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|  | **azeotropic distillation process** |

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The thesis was carried out in a short time and I had faced impediments to first applying my knowledge at school to practical situations, therefore, mistakes and deficits are inevitable. Thus I am willing to receive comments and assessments from teachers so that I can improve my project later on.

Student

Quang Khoa LE

**Abstract**

Acetic acid dehydration is so far an important step in the production of purified isophthalic acid. Although Acetic Acid and Water do not form an azeotrope at atmospheric pressure, this system (acetic acid-water) cannot be separated easily by using a normal distillation. In this paper, an industrial separation acetic acid and water system via heterogeneous azeotropic distillation is carried out by using Aspen Plus software. The entrainer using to facilitate the separation is isobutyl acetate. Adding another component to the column, in order to form azeotrope and alter the relative volatility of these components, leads to change the behavior of column and make the process be more difficult to be operated. A good understanding of vapor liquid equilibrium (VLE) and vapor liquid liquid equilibrium (VLLE) is really essential to have a good design then a thermodynamic model analysis is put in place in order to make a good choice of model using for this simulation. A process description gives all parameter needed for simulation. Three manipulated variables in this process are bottom flow rate, IBA reflux flow rate and water reflux ratio. Multiple steady states are observed via different solution branches. An analysis of sensitivity on multiple steady states is carried out to see how the performance of the column is under different steady state.

*Keywords* : acetic acid dehydration, heterogeneous azeotropic distillation, multiple steady states, binary analysis, residue curve.

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# Introduction

In chemical industry, distillation is one of the most popular processes. It is also a useful tool to separate two or several components of a mixture. Nowadays, engineers are quite familiar with distillation process; however, there are always some difficulties concerning the composition of feed stream, one is azeotropic mixture. This mixture is not easy to be separated, so that another component which is called entrainer is added to facilitate the separation. In fact, these entrainers form heterogeneous (or homogeneous) azeotropes with the valuable products and alter their relative volatility. For example, Acetic acid (HAC) dehydration is so far an important step in the production of purified isophthalic acid (PIA). Although acetic acid and water do not form an azeotrope at atmospheric pressure, this system (HAC-water) cannot be separated easily by using a normal distillation. It may lead to the high requirement of operating cost (due to high number of tray in a column, or backup stream (entrainer)…). By tracing vapor liquid equilibrium(figure 1), it is easy to see that this mixture form a pinch area on the pure water end where the liquid composition and vapor composition are very closed together, that is why Isobutyl Acetate (IBA) is used as an entrainer introduced to the system to make the separation easier.

However, the use of IBA as an entrainer also makes the column extremely difficult to operate and simulate because of distillation boundaries, phase split, multi component presenting in the column and the possible existence of multiple steady states.

In fact, in the production of purified isophthalic acid, Acetic acid is used as a solvent throughout the process, where isophthalic acid is produced when m-xylène is oxidized in acetic acid solvent. Then it is necessary to remove water producing during the process from acetic acid by sending this mixture of acetic acid-water to an acetic acid dehydrating column. Then HAC is returned to the oxidation step Nevertheless, a small amount of m-xylène may be present in the feed leading to this HAC dehydrating column as a tiny amount of impurity.

In the first part of this paper, the choice of thermodynamic model will be discussed as well as the choice of IBA as entrainer. Then in the latter part of this paper, the whole industrial process will be described and simulated, an analysis of the sensitivity on multiple steady states will be also mentioned.

# Thermodynamique model analysis

## What is an azeotrope ?

In a multicomponent mixture, nonideal interations between molecules of two or more species can cause azeotropic behavior, where there is a critical composition for this, the vapor and liquid composition is identical. Then the components cannot be separated by using a normal distillation process at a given pressure.

Each azeotrope has a specific boiling point, which is either less than temperature boiling point of any of its constituents (this case is called a minimum boiling azeotrope, and can be found on the top of the column), or greater than temperature boiling point of any of its constituents (this case is called maximum boiling azeotrope and leaves in the bottom of the column).

If at the equilibrium temperature the liquid mixture is homogeneous (containing one liquid phase), the azeotrope is called a homoazeotrope, where the entrainer changes the relative volatility of the azeotropic constituent but not cause liquid-liquid immiscibility. If the vapor phase coexists with two liquid phases, it is called a heteroazeotrope, where the entrainer alters the relative volatility and induces liquid phase separation

Heterogeneous azeotropic distillation[1,2,3] is a widely used separation process in the chemical industrial process for the dehydration of a various range of material such as acetic acid, chloroform, and many types of alcohol. Separating close boiling point involves adding a third component which is called entrainer, in order to form a minimum boiling, water is sent to the overhead and pure desired product is taken off from the bottom.

An entrainer is usually used to facilitate the separation of an Azeotropic mixture. The selection of entrainer [4] must be a critical step since the choice of entrainer determines the separation sequence (number of distillation column, decanter …).

However, the use of another component as an entrainer can be extremely difficult to operate and to simulate due to distillation boundaries, phase split, multi component…

In this study, an industrial process for acetic acid dehydration via heterogeneous azeotropic distillation will be discussed. HAC– water separation is very difficult due to the existence of a tangent pinch on the pure water end, where the liquid composition and vapor composition are really close together. That leads to conclude that it is necessary to use an entrainer via a heterogeneous azeotropic distillation column system in case of producing high-purity water. This entrainer will form azeotrope with water, and its boiling point is lower than pure water’s (100°C, at atmospheric pressure).

By using Aspen plus (a simulator program), we can plot the vapor liquid equilibrium of system Acetic acid-water.



***Figure 1***: T-xy diagram for Acetic acid

Many entrainers have been studied so far by several researchers (Luyben W.L, ChienI-L.[5], San-Jang Wang, Kejin Huang[6]) in order to find out which one gives the best economical process design. IBA was chosen by most of the researchers, in this study, instead of carrying out an entrainer analysis, we chose to use/adopted IBA as entrainer, the explanation is given in the later part of this work.

First of all, a model analysis must be carried out to help understand and figure out which thermodynamic methodology should be used for this separation.

* 1. Choice for thermodynamic methodology

The basic of distillations is phase equilibrium, such as: vapor-liquid equilibrium (VLE), vapor-liquid-liquid equilibrium (VLLE). A good understanding of VLE and VLLE is really essential to have a good analysis, design, and control of distillation column. **Aspen plus** [7]simulator software is used to describe the VLE and VLLE system.

### Binary system

Some thermodynamic models will be discussed in this section in order to make a good choice of model for the calculation. In this case, there is a non-ideal mixture: HAC, Water, and IBA, so it is required to use a model which is capable of calculating the activity coefficient, as function of mole fractions and system temperature, for highly non-ideal chemical system. Aspen simulator provides some models: UNIQUAC, UNIFAC, NRTL (nonrandom two liquids). By using “Diagrams for Binary systems” feature on Aspen Plus v8.2, vapor-liquid equilibrium (VLE) curve of two components can be traced, then these values are exported and plotted on Excel, in order to compare the VLE obtained by software and VLE obtained from experimental data (“vapor liquid equilibrium data collection” [8])

***HAC- water system:***

***Figure 2***: VLE curve of system HAC-water obtained by different models

The binary system of Acetic Acid-Isobutyl Acetate can be found nowhere, but the others system can be considered instead such as Acetic Acid-nButyl Acetate, and Acetic Acid-isopropyl Acetate. The VLE of these binary systems are plotted on Excel and compared to the experimental data values by doing exactly the same works like before (*appendix 1*). It is now clear that NRTL parameters provide a good match between predicted and experimental data for binary system so that NRTL model is recommended for this system.

The equation for the NRTL model [9] resulting expression for the activity coefficient of component 1 and 2 in a binary mixture:





Where:

,

,

Aspen physical Property System has a large number of built-in binary parameters for the NRTL. The form of the equation for NRTL model in Aspen plus [10] is:



Moreover, vapor phase non ideality caused by the dimerization of Acetic Acid is taken into consideration by using the Hayden-O’connell [11]. This correlation is used to obtain the second virial coefficient for acetic acid. The other missing parameters are estimated by UNIFAC.

### Ternary system

NRTL parameters were used to describe the vapor-liquid-liquid equilibrium of this system and Hayden-O’Connell equation was used to take into account the vapor association. Azeotrope report is obtained from an Aspen plus feature “Ternary plot”. Two Azeotropes were found for the mixture of three components (HAC-water-IBA), see the table below:

|  |
| --- |
| **AZEOTROPE SEARCH REPORT** |

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

***Mixture Investigated For Azeotropes At A Pressure Of 101325 N/SQM***

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| |  |  |  |  | | --- | --- | --- | --- | | **Comp ID** | **Component Name** | **Classification** | **Temperature** | | **ACETI-01** | **ACETIC-ACID** | **Saddle** | **118.01 C** | | **WATER** | **WATER** | **Saddle** | **100.02 C** | | **ISOBU-01** | **ISOBUTYL-ACETATE** | **Saddle** | **116.40 C** | |

***2 Azeotropes found***

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 01 | |  |  |  | | --- | --- | --- | | **Number Of Components: 2** | **Temperature 122.72 C** | | | **Homogeneous** | **Classification: Stable node** | | |  | **MOLE BASIS** | **MASS BASIS** | | **ACETI-01** | 0.5326 | 0.3707 | | **ISOBU-01** | 0.4674 | 0.6293 | |

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 02 | |  |  |  | | --- | --- | --- | | **Number Of Components: 2** | **Temperature 88.06 C** | | | **Heterogeneous** | **Classification: Unstable node** | | |  | **MOLE BASIS** | **MASS BASIS** | | **WATER** | 0.6419 | 0.2176 | | **ISOBU-01** | 0.3581 | 0.7824 | |

***Table 1***: Azeotrope research

Triangular diagrams (especially so-called Residue Curve Map (RCM) [12, 13]) are often used to describe the equilibrium of a ternary mixture.

A RCM begins and ends at nodes, and there are some notations used in the RCM as well as in the Azeotropic search report above:

* A stable node is highest boiling point in a distillation region, there are only arrows pointing inward at this point.
* An unstable node is lowest boiling point in a distillation region, there are only arrows pointing outward at this point.
* Saddles have both arrows pointing inward and pointing outward. Pure components and azeotropes which have a boiling point between the stable nodes and unstable nodes are saddles.

Residue curve runs from unstable node to stable node via a saddle node.

Distillation boundary is a line between stable node and an azeotrope in the system or between two azeotropes. It divides ternary plot into different distillation regions.



***Figure 3***: ternary map

Here again, a tangent pinch is observed on the pure water end. The binary azeotrope Water-IBA has temperature boiling point 88.06°C, at 101 325 kPa, is an unstable node. The binary azeotrope HAC-IBA has temperature boiling point 122.71°C at 101 325 kPa is a stable node.

Due to the presence of the azeotropes, ternary diagram is divided into three distillation regions. One of two distillation region boundaries is formed between HAC and Water-IBA azeotrope, another is formed between Water-IBA azeotrope and HAC-IBA azeotrope.

* Region 1 has a stable node (HAC), an unstable node (water-IBA azeotrope) and a saddle point (water).
* Region 2 has a stable node (HAC-IBA azeotrope), an unstable node (water-IBA azeotrope) and a saddle point (HAC).
* Region 3 has a stable node (HAC-IBA azeotrope), an unstable node (water-IBA azeotrope) and a saddle point (IBA).

In region 2 and region 3, stable point is HAC-IBA azeotrope (122.71°C at 101 325 kPa) . Operating in these regions, we risk losing of IBA in the bottom stream, which is undesirable. Distillation in region 1 is expected to be operated, since acetic acid pure can be obtained in the bottom product and product specifications could be respected.

It is now necessary to verify if the chosen model NRTL-HOC gives a good match between predicted and experimental data for the ternary system. The values obtained from the model on Aspen are collected then plotted on Excel and compare with experimental values (from “Liquid-liquid equilibrium data collection, ternary system” [14])). We want to plot Acetic Acid mole fraction as a function of Water mole fraction (then IBA mole fraction can be deduced easily by using the relation: xIBA+xHAC+xwater =1):

***Figure 4***: ternary system, Acetic Acid mole fraction as a function of Water mole fraction

As we can see that using the chosen model does not give a good match between predicted and experimental data. To correct this inconvenience, the other NRTL parameters proposed by William L. Luyben and I-Lung Chien were used[5] (*table 2*) but that could not bring about better results. After a great effort, we can conclude that although the values obtained from the NRTL-HOC model does not fit very well to the experimental data for ternary system, but this model is the best among the models chosen to study.

|  |  |  |  |
| --- | --- | --- | --- |
| **Comp. i** | **Acetic acid** | **Acetic acid** | **Isobutyl Acetate** |
| **Comp. j** | **Water** | **Isobutyl Acetate** | **Water** |
| aij | 0 | 0 | 0 |
| aji | 0 | 0 | 0 |
| bij(K) | -211.310 | 90.268 | 489.609 |
| bji(K) | 652.995 | 194.416 | 1809.079 |
|  | 0.3 | 0.3 | 0.2505 |

***Table 2*:** NRTL Parameters for HAC-water-IBA system

## 2.3 Case study:

Before doing the simulation with the true data, a case study was done in order to make sure whether the chosen model works well by comparing the result obtained from Aspen Plus with the result in document given by Perstorp employees while using the same data input. The stream table, vapor composition profiles, temperature profile and the process design are shown in *appendix 2*.

Some observations can be made from the results obtained: the mass flow and mass fraction of two product streams (bottom and top) are not exactly the same but really close together between the result in the data given and simulation result. The vapor composition profiles look like the same appearance comparing to the given figure. However the temperature plot does not match very well, except that the bottom and the top temperature are quite the same.

# Process simulation

## Isobutyl Acetate (IBA) is used as the entrainer for this system

Firstly, HAC has a highest boiling point in ternary system, it means that high-purity acetic acid can be obtained in the bottom of column while the azeotrope of Water-IBA (blue dot in the figure) can be found on the top product, and also the slippage of the entrainer into the bottom is excluded. A large temperature difference between the two desired products presented in the bottom and the top of the column makes the separation easier.

Secondly, by looking at the RCM, we can see that the azeotrope composition contains more water in the mixture; it means that IBA entrainer is more capable of carrying water to the top of the column, or the smaller composition of entrainer in the mixture, the less entrainer is needed in the column. On the other hand, from the RCM, the aqueous phase contains little IBA but almost water, then the loss of IBA entrainer in the rejected aqueous phase is minimized, so that an IBA makeup stream is needed. Consequently, from economical point of view, cost of the process would be decreased.

## Process description

In this study, a heterogeneous azeotropic distillation process used for HAC dehydration is investigated.

The liquid feed and vapor feed are sent to the C3301 column at tray number 37 and 45, respectively, the composition and flow rate are given in the *table 3*.



***Figure 5*:** Process flow sheet

By using isobutyl acetate as entrainer for this system, high purity acetic acid can be obtained in the bottom product while minimum boiling azeotrope water-IBA exits the HAC column via overhead product. From the top of column, the vapor passes through an exchanger to decrease its temperature to 40°C and then enter to the decanter. Here, the overhead stream is condensed and separated into two liquid phases, since the Water-IBA azeotrope is heterogeneous. The organic phase which is rich on entrainer will be refluxed partially, back to the heterogeneous azeotropic column, and the rest will be sent to an IBA-MA (isobutyl acetate-methyl acetate) column to eliminate MA. IBA leaving this column will be sent back to the decanter, but in this study this column will not be discussed, and IBA-pure stream is needed to compensate the loss of IBA during the simulation. The aqueous phase which gets out the decanter will be partially refluxed to the HAC column while another part is sent to another decanter to extract waste water again, however, this last decanter is not interesting to be discussed either and we consider this stream as a product stream (or so-called “top product” which contains mostly water). The water reflux stream is back to the dehydration column at the first stage in order to meet the product specification.

## Process simulation

The system is simulated by using Aspen Plus. The setting data for this process (number of trays, feed tray, pressure, vapor composition, feed flow rate, feed composition) as well as the product specification is taken from a real industry plant. The column consists of 51 trays (including the reboiler and numbering from the top of column to the bottom), its top pressure is at 1.3 bars and column pressure drop is 0.24 bars. All the other setting data can be found in the table below:

|  |  |
| --- | --- |
| Column total tray | 51 |
| Column top pressure(stage 1) (bar) | 1.3 |
| Column drop pressure (bar) | 0.24 |
| Liquid feed stage | 37 |
| Liquid feed flow rate (kg/h) | 26150 |
| Liquid feed composition | 0.73; 0.2527; 0.002; 0.015; 0.0002; 0.0001 |
| Vapor feed stage | 45 |
| Vapor feed flow rate(kg/h) | 5830 |
| Vapor feed composition | 0.907; 0.085; 0; 0.008; 0; 0 |
| Reflux stage | 1 |
| IBA-ref flow rate (kg/h) | 22000 |
| Water ref ratio | 0.17 |
| Bottom flow rate (kg/h) | 25500 |

***Table 3***: base-case condition of the system

***Note***: mass fraction composition (HAC, Water, IBA, MA, MX, and Methanol). The product specification is given in the table below:

**Product Specification:**

Top: Bottom:

HAC < 0.1% Water 6 – 7%

IBA < 0.4 %

After completing all input required, the simulation was run several time, an important remark is that more than one steady state in the system was observed. In fact there are three steady states for this system; it refers to the phenomenon multiple steady states (MSS) which is considered as one of the problem that may encounter when running a heterogeneous azeotropic distillation. Its existence has been proved experimentally by several researchers [15, 16]. Three steady states presence in this system: the low (SS1), intermediate (SS3) and high (SS2) steady state.

**Legend:**

HAC: *Acetic Acid* MX: *Metaxylene* IBOH: *Isobutanol*

MA: *Methyl Acetate*  IBA: *Isobutyl Acetate* MeOH: *Methanol*

### Steady state SS1

This steady state solution is undesired, since the product specification is not respected. According to the results given in *table 4*, a significant amount of HAC presences in the top product (or water stream product), that leads to an important loss of HAC. On the other hand, 10% of water is found in the bottom product, it means that the HAC product obtained is not pure enough.

Furthermore, from the vapor composition profiles in *appendix 3*, it is remarkable that IBA die out just after tray number 6, IBA do not go down in the column as far as enough to give a good separation water-HAC. This confirms a conclusion made before: this steady state is undesired.

|  |  |  |
| --- | --- | --- |
| **L\_w (water ref) (kg/h)** | 1183.236(0.17) | 1201.445(0.17) |
| **L\_IBA (IBA ref) (kg/h)** | 20000 | 24000 |
| **B (bottom kg/h)** | 25500 | 25500 |
| **Xwater** | **0.108995** | **0.09803** |
| **X IBA** | 3.7E-06 | 2.3E-06 |
| **XHAC** | 0.891001 | 0.901968 |
| **D (top product kg/h)** | 5776.977 | 5865.878 |
| **Xwater** | 0.726584 | 0.767234 |
| **XHAC** | **0.214185** | **0.180826** |
| **Q( heat duty MW)** | 5.808516 | 6.476562 |
| **steam (ton/h)** | 8.974532 | 10.00671 |
| **T BOT** | 121.1225 | 121.7559 |
| **T TOP** | 102.2339 | 101.3169 |

***Table 4***: Steady state SS1 undesired

### Steady state SS2

This steady state solution gives better results. The vapor composition profiles are quite correct, *appendix 3* (it is quite similar to the composition profile in “case study” we studied above). The water composition (1%-3%) is even much better than expected (6%-7%). However, a significant amount of entrainer IBA is found in the bottom product (contains 3% of IBA, while the specification for this stream is less than 0.4% of IBA), that leads to an important loss of IBA. The temperature in the bottom of HAC column (128-130°C) is much higher than expected (at around 122.22°C). That explains why this steady state is not desired.

|  |  |  |
| --- | --- | --- |
| **Lw(water ref)** | 1410.021(0.17) | 1343.007(0.17) |
| **LIBA(IBA ref)** | 20000 | 18000 |
| **B (bottom kg/h)** | 25500 | 25500 |
| **Xwater** | 0.0155268 | 0.0274451 |
| **X IBA** | **0.028294502** | **0.016377263** |
| **XHAC** | 0.9559729 | 0.9559729 |
| **D (top product kg/h)** | 6884.22 | 6557.035 |
| **Xwater** | 0.9688071 | 0.9701339 |
| **XHAC** | 2.16E-09 | 2.25E-08 |
| **Q( heat duty MW)** | 6.875681295 | 6.386644157 |
| **steam (ton/h)** | 10.62337024 | 9.867776379 |
| **T BOT** | **130** | **128** |
| **T TOP** | 86 | 85 |

***Table 5***: Steady state SS2 undesired

### Steady state SS3

This steady state solution gives the best result of all. Product specification is respected. Temperature in the bottom is still high (around 124-126°C) but it closes to the target (122.22°C)). On the other hand, top temperature is quite good; it closes to the temperature of Water-IBA azeotrope (88°C) as expected. The big difference between SS2 and SS3 is that IBA composition in the bottom stream in SS3 is much less than the one in SS2, then much less loss of IBA in SS3. It is the reason why SS3 is a desired steady state solution of this process.

|  |  |  |
| --- | --- | --- |
| **Lw(water ref)** | 1257.025(0.17) | 1265.647(0.17) |
| **LIBA(IBA ref)** | 22000 | 19000 |
| **B (bottom kg/h)** | 25500 | 25500 |
| **Xwater (%)** | 0.04296 | 0.041327 |
| **X IBA (%)** | 0.001192 | 0.002708 |
| **XHAC (%)** | 0.955843 | 0.955936 |
| **D (top product kg/h)** | 6137.241 | 6179.337 |
| **Xwater (%)** | 0.971139 | 0.971354 |
| **XHAC (%)** | **0.000457** | **0.000131** |
| **Q( heat duty MW)** | 6.652795 | 6.273144 |
| **steam (ton/h)** | 10.279 | 9.692412 |
| **T BOT** | **126** | **126** |
| **T TOP** | **89.5** | **87.5** |

***Table 6***: Steady state SS3 desired

*Note that the tables above (5, 6 and 7) do not display the final results; but they give us a general view of the behaviors of each steady state solution.*

In the last context, an analysis of sensitivity on multiple steady states will be carried out to give a good understanding.

# Analysis on multiple steady states

The two manipulated variables chosen here are IBA reflux flow rate and water reflux ratio. We are interested in observing the variation of the purity of HAC in the bottom stream product and the heat duty of reboiler.

Firstly, in *figure 6*, IBA reflux flow rate is selected as manipulated variable while water reflux ratio and bottom flow rate are kept constant at 0.17 and 25500, respectively. IBA ref flow rate varies between 15000 kg/h and 28000 kg/h. The increment in each step is set at 100kg/h.

Some observations can be made, steady state 1 (SS1) needs less energy introduced to reboiler but gives the worst purity of HAC. It is eventually not a good choice. Steady state 2 (SS2) and 3 (SS3) give almost the same purity of HAC product, but steady state 3 needs less heat duty than steady state 2 does.

***Figure 6***: manipulated variable: IBA reflux flow rate

***Figure 7***: manipulated variable: water reflux ratio

Secondly, in *figure 7*, water reflux ratio is selected as manipulated variable, IBA reflux stream is kept constant at 20000 kg/h, and bottom flow rate is always the same (25500 kg/h).This figure has the same appearance as *figure 6*; SS1 gives the worst HAC composition in bottom product stream. Heat duty and HAC composition are quite similar for the two other steady states (SS2 and SS3). If water reflux ratio is greater than 0.22, steady state 2 solution will never be obtained.

Conclusion, steady state SS3 solution is desired. Product specification is sucessfully respected however energy needed to put into reboiler (from 9 to 10 t/h LS) is still higher than energy used for the real process (6.79 t/h LS).

It is worth noting from the two figures above that the solution branch jumps from high branch SS2 to lower branch SS3 (desired) at flow rate of 19500kg/h of IBA reflux flow rate. Then, it jumps from branch SS3 to SS1 (undesired) at flow rate of 17600 kg/h of IBA reflux; so that it is necessary to operate the heterogeneous distillation column with an IBA reflux flow rate greater than 18000 kg/h. On the other hand, any important change in IBA reflux flow rate (increase or decrease at least 7000kg/h) may cause a jump from SS2 or SS3 to SS1 (undesired), so that during column operation, any change or disturbance on this stream flow rate should not be too big to avoid the jump from high steady states to low steady state.

Unfortunately, in this simulation, the system often works at the low steady state SS1 which is undesired, while the desired steady state SS3 is not easy to achieve. From the figure 5 and 6, we can see that the low steady state SS1 can be always achieved during the variation of two chosen manipulated variables with a step size of 100 kg/h for IBA reflux stream and 0.01 for water reflux ratio. This simulation always starts up with steady state solution SS1. We would like to know how to jump from this stead state (SS1) to steady state SS3 (desired) by adjusting IBA reflux flow rate. Another remark is that during the simulation, a jump from one steady state to another may be occurred when there is an important change in IBA reflux stream.

Although a great effort has been made to find out how to jump from SS1 (undesired) to SS3 (desired), a general method with a good and logic explanation could not be found. However, a particular solution is found and it works for all time. The simulation is start up with:

IBA reflux flow rate: 20000 kg/h  
Bottom flow rate : 26500 kg/h  
Water reflux ratio : 0.17

The low steady state SS1 is achieved first, then we increase IBA reflux up to 32000 kg/h while the others parameter are kept constant, we are still at SS1 solution branch. Finally, we increase IBA reflux up to 37000 kg/h, and here we jump to the high steady state SS2. Then IBA reflux is decreased gradually with a step of 2000 kg/h until reach SS3 at about 19000 kg/h. This is the desirable steady state solution, and then we can change the parameters (inputs) to obtain result expected while respecting all product specification and reduce reboiler duty.

*Note that at the key point where there is a jump from one steady state to another, the divergence will occur.*

# Result

The result obtained from the simulation is presented in *appendix 4*. IBA reflux flow rate is 19000 kg/h, bottom flow rate is 25500 kg/h, and water reflux ratio is 0.2 (1236.3 kg/h). The profiles of composition show that IBA goes downward in the column and die out to a small quantity at some trays after vapor feed. All product specifications are respected, however energy required (9.2 t/h LS) is still higher than expected (6.79 t/h LS).

It is remarkable that m-xylene (MX), impurity presents in the feed stream, accumulate in the column and attaint its highest composition at tray 34, then in practice, a side stream in order to draw off MX from the column at this tray. Since the increasing of MX leads to an area of the column will be occupied, it has an effect on AA-water separation.

# Conclusion

By using simulator software Aspen plus, a heterogeneous azeotropic distillation (HAD) process is investigated. However, it is difficult to understand and operate a HAC column, so that an accordant thermodynamic model is really necessary to give a good description of VLE and VLLE for binary and ternary system. Among the physical model proposed by Aspen software, it is necessary to put in place a model analysis to find out which model gives a good match between predicted and experimental data.

During the process simulation, a multiple steady states are observed via different solution branches. A sensitivity analysis was carried out to help understanding how the performance of the column distillation under the different steady states is. This analysis is useful for operating a heterogeneous azeotropic distillation process. We figure out that the desired operating point is at the high steady state SS3, and it is not easy to be achieved. When starting up the process, we are always at the undesired steady state SS1, however the desired steady state SS3 can be achieved by adjusting the IBA reflux flow rate (different star-up strategies).

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# Appendix 1: Thermodynamique models

***Acetic acid- Isopropyl acetate system:***

***Acetic acid-butyl acetate system:***

Appendix 2: Case study

**Process flow sheet**



**Results obtained by simulating on Aspen Plus:**

|  |  |  |
| --- | --- | --- |
|  | BOTTOM | OVERHEAD |
| **Mass Flow kg/hr** |  |  |
| ACETI-01 | 20418.29 | 6.612727 |
| WATER | 848.7119 | 5510.988 |
| ISOBU-01 | 73.70905 | 18108.19 |
| METHY-01 | 0.00214493 | 1803.398 |
| M-XYL-01 | 809.2896 | 699.9104 |
| **Mass Frac** |  |  |
| ACETI-01 | 0.9218188 | 0.000253079 |
| WATER | 0.0383165 | 0.2109138 |
| ISOBU-01 | 0.00332772 | 0.6930277 |
| METHY-01 | 9.68E-08 | 0.0690187 |
| M-XYL-01 | 0.0365367 | 0.0267866 |
| **Total Flow kg/hr** | 22150 | 26129.1 |
| **Temperature C** | 122.5708 | 86.92196 |



Composition profiles



Temperature profile

# Appendix 3: Multiple steady states

1. **Steady state SS1**



Composition profile



Temperature profile

1. **Steady state SS2**



Composition profile



Temperature profile

# Appendix 4: Final result

|  |  |  |  |
| --- | --- | --- | --- |
|  | **Bottom product** | **top product** | **IBA\_ref** |
| **Flow rate (kg/h)** | 26000 | 5627.608 | 19000 |
| **HAC** | 0.9374948 | 0.000363247 | 0.00012 |
| **WATER** | 0.0612502 | 0.9707089 | 0.014431 |
| **IBA** | 0.00125061 | 0.00640666 | 0.890028 |
| **METHY ACETATE** | 5.55E-07 | 0.0220899 | 0.093834 |
| **M-XYLENE** | 3.10E-06 | 5.09E-07 | 0.001535 |
| **METHANOL** | 7.31E-07 | 0.000430718 | 5.13E-05 |
| **Q heat duty (MW)** | 5.977910726 |  |  |
| **steam (t/h)** | **9.236256915** |  |  |
| **T BOT\_Column** | 124.424238 |  |  |
| **T TOP\_Column** | 88.3736279 |  |  |

stream property



vapor composition profiles



Temperature profile