amount of water leaving the system through the output streams at the top of the column (organic phase purge, organic phase recirculation and aqueous phase) becomes fixed according to the overall mass balance. The overall mass balance equations are:

$$W_{\text{FEED}} = W_{\text{HAC PURE STREAM}} + W_{\text{ORG. PHASE PURGE}} + W_{\text{AQU. PHASE PURGE}} \quad (6)$$

$$W_{\text{FEED}} \cdot X_{\text{FEED}}^{\text{HAC}} = W_{\text{HAC PURE STREAM}} \cdot X_{\text{HAC PURE STREAM}}^{\text{HAC}} \quad (7)$$

$$W_{\text{FEED}} \cdot X_{\text{FEED}}^{\text{H}_2\text{O}} = W_{\text{HAC PURE STREAM}} \cdot X_{\text{HAC PURE STREAM}}^{\text{H}_2\text{O}} + W_{\text{ORG. PHASE PURGE}} \cdot X_{\text{ORG. PHASE PURGE}}^{\text{H}_2\text{O}} + W_{\text{AQU. PHASE PURGE}} \cdot X_{\text{AQU. PHASE PURGE}}^{\text{H}_2\text{O}} \quad (8)$$

$$W_{\text{FEED}} \cdot X_{\text{FEED}}^{\text{MA}} = W_{\text{ORG. PHASE PURGE}} \cdot X_{\text{ORG. PHASE PURGE}}^{\text{MA}} + W_{\text{AQU. PHASE PURGE}} \cdot X_{\text{AQU. PHASE PURGE}}^{\text{MA}} \quad (9)$$

$$W_{\text{FEED}} \cdot X_{\text{FEED}}^{\text{PX}} = W_{\text{ORG. PHASE PURGE}} \cdot X_{\text{ORG. PHASE PURGE}}^{\text{PX}} + W_{\text{AQU. PHASE PURGE}} \cdot X_{\text{AQU. PHASE PURGE}}^{\text{PX}} \quad (10)$$

To formulate the overall mass balance, even considering the two assumptions, it is really important to provide clear information about the inputs and outputs of the system, because these influence all the subsequent steps.

The first scheme approach to the system is shown in Figure 22. The scheme consists of a distillation column, a decanter, an organic phase purge and a recirculation of part of the organic phase as reflux. The aqueous phase is treated as waste.

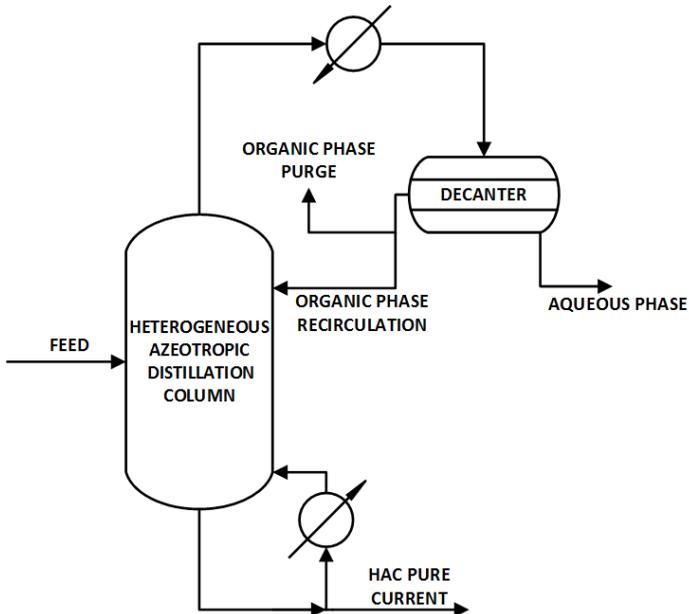


Figure 22. First column scheme design.

Simulating several times the distillation process while using this scheme (Figure 22), the HAc purity did not reach values above 80%, even increasing the column number of stages and the recirculation flow rate to high values. These results were unexpected because PX, considered to be entrainer of the mixture, did not help to increase the HAc purity. Actually, when PX was recirculated with a high flow rate, HAc started leaving only through the top of the column, and PX through the bottom of the column. The reason of what was occurring was found while looking to the ternary diagram and the residue curves map. Figure 23 shows the ternary diagram that indicates each region and explains the reasons of the obtained purity results.

When the organic phase was recirculated with a low flow rate, the system was found in the desired distillation region but, at the same time, the system did not have enough reflux to reach the desired purities. Increasing the recirculation flow rate to high values, the system increased the reflux but, at the same time, the overall feed composition crossed to the undesired distillation region. In conclusion, when recirculating only the organic phase with the overall feed composition in the desired distillation region, even at the limit, the system needs more reflux to achieve the desired separation.

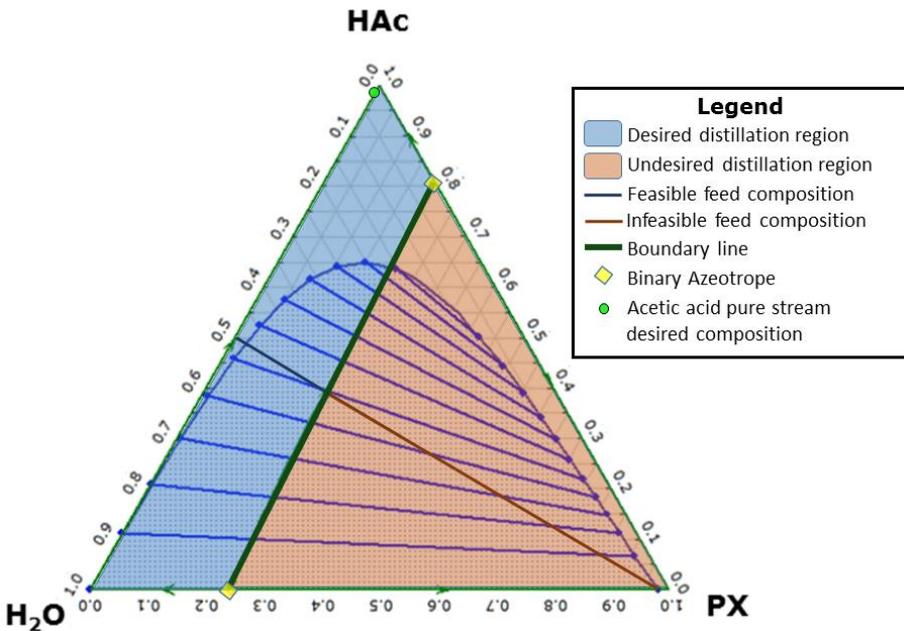


Figure 23. Overall ternary diagram with distillation regions.

The only way to remain in the desired distillation region and have enough reflux to achieve the desired separation is recirculating part of the aqueous phase too, composed most of water. Thus, the composition of the overall feed could be carried to the feasible feed composition and the reflux could be carried to enough values to reach the desired purity.

The modification on the distillation process is shown in Figure 24. Figure 25 shows the behaviour of the system when the aqueous phase is recirculated too. Depending on the ratio between the organic phase and the aqueous phase recirculation, the overall feed will be found in the darkest coloured regions.

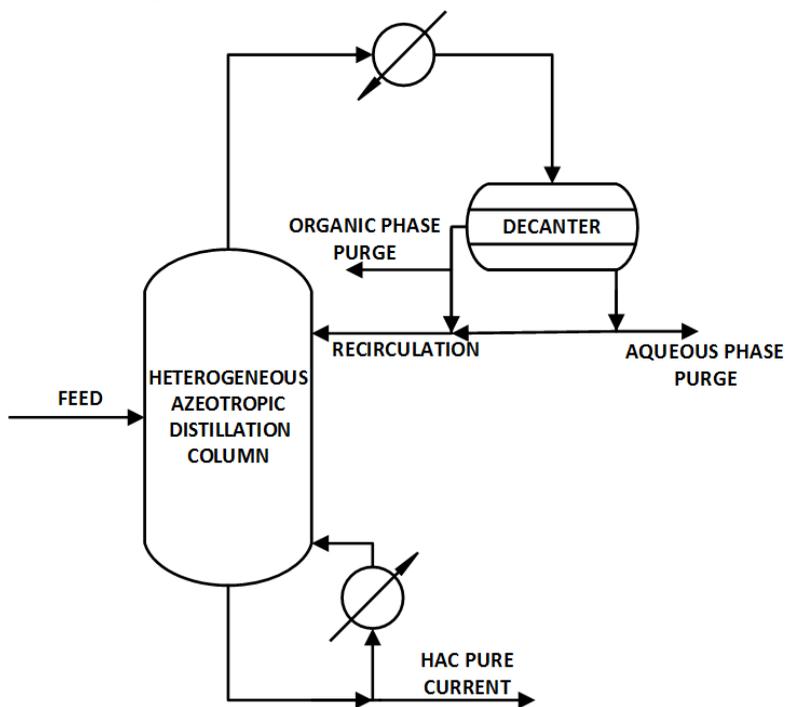


Figure 24. Final column scheme design.

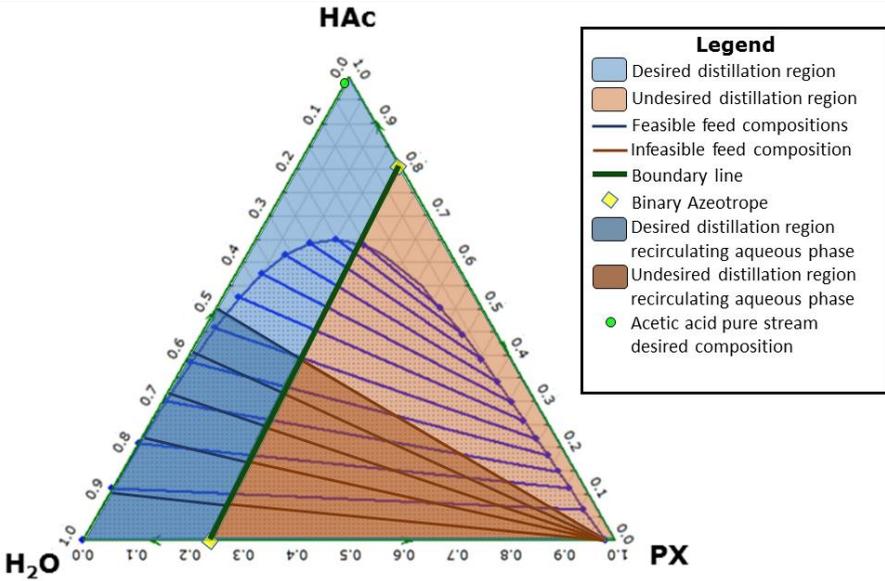


Figure 25. Overall ternary diagram with distillation regions recirculating aqueous phase.

6.2.3. Select the tie line (liquid-liquid equilibrium) of the decanter system MA/water/PX that fulfils the overall mass balance

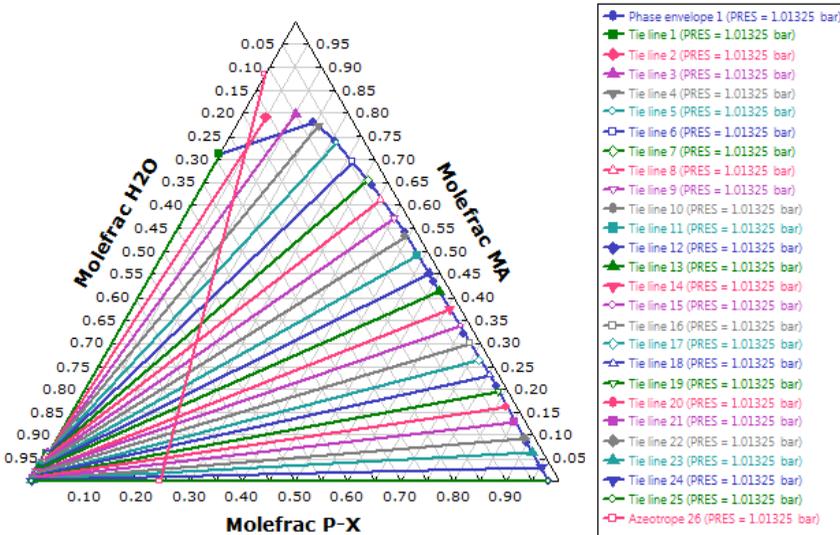


Figure 26. Ternary diagram decanter MA/H₂O/PX.

To select the tie line that fulfils the overall mass balance, first the ternary diagram of the decanter system is plotted (Figure 26). HAc does not appear in the diagram because of considering that the main component, the HAc, only leaves the system through the column bottom stream (section 6.1). The tie line ends indicate the equilibrium concentrations of the separated liquid phases of a point that is situated inside an immiscible region. Tie lines values are shown in Appendix 1.

To know which tie lines fulfil the overall mass balance, two equations of the overall mass balance were selected:

$$W_{\text{FEED}} \cdot X_{\text{FEED}}^{\text{MA}} = W_{\text{ORG. PHASE PURGE}} \cdot X_{\text{ORG. PHASE PURGE}}^{\text{MA}} + W_{\text{AQU. PHASE PURGE}} \cdot X_{\text{AQU. PHASE PURGE}}^{\text{MA}} \quad (9)$$

$$W_{\text{FEED}} \cdot X_{\text{FEED}}^{\text{PX}} = W_{\text{ORG. PHASE PURGE}} \cdot X_{\text{ORG. PHASE PURGE}}^{\text{PX}} + W_{\text{AQU. PHASE PURGE}} \cdot X_{\text{AQU. PHASE PURGE}}^{\text{PX}} \quad (10)$$

Knowing the composition in each phase at the tie line ends, the flow rates of both phases purge streams are found for each tie line. The column bottom stream flow rate is found for each tie line applying the following overall mass balance equation:

$$W_{\text{FEED}} = W_{\text{HAC PURE STREAM}} + W_{\text{ORG. PHASE PURGE}} + W_{\text{AQU. PHASE PURGE}} \quad (6)$$

Finally, the purity of HAc is found for each tie line from Equation 7:

$$X_{\text{HAC PURE STREAM}}^{\text{HAc}} = W_{\text{HAC PURE STREAM}} - W_{\text{FEED}} \cdot X_{\text{FEED}}^{\text{HAc}} \quad (11)$$

Due to the fact that Aspen Plus® software draws a maximum of 25 tie lines on the ternary diagram, the study specifications are found between two tie lines. Hence, the way that is used to select a more accurate tie line is simulating a decanter with the three components. The selected tie line composition that fulfils the desired specifications is indicated in Table 5, while the stream results and HAc purity using the selected tie line are shown in Table 6.

Table 5. Selected tie line equilibrium compositions of the separated liquid phases.

MOLEFRAC ORG. MEAC	0.3827
MOLEFRAC ORG. WATER	0.0257
MOLEFRAC ORG. P-X	0.5915
MOLEFRAC AQU. MEAC	0.0291
MOLEFRAC AQU. WATER	0.9707
MOLEFRAC AQU. P-X	traces

Table 6. Selected tie line streams results and HAC purity.

$W_{\text{AQU. PHASE PURGE}}$ [kmol/h]	1025
$W_{\text{ORG. PHASE PURGE}}$ [kmol/h]	0.3710
$W_{\text{HAC PURE STREAM}}$ [kmol/h]	1005
$X_{\text{HAC HAC PURE STREAM}}^{\text{HAC}}$	0.9950

6.2.4. Formulate the decanter mass balance taking into account the organic and aqueous purge and recirculation currents.

As it is explained in the methodology (Section 5.4), the recirculation of information is cut in order to eliminate the iteration problems and propose an easier system to converge to Aspen Plus® software. However, this action involves: (1) the output stream of the cut (Figure 8), in this case the decanter input stream specifications, have to be introduced by the user in order to obtain results; (2) the introduced values of the output stream of the cut have to be equal to the results of the input stream of the cut. Therefore, to comply with the previous consequences, the introduced values for the decanter input stream specifications cannot be random, they have to fulfil the mass balances. Figure 27 shows the streams that are involved in the mass balance.

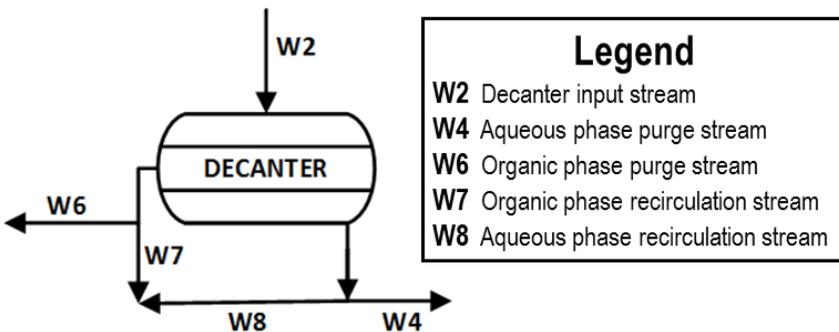


Figure 27. Decanter mass balance scheme.

The equations 12-15 describe the decanter mass balances:

$$W2 = W7 + W6 + W4 + W8 \quad (12)$$

$$W2 \cdot X2^{H2O} = W7 \cdot X7^{H2O} + W6 \cdot X6^{H2O} + W4 \cdot X4^{H2O} + W8 \cdot X8^{H2O} \quad (13)$$

$$W2 \cdot X2^{MA} = W7 \cdot X7^{MA} + W6 \cdot X6^{MA} + W4 \cdot X4^{MA} + W8 \cdot X8^{MA} \quad (14)$$

$$W2 \cdot X2^{PX} = W7 \cdot X7^{PX} + W6 \cdot X6^{PX} + W4 \cdot X4^{PX} + W8 \cdot X8^{PX} \quad (15)$$

The unknowns of the mass balance are: both phases recirculation streams ($W7$, $W8$), the decanter input stream ($W2$) and the molar fraction of each component in the decanter input stream ($X2^{H2O}$, $X2^{MA}$, $X2^{PX}$).

Due to the fact that there are not enough independent equations to solve the mass balance and determine all the unknowns, two independent variables are introduced: the decanter input stream ($W2$) and the molar fraction of PX in the decanter input stream ($X2^{PX}$). The first variable is chosen because it allows to regulate the column reflux, and can be used later to establish a ratio between the reflux rate and the HAc purity. The second variable is chosen because it is the molar fraction of the component considered as the entrainer in the system. As it is explained in Section 6.2.2, the concentration of this component must be controlled in order not to move to the undesired distillation region. Hence, the concentration of this component at the top of the column can be fixed through $W2$ stream.

In order to formulate the decanter mass balance with clearer equations to solve, two equations of the initial decanter mass balance (13, 15) are replaced by the following two equations: (1) the selected tie line equation (16), in which the decanter input stream composition has to be situated to comply with the phase split equilibrium compositions (Table 5); (2) the sum of molar fractions in the decanter input stream (17):

$$X2^{MA} = 0.5978 \cdot X2^{PX} + 0.0291 \quad (16)$$

$$X2^{H2O} + X2^{MA} + X2^{PX} = 1 \quad (17)$$

Finally the decanter mass balance is formulated using the following equations:

$$W2 = W7 + W6 + W4 + W8 \quad (12)$$

$$W2 \cdot X2^{MA} = W7 \cdot X7^{MA} + W6 \cdot X6^{MA} + W4 \cdot X4^{MA} + W8 \cdot X8^{MA} \quad (14)$$

$$X2^{MA} = 0.5978 \cdot X2^{PX} + 0.0291 \quad (16)$$

$$X2^{H2O} + X2^{MA} + X2^{PX} = 1 \quad (17)$$

Once the balance is solved, the result equations obtained with Xcas software for each unknown are:

$$W7 = 2.8281 \cdot (0.5978 \cdot W2 \cdot X2^{PX} - 4.1151e - 05 \cdot W2 - 0.1312) \quad (18)$$

$$W8 = 2.8281 \cdot (-0.5978 \cdot W2 \cdot X2^{PX} + 0.3536 \cdot W2 - 362.3889) \quad (19)$$

$$X2^{H2O} = 2.8281 \cdot (-0.5649 \cdot X2^{PX} + 0.3433) \quad (20)$$

$$X2^{MA} = 2.8281 \cdot (0.2114 \cdot X2^{PX} + 0.0103) \quad (21)$$

To know the behavior of the unknowns versus $W2$ and $X2^{PX}$, 3-D graphics have been plotted using MATLAB® software. The results are shown in Figure 28 for $W7$, Figure 29 for $W8$, Figure 30 for $X2^{H2O}$ and Figure 31 for $X2^{MA}$.

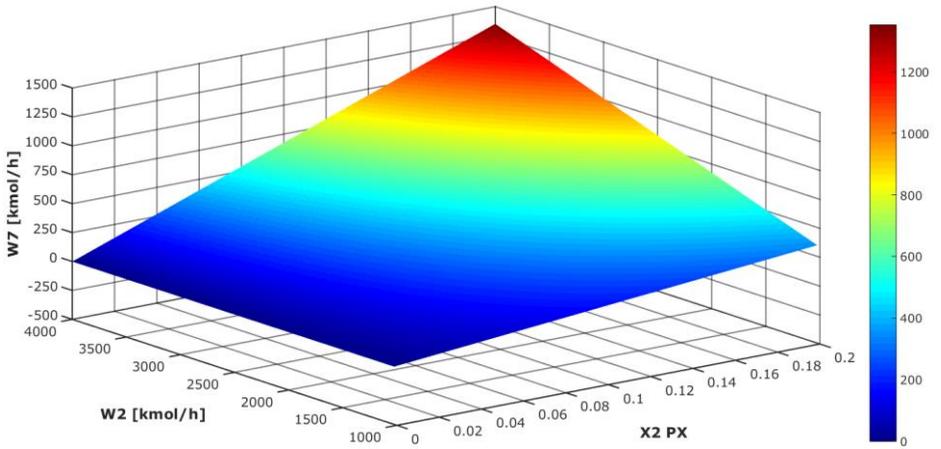


Figure 28. W7 behaviour in front of W2 an X2PX.

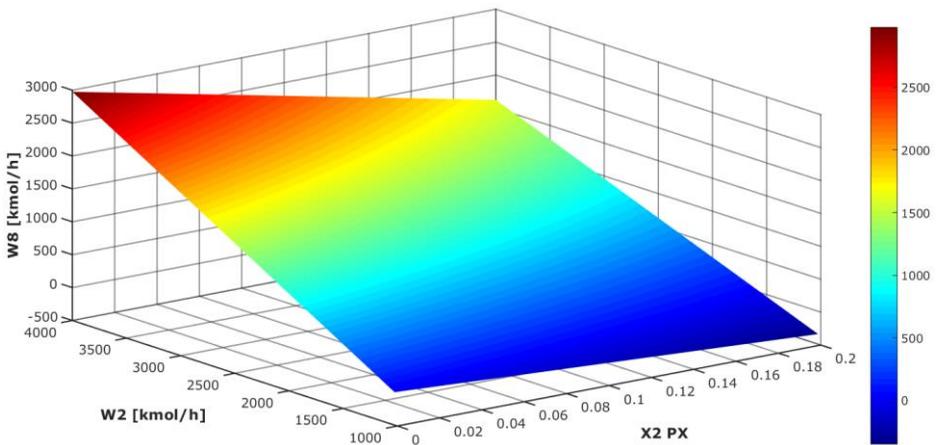
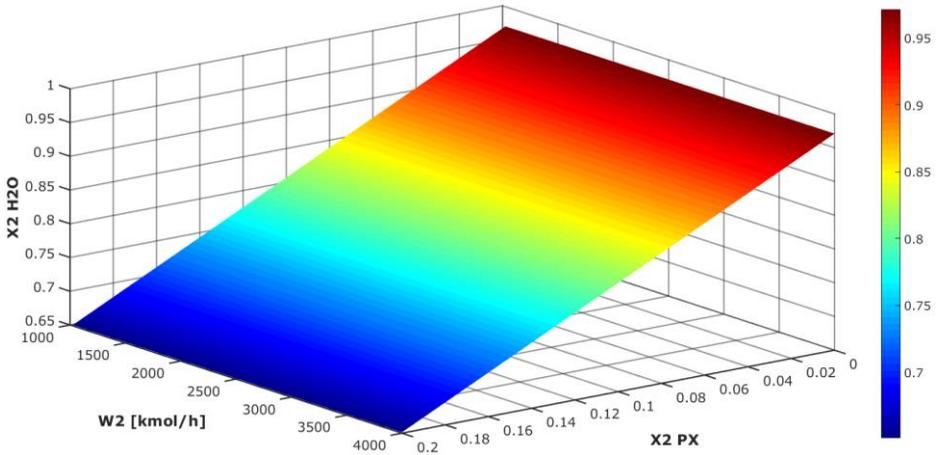
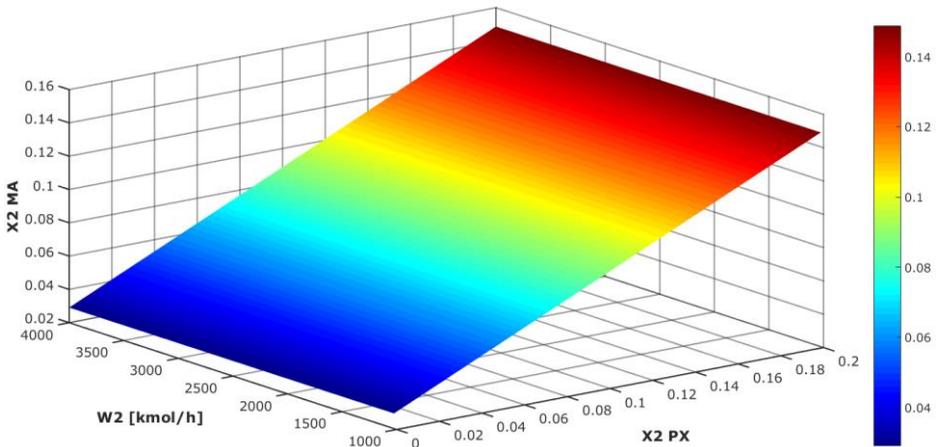


Figure 29. W8 behaviour in front of W2 an X2PX.

Figure 30. $X_2^{H_2O}$ behaviour in front of W_2 an X_2^{PX} .Figure 31. X_2^{MA} behaviour in front of W_2 an X_2^{PX} .

As it is shown in Figure 18, the molar fraction value of PX at the column distillate stream has to be under 0.2425 in the mixture of water-PX to have the system situated in the desired distillation region. This ternary diagram does not account with the presence of MA and as the behaviour of the real system formed with the four components is unknown, the real composition of PX in the system has to be situated in the desired distillation region. For this reason, in order to avoid the risk of being situated in the boundary line or in the undesired distillation region, the molar fraction value of PX at the decanter input stream is fixed at 0.20.

6.2.5. Find the optimal relation between feed stage and the decanter input stream flow rate.

To find the optimal relation between feed stage and the decanter input stream flow which provides the desired HAc purity and a low column heat duty, several accurate simulations are performed using Aspen Plus® software. The column number of stages is fixed in Section 5.2. The parameters introduced into the software in order to perform the accurate simulations are:

- The decanter input stream flow rate (W_2) and composition (X_{H_2O} , X_{MA} , X_{PX})
- Both phases purge stream flow rates (W_4 , W_6)
- The feed flow rate and composition
- The column number of stages
- The column bottom stream flow rate ($W_{HAc \text{ PURE STREAM}}$)
- The column pressure (atmospheric)
- The column feed stage

Figure 32 shows a scheme of these parameters introduced to the simulation software to perform the accurate simulations of the study.

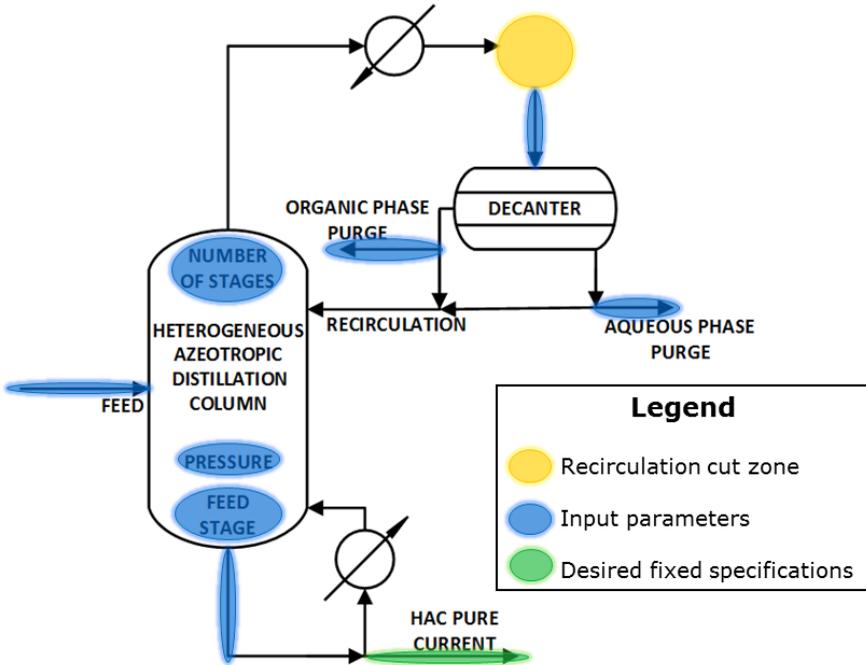


Figure 32. Graphical representation of input parameters to perform the study accurate simulations.

Due to the fact that around 2,500 rigorous simulations are performed, the most appropriate representation of all the obtained results is plotting them in a 3-D diagram. The desired specifications, in this case the HAC purity and the column heat duty (Q) are represented versus the feed stage and the decanter input stream flow rate (W_2). Figures 33 and 34 illustrate the 3-D and 2-D representation of HAC versus the feed stage and W_2 . Figures 35 and 36 illustrate the 3-D and 2-D representation of the column heat duty (Q) versus the feed stage and W_2 . The blue dots are the results of each converged simulation. The area of each plot is produced by interpolation of the simulation results.

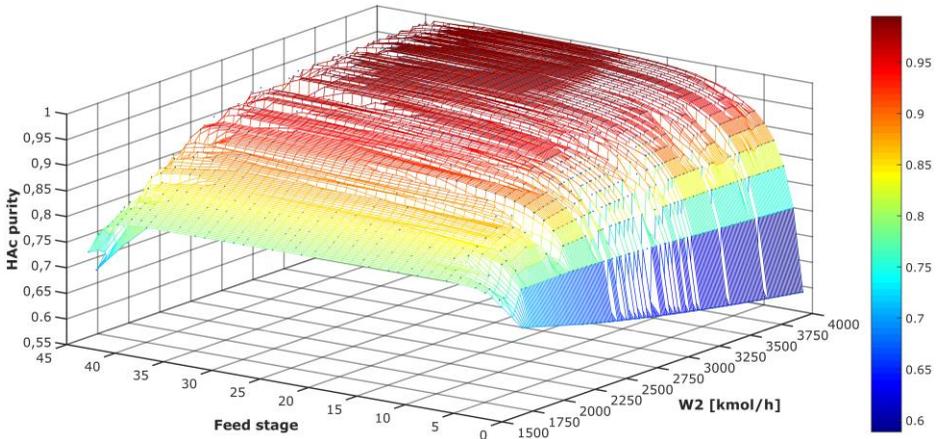


Figure 33. 3-D representation of HAC purity in front of the feed stage and W2.

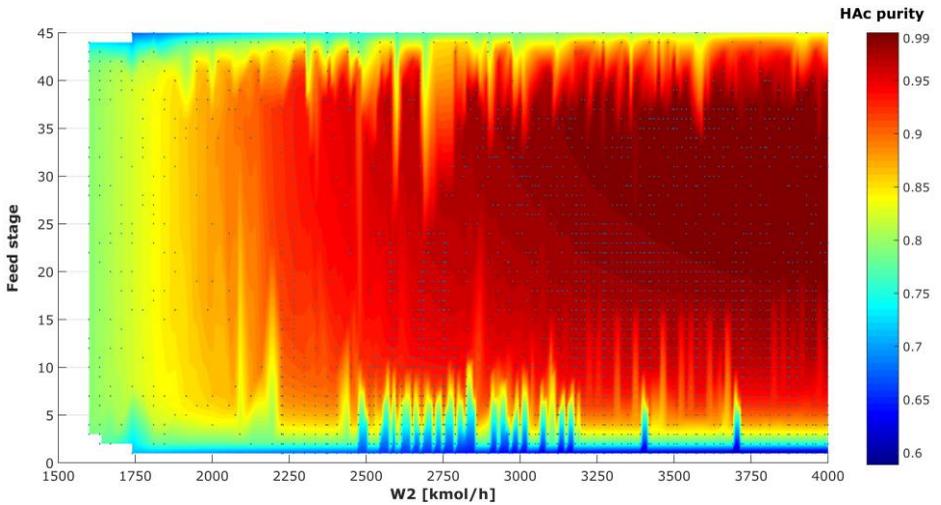


Figure 34. 2-D representation of HAC purity in front of the feed stage and W2.

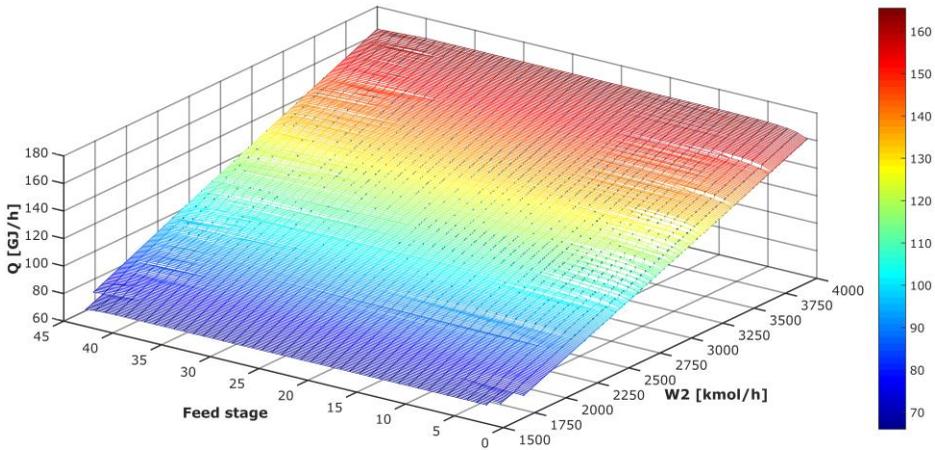


Figure 35. 3-D representation of column heat duty (Q) in front of the feed stage and W2.

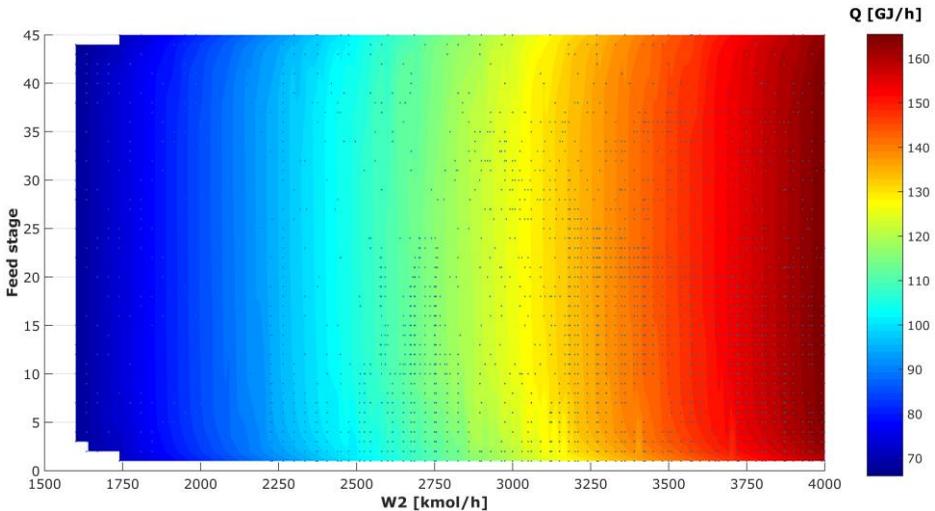


Figure 36. 2-D representation of column heat duty (Q) in front of the feed stage and W2.

Considering the obtained results of HAc purity and column heat duty (Q) versus the feed stage and the decanter input stream flow rate (W2), it is shown that to obtain an acetic acid purity of 99.5%, the minimum decanter input stream flow rate (W2) is 3,450 kmol/h, feeding at the stage 40. Its respective column heat duty is 143.72 GJ/h. Figure 37 shows the distillation process represented in the ternary diagram and in the column scheme.

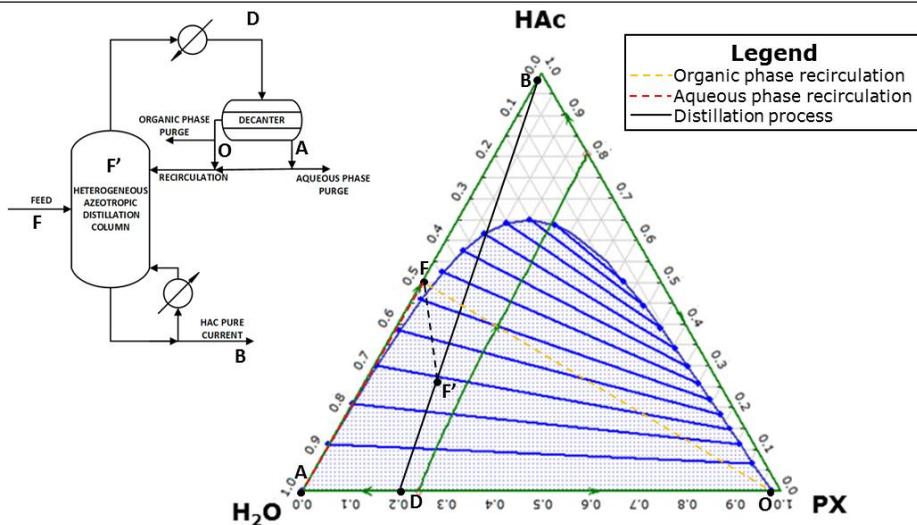


Figure 37. Distillation process scheme.

6.3. COMPARISON OF RESULTS

In the Appendices 2 and 3 the process scheme of the heterogeneous azeotropic distillation (HAD) columns from previous works of Wang and Huang (2012) and Wang and Wong (2013) are shown. The same thermodynamic model parameters are implemented. In the work of Wang and Wong (2013) there is a side-draw instead of an organic phase purge. Both of them use a p-xylene make up in the decanter. In this study, this make up of p-xylene is not considered to be essential for the process, as the similar results were obtained using it or not.

The results of the previous works are:

- Wang and Huang (2012): 99.5% HAC purity feeding at the stage 9 and with a decanter input stream flow rate of 1,861.77 kmol/h. Its respective column heat duty is 85.42 GJ/h.
- Wang and Wong (2013): 99.5% HAC purity feeding at the stage 9 and with a decanter input stream flow rate of 1,690.81 kmol/h. Its respective column heat duty is 79.92 GJ/h.

Both previous works were simulated. Nevertheless, the final results reached a HAC purity of 83% with its respective column heat duty of 79.9 GJ/h.

7. CONCLUSIONS

The behaviour of the system is represented in a tetrahedron and shows an unstable node and two stable nodes. Therefore, there are two distillation regions and only one of them is suitable to collect acetic acid at the bottom of the column. The PX amount on the top of the column defines the distillation region where the column operates. Two assumptions simplify the mass balances: HAc is only collected at the bottom of the column and MA and PX are only collected at the top of the column.

The novelty of the resolution method proposed in the present study is that the HAc product purity is introduced as input variable and the simulation is performed without any tear stream. To obtain the HAc desired purity, both split phases from the decanter have to be recirculated to the column. Only the aqueous phase is collected as distillate, and a purge is placed in the recirculated organic phase stream.

All the flow rates and compositions are represented in function of the decanter input stream and its p-xylene molar fraction.

Rigorous simulations have been performed to find the optimal relation between feed stage and the decanter input stream flow. Around 2,500 rigorous simulations are performed to check the behaviour of the system. To obtain an acetic acid purity of 99.5%, the minimum decanter input stream flow rate (W_2) is 3,450 kmol/h, feeding at the stage 40. Its respective column heat duty is 143.72 GJ/h.

The results are compared with two previous works using the same thermodynamic model and inputs. The authors claim that the HAc 99.5% purity is achievable with a heat duty around 80 GJ/h and feeding at the stage 9. Nevertheless, when these studies are reproduced again here with the indicated heat duty, only an HAc purity of 83% is reached.

8. REFERENCES AND NOTES

- Aspen® Technology, Inc., 2015, <http://www.aspentech.com/products/aspen-plus.aspx> (accessed Feb 3, 2015).
- Bonet-Ruiz A. -E, J. Bonet, G. Bozga, J.-Ll. Llacuna, V. Plesu, Number of Transfer Units Information on Residue Curve Maps, *Chemical Engineering Transactions* Volume 21 **2010** pp 1417-1422.
- Bonet-Ruiz A.-E., Modelling and simulation of continuous catalytic distillation processes, PhD Dissertation, University "Politehnica" of Bucarest, **2012**.
- Cano E., Rectificación del ácido acético acuoso utilizando metil acetate como entrainer, Trabajo de Final de Carrera Ingeniería Química de la Universidad de Barcelona **2014**.
- ChemStation®, online available technical article, http://www.chemstations.com/content/documents/Technical_Articles/DISTILLATION.PDF (accessed Mar 4, 2015).
- Chien I.L., H.P. Huang, T.K. Gau, C.H. Wang, Influence of feed impurity on the design and operation of an industrial acetic acid dehydration column, *Industrial & Engineering Chemistry Research* 44 **2005** pp 3510–3521.
- Chien I.L., K.L. Zeng, H.Y. Chao, J.H. Liu, Design and control of acetic acid dehydration system via heterogeneous azeotropic distillation, *Chemical Engineering Science* 59 **2004** pp 4547–4567.
- Górák A., E. Sorensen, *Distillation: Fundamentals and Principles*, Elsevier: Academic Press UK, **2014**.
- Górák A., Z. Olujic, *Distillation: Equipment and Processes*, Elsevier: Academic Press UK, **2014**.
- Huang H.P., H.Y. Lee, T.K. Gau, I.L. Chien, Design and control of acetic acid dehydration column with p-xylene or m-xylene feed impurity. 1. Importance of feed tray location on the process design, *Industrial & Engineering Chemistry Research* 46 **2007** pp 505–517.
- Huang X., W. Zhong, W. Du, F. Qian, Thermodynamic Analysis and Process Simulation of an Industrial Acetic Acid Dehydration System via Heterogeneous Azeotropic Distillation, *Ind. Eng. Chem. Res.* 52 **2013** pp 2944–2957.
- Institut Fourier, 2015, <http://www-fourier.ujf-grenoble.fr/~parisse/giac.html> (accessed Mar 4, 2015).
- Kurooka T., Y. Yamashita, H. Nishitani, Y. Hashimoto, M. Yoshida, M. Numata, Dynamic simulation and nonlinear control system design of a heterogeneous azeotropic distillation column, *Computers and Chemical Engineering* 24 **2000** pp 887–892.
- Lee H.Y., H.P. Huang, I.L. Chien, Design and control of acetic acid dehydration column with p-xylene or m-xylene feed impurity. 2. Bifurcation analysis and control, *Industrial & Engineering Chemistry Research* 47 **2008** pp 3046–3059.
- Lee M.M., D.J. Kwon, D.W. Lee, A.J. Lee, Azeotropic distillation process for separating acetic acid, methyl acetate and water in the production of an aromatic carboxylic acid, US Patent Number 0,027,340 **2007**.
- Li C., Dynamic simulation and analysis of industrial purified terephthalic acid solvent dehydration process, *Chinese Journal of Chemical Engineering* 19 **2011** pp 89–96.
- Li S., D. Huang, Simulation and analysis on multiple steady states of an industrial acetic acid dehydration system, *Chinese Journal of Chemical Engineering* 19 **2011** pp 983–989.
- Parten W.D., A.M. Ure, Dehydration of acetic acid by azeotropic distillation in the production of an aromatic acid, US Patent Number 5,980,696 **1999**.
- Sirola J.J., An industrial perspective on process synthesis, *AIChE Symposium Series* 91 (304) **1995** pp 222–233.

- The MathWorks, Inc., 2015, http://es.mathworks.com/products/new_products/release2008b.html (accessed Apr 7, 2015).
- Wang S.J., C.J. Lee, S.S. Jang, S.S. Shieh, Plant-wide design and control of acetic acid dehydration system via heterogeneous azeotropic distillation and divided wall distillation, *Journal of Process Control* 18 **2008** pp 45–60.
- Wang S.J., D.S.H. Wong, Online switching of entrainers for acetic acid dehydration by heterogeneous azeotropic distillation, *Journal of Process Control* 23 **2013** pp 78– 88.
- Wang S.J., K. Huang, Design and control of acetic acid dehydration system via heterogeneous azeotropic distillation using p-xylene as an entrainer, *Chemical Engineering and Processing* 60 **2012** pp 65– 76.
- Wasylikiewicz S.K., L.C. Kobylka, F.J.L. Castillo, Optimal design of complex azeotropic distillation columns, *Chemical Engineering Journal* 79 **2000** pp 219–227.
- Wolfram® Research Europe Ltd., 2015, <http://www.wolfram.com/mathematica/> (accessed Feb 21, 2015).

Atès el caràcter no lucratiu i la finalitat exclusivament docent i eminentment il·lustrativa dels materials disponibles en aquest Treball de Final de Grau, m'acullo a l'article 32 de la Llei de Propietat Intel·lectual vigent respecte de l'ús parcial d'obres alienes com ara imatges, gràfics, texts o altre material utilitzat en el present Treball de Final de Grau.

9. ACRONYMS

PET = polyethylene terephthalate

TA = Terephthalic acid

HAc = Acetic acid

H₂O = Water

MA = Methyl acetate

PX = p-Xylene

HAD = Heterogeneous Azeotropic Distillation

PET = polyethylene terephthalate

EA = Ethyl acetate

NBA = n-Butyl acetate

IBA = isobutyl acetate

NPA = n-Propyl acetate

NTU = Number of Transfer Units

NRTL = Nonrandom two-liquid

3-D = Three-dimensional

2-D = Two-dimensional

W = molar flow rate

X(stream)^(component) = Molar fraction of the component at the stream

W2 = Decanter input stream molar flow rate

W4 = Aqueous phase purge stream molar flow rate

W6 = Organic phase purge stream molar flow rate

W7 = Organic phase recirculation stream molar flow rate

W8 = Aqueous phase recirculation stream molar flow rate

APPENDICES

APPENDIX 1: TIE LINES VALUES

Table A1. Tie lines values of MA/H₂O/PX phase split.

TIE LINE #	MOLEFR AC ORG. MA	MOLEFR AC ORG. H ₂ O	MOLEFR AC ORG. PX	MOLEFR AC AQU. MA	MOLEFR AC AQU. H ₂ O	MOLEFR AC AQU. PX
1	0.71199	0.28800	0	0.06157	0.93842	0.00E+00
2	0.79192	0.16010	0.04796	0.05832	0.94163	4.23E-05
3	0.79729	0.10030	0.10239	0.06048	0.93947	3.77E-05
4	0.77277	0.06951	0.15771	0.06217	0.93778	3.63E-05
5	0.73646	0.05203	0.21150	0.06134	0.93861	3.65E-05
6	0.69594	0.04134	0.26270	0.05802	0.94193	3.71E-05
7	0.65433	0.03436	0.31130	0.05327	0.94668	3.77E-05
8	0.61274	0.02956	0.35768	0.04806	0.95189	3.83E-05
9	0.57160	0.02612	0.40227	0.04292	0.95703	3.92E-05
10	0.53104	0.02358	0.44537	0.03810	0.96185	4.03E-05
11	0.49111	0.02168	0.48720	0.03368	0.96627	4.16E-05
12	0.45185	0.02024	0.52790	0.02966	0.97029	4.32E-05
13	0.41325	0.01915	0.56758	0.02602	0.97393	4.49E-05
14	0.37532	0.01834	0.60632	0.02272	0.97723	4.68E-05
15	0.33806	0.01775	0.64418	0.01972	0.98022	4.89E-05
16	0.30145	0.01733	0.68120	0.01698	0.98296	5.11E-05
17	0.26549	0.01707	0.71742	0.01448	0.98546	5.34E-05
18	0.23017	0.01695	0.75287	0.01218	0.98776	5.59E-05
19	0.19548	0.01693	0.78757	0.01005	0.98988	5.85E-05
20	0.16141	0.01702	0.82155	0.00808	0.99185	6.12E-05
21	0.12795	0.01720	0.85483	0.00625	0.99368	6.40E-05
22	0.09509	0.01746	0.88743	0.00453	0.99539	6.68E-05
23	0.06282	0.01780	0.91936	0.00293	0.99699	6.98E-05
24	0.03112	0.01822	0.95064	0.00142	0.99850	7.28E-05
25	0	0.01869	0.98130	0	0.99992	7.58E-05

APPENDIX 2: SIMULATION WANG AND HUANG (2012)

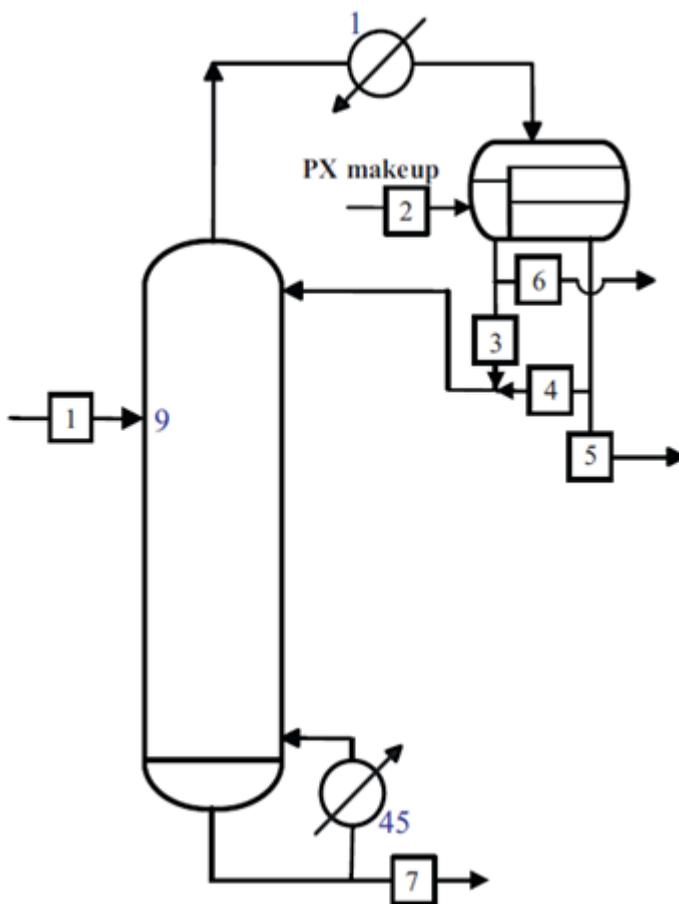


Figure A2. Wang and Huang distillation process scheme.

Table A2. Wang and Huang distillation process values.

Stream no.	1	2	3	4	5	6	7
Temperature (°C)	70.0	35.0	35.0	35.0	35.0	35.0	125.8
Mole flow (kmol/h)							
HAc	1000.000	0.000	0.029	0.019	0.067	0.000	999.933
H ₂ O	1000.000	0.000	8.843	280.624	994.938	0.038	5.025
MA	30.000	0.000	299.021	8.099	28.717	1.282	0.000
PX	0.290	0.760	239.796	0.006	0.022	1.028	0.000
Total	2030.290	0.760	547.689	288.748	1023.744	2.348	1004.958
Mole percent							
HAc	49.254	0.000	5.331E-03	6.525E-03	6.525E-03	5.331E-03	99.500
H ₂ O	49.254	0.000	1.615	97.186	97.186	1.615	0.500
MA	1.478	0.000	54.597	2.805	2.805	54.597	0.000
PX	0.014	100.000	43.783	2.165E-03	2.165E-03	43.783	0.000

APPENDIX 3: SIMULATION WANG AND WONG (2013)

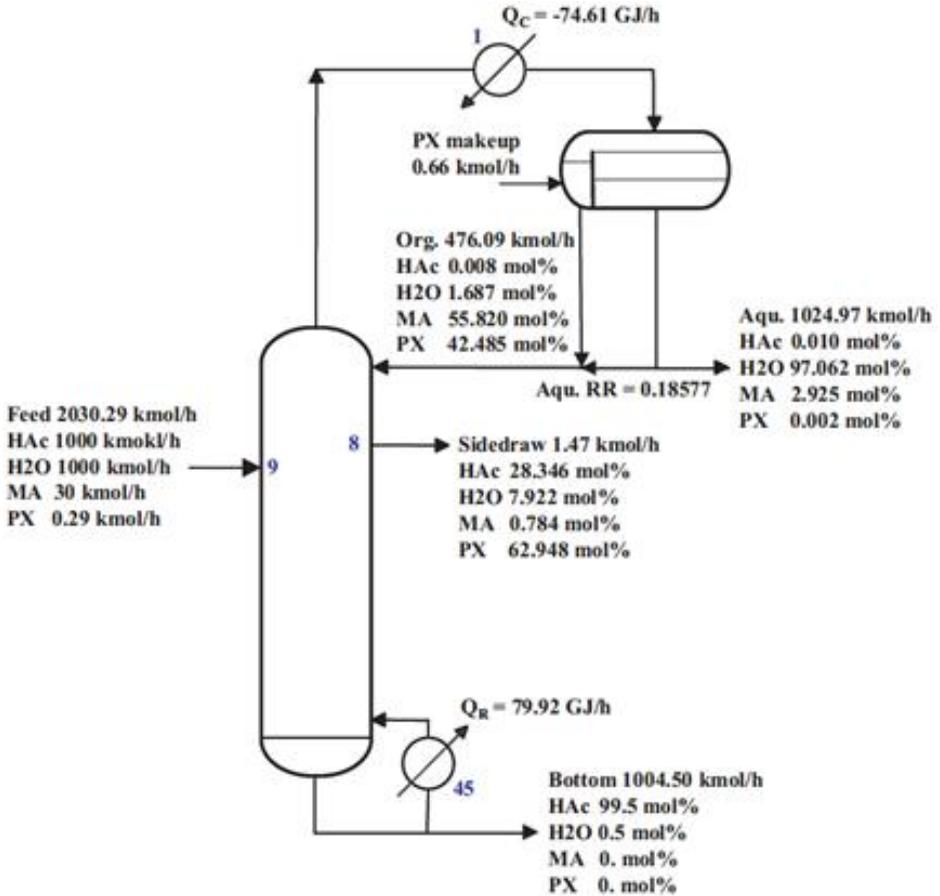


Figure A3. Wang and Wong distillation process scheme.

