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Design and simulation of dividing wall column for ternary heterogeneous distillation

Master’s thesis in Chemical Engineering

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Abstract

Heterogeneous azeotropic distillation is routinely used in chemical industry to separate close boiling point mixtures and azeotropes, which are not easily separated in a normal distillation process.

Dividing wall column is one of the most promising technologies to minimize the energy consumption that leads to minimize the operating cost. Dividing wall column provide a large potential energy saving up to more than 30% compared to the conventional column sequences.

The aim of this work is to figure out a novel approach to apply the dividing wall column in heterogeneous azeotropic distillation as well as minimize energy required. In this paper, four-component heterogeneous system was investigated: water, acetic acid (HAC), component X, and heavy organics. Water, acetic acid and component X form a two-liquid phase system.

Two alternatives were investigated. Both of them allow downsizing the chemical plant but only with the Petlyuk arrangement we can achieve an energy saving up to 18.3% compared to the conventional design. Energy saving achieved in this work is not as much as expected, but at least it shows the significant potential for the combination of Petlyuk arrangement and ternary heterogeneous distillation.

Acknowledgments

This master thesis could not have been completed without support of several individuals. Firstly and mainly, I would like to thank my supervisor, Prof. Sigurd Skogestad at Chemical Engineering department, NTNU, for his willingness to give guidance and orientation. I came to Norway one year ago with a lot of difficulties in speaking an understanding English, but he has been always explaining and answering all my questions with patience and enthusiasm. His door was always open for advices and suggestion. I have learned a lot from working with him, not only professional skill but also the attitude towards research work. He is a great and brilliant team leader in the Process Control group. Especially, I will never forget his nice and social smile whenever I came to ask for help. Working with him is one of my most beautiful souvenirs from Norway.

I would like to express my great appreciation to my co-supervisor, Dr Ivar J halvorsen (from Sintef). He has given me some brilliant ideas about my project and he also helped me to tackle with simulating problem. Next, my special thank is extended to O.Pajalic (from Perstorp), for entrusting me with this project. I know he is very busy with his works in Perstorp, but he always has replied my e-mail quickly. It was such a nice experience working with him.

Finally, I would like to thank my parents who have been always standing by my side to support and encourage me, and my two sisters who has been always motivating me to work harder and sharing their experience to help me deal with personal life when I am living far away

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.

I declare that this is an independent work according to the exam regulations of the Norwegian University of Sience and technology (NTNU)

Date and signature

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I. Introduction:

Heterogeneous azeotropic distillation (1,2,3) is widely used in chemical industry to separate close boiling point mixtures and azeotropes, which are not easily separated in a normal distillation process. In reality, this technique is routinely employed for dehydration of a various range of material includes acetic acid (HAC), chloroform, and many types of alcohol. Among these, acetic acid dehydration is most frequent seen in industry. It usually is difficult to separate acetic acid and water by a conventional distillation column, even though they do not form an azeotrope at atmospheric pressure. Furthermore, HAC and water can form a pinch area on the pure water end, where the liquid and vapor composition are much closer to one another (*figure I.1*). Therefore, using a conventional column may require a large number of trays and a large boil-up flow rate that leads to the high operating cost.

This problem could be circumvented by the heterogeneous azeotropic distillation technology. It is a special technique, which introduces a third component called entrainer to the azeotropic system to make the separation easier by creating a new lower or higher boiling point azeotrope. However, entrainer addition makes the column extremely difficult to operate and simulate because of distillation boundaries, phase split, non-linear dynamics, and the possible existence of multiple steady states. Previous review by Widagdo and Seider (4) gives a comprehensive overview of azeotropic distillation.

In most distillation processes, the major operating cost is re-boiler heat duty supplied to the distillation column. Therefore minimizing the re-boiler heat input could results in minimizing the operating cost. Up until now, there are a few distillation technologies, which can reduce energy consumption for a multicomponent system. One of the most promising technologies is dividing wall column (DWC) configuration. However, there was no experimental work or very few studies conducted on dividing wall column for a ternary heterogeneous distillation.

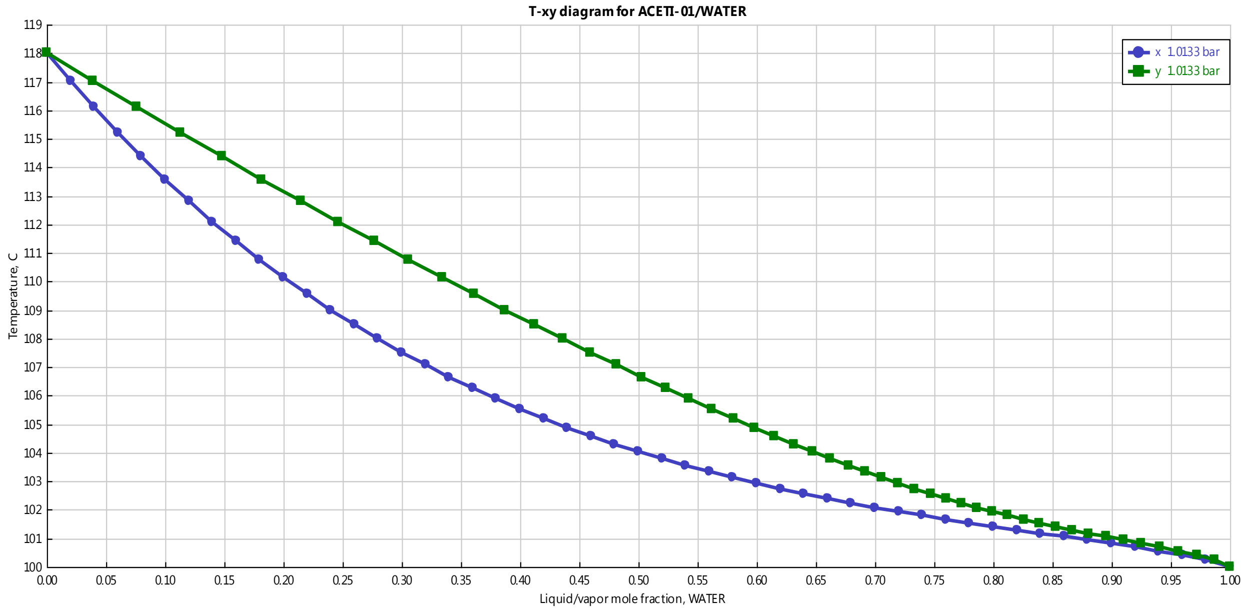

Figure I.1 T-xy diagram for acetic acid/water system

Richard Wright developed the DWC in 1946. Since the first industrial DWC implemented in 1985 by BASF SE (5), there have been more than 100 industrial applications of DWC in 2006 (6), and more than 200 DWC installed in 2013. Specifically, for a three-component separation, there are two different types of DWC. The first type shown in *figure 1.2a* is the most common (7). The second one illustrated in *figure I.2b and I.2c*, in which the shell is located either at the upper or at the lower part of the column.

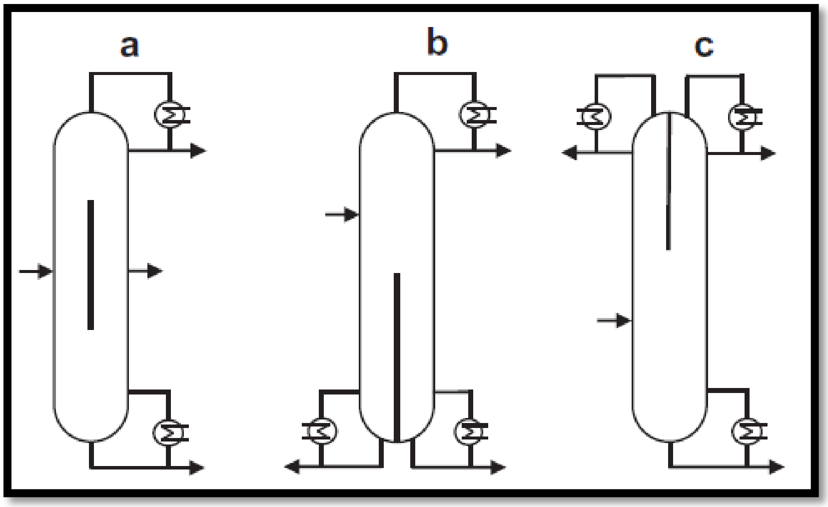

Figure I.2 Different basic types of DWC

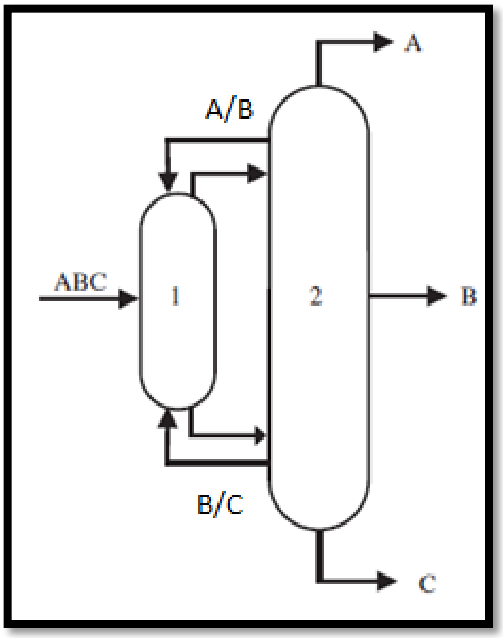

Figure I.3 Thermally coupled (Petlyuk)

In the most common DWC configuration, namely Petlyuk column or fully thermally coupled distillation column (*figure I.3*), the multicomponent feed is introduced to the pre-fractionator. This column carries out a sharp separation between heavy and light components. In fact, the low-boiling point component (A) goes to the top, the high-boiling point component (C) goes to the bottom, while the middle-boiling point component (B) distributes at both places. Then high purity of B can be drawn out as a side draw (*figure I.3*), while the heavy component C and light component A can be withdrawn at theirs maximum concentration from the bottom and the top section of main column, respectively.

DWC technique can also be employed to perform the separation of three or more components. The advantage of DWC is not only saving energy but also using less equipment leads to less capital investment and less maintenance compared to the conventional configuration. However, there are some drawbacks of DWC limiting its industrial application such as taller distillation column, higher-pressure drop, and higher temperature difference.

The aim of this work is to figure out a novel approach to apply the dividing wall column in heterogeneous azeotropic distillation as well as minimize energy required. In this paper, four-component heterogeneous system was investigated. It includes water (W) (boiling point is

100°C), acetic acid (HAC) (boiling point is 118°C), component X (boiling point is about 150°C), and heavy organics (HO), which include two subsequent components named HO1 and HO2. Among these, component X, water, and acetic acid constitute a two liquid phase system.

A comprehensive thermodynamic analysis was performed in order to understand and utilize the most suitable thermodynamic model. The conventional process was then built and simulated on Aspen Plus using the real data produced by Perstorp (0). Once the process successfully converges and all the product purities had achieved, an optimization phase was indispensable to minimize energy usage for the conventional design. Finally, the application of a DWC for a ternary heterogeneous azeotropic distillation was examined. Furthermore, two alternatives were also investigated in this paper: one with the wall placed at the middle of the column or so-called Petlyuk column, and the other one with the wall placed at the upper part of the column.

II. Azeotrope :

Before going to the detailed analysis, an overview of azeotrope is indispensable to understand azeotrope mixtures formation and their specific characteristics. Hence their behavior in a distillation column can be predicted and investigated.

1. What is an azeotrope?

In a multicomponent mixture, non-ideal interactions between molecules of two or more species may cause azeotropic behavior, where there is a critical composition. More specifically, the equilibrium vapor composition and liquid composition are identical at a given pressure and temperature. Therefore the components cannot be easily separated by a normal distillation. Sometimes people get confused between azeotropes and single component, because they boil at a specific temperature. In addition, the boiling point of these azeotropes is different from that of the pure components

If at equilibrium temperature, the liquid mixture is homogeneous (containing one liquid phase); the azeotrope is called a homo-azeotrope, where the entrainer alters the relative volatility of the azeotropic constituent but not cause liquid-liquid immiscibility. If the vapor phase coexists with two liquid phases, the mixture is called a hetero-azeotrope, where the entrainer alters the relative volatility and induces two liquid phases, which can be separated easily using a decanter.

Each azeotrope has a specific boiling point, which is either less than temperature boiling point of any of its constituents (named minimum boiling azeotrope), or greater than temperature boiling point of any of its constituents (called maximum boiling azeotrope).

2. Vapor-liquid phase equilibrium calculation and azeotropy:

At a moderate pressure (less than 10 bars), the vapor-liquid phase equilibrium for a non-ideal mixture can be expressed as:

$$y_i P = x_i \gamma_i (x,T) P_i^{sat}(T) \qquad \text{i = 1, 2, …,n}$$

Where: y_i and x_i are vapor and liquid fraction of component i respectively.

T and P are temperature and pressure of the system.

γ_i is the activity coefficient of component i in the liquid phase.

P_i^{sat} is the saturated vapor pressure of component i.

The mixture is said to be ideal when $\gamma_i = 1$, the equation above simplifies to Raoult's law:

$$y_i P = x_i P_i^{sat}(T) \qquad \text{i = 1, 2, …, n}$$

If the deviations from Raoult's law (positive ($\gamma_i > 1$), or negative ($\gamma_i < 1$)) become large enough, the azeotropic behavior can be observed. At the azeotropic point, the liquid phase has the same composition as its equilibrium vapor phase: $x = y$.

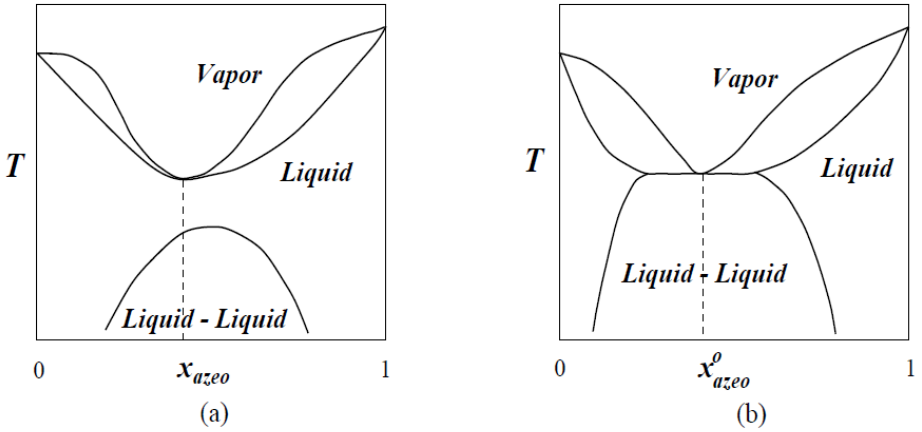

Figure II.1 Azeotropes can be homogeneous (a) or heterogeneous (b)

If the deviation is positive and sufficient large ($\gamma_i > 4$), the system may form a hetero-azeotrop where vapor phase is coexists with two liquid phases (*figure II.1b*)

The non-ideal behavior is caused by the interaction between the molecules of system. More specifically we have three cases:

- Positive deviation from Raoul's law: the force of attraction between identical molecules (A-A and B-B) is stronger than between different molecules (A-B). This leads to the formation of minimum-boiling azeotrope.
- Negative deviation from Raoul's law: the force of attraction between different molecules (A-B) is stronger than between identical molecules (A-A and B-B). This leads to the formation of maximum-boiling azeotrope.
- Obey Raoul's law or ideal mixture: all the intermolecular forces in the system are equal.

III. Thermodynamic methodology:

1. Aspen Plus:

Aspen Plus simulator is employed to perform the thermodynamic analysis and to simulate the process.

Aspen, or Advanced System for Process Engineering, was the first time developed in 1970s by researchers at MIT's Energy Laboratory, US. Since its invention, Aspen has been commercialized all over the world by a company named Aspen Tech. This software has been being used by process manufacturers to optimize their supply, engineering, manufacturing chains. It has a large scale of built-in model library for almost all equipment in industry such as: distillation columns, heat exchangers, reactors, separators, splitters/mixers, pressure changers. Aspen also provides a huge built-in databank for thermodynamic and physical parameters.

Aspen Plus is so far known as an effective simulator to carry out a wide range of tasks for almost every aspect of process engineering, such as: regressing and estimating physical properties, constructing and optimizing the process industrial, performing steady state result or dynamical result…. Moreover, this software is widely used in industry from designing the process to estimating annual operating cost.

2. Thermodynamic analysis:

The basic of distillations is phase equilibrium, such as: vapor-liquid equilibrium (VLE), vapor-liquid-liquid equilibrium (VLLE). Therefore a comprehensive analysis on VLE and VLLE is indispensable to understand and operate the distillation columns.

NRTL (Non Random Two-Liquid) is usually recommended for highly non-ideal system Aspen Plus physical property system has a large number of built-in binary parameters for the NRTL model. The equation for NRTL model in Aspen plus (8) is given below. Note that for NRTL model, three parameters need to be specified: b_{ij}, b_{ji} and an additional symmetrical parameter c_{ij}. In Aspen Plus, the binary parameters are named A12, A21 which are related to b_{ij}, b_{ji} in the equation below, and the ALPHA12 corresponds to the c_{ij} parameter in the NRTL model.

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \tau_{ij} \right)$$

$$\begin{aligned}
&where: \\
&G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \\
&\tau_{ij} = \alpha_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + f_{ij} T \\
&\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15K) \\
&\tau_{ij} = 0 \\
&G_{ij} = 1
\end{aligned}$$

The equilibrium data for the ternary system water-acetic acid-component X were carried out in Perstorp (9), and the other missing parameters are estimated by UNIFAC.

In addition, the vapor phase non ideality caused by the dimerization of Acetic Acid has to be taken into consideration by using the Hayden-O'connell (10). This correlation is used to obtain the second virial coefficient for acetic acid.

The Aspen feature "Diagrams for Binary systems" uses the thermodynamic parameters which is either provided by user or predicted by Aspen Plus to plot the vapor-liquid equilibrium (VLE) curve of two-component mixture. Then these values are exported and plotted on Excel in order to compare the VLE obtained by Aspen Plus with the VLE obtained from experimental data (11).

Finally, NRTL-HOC is chosen as thermodynamic model for this ternary system (W-HAC-X). From the *figures 3.1 and 3.2* below, we can see that the parameters of the model chosen provide a good match between predicted and experimental data.

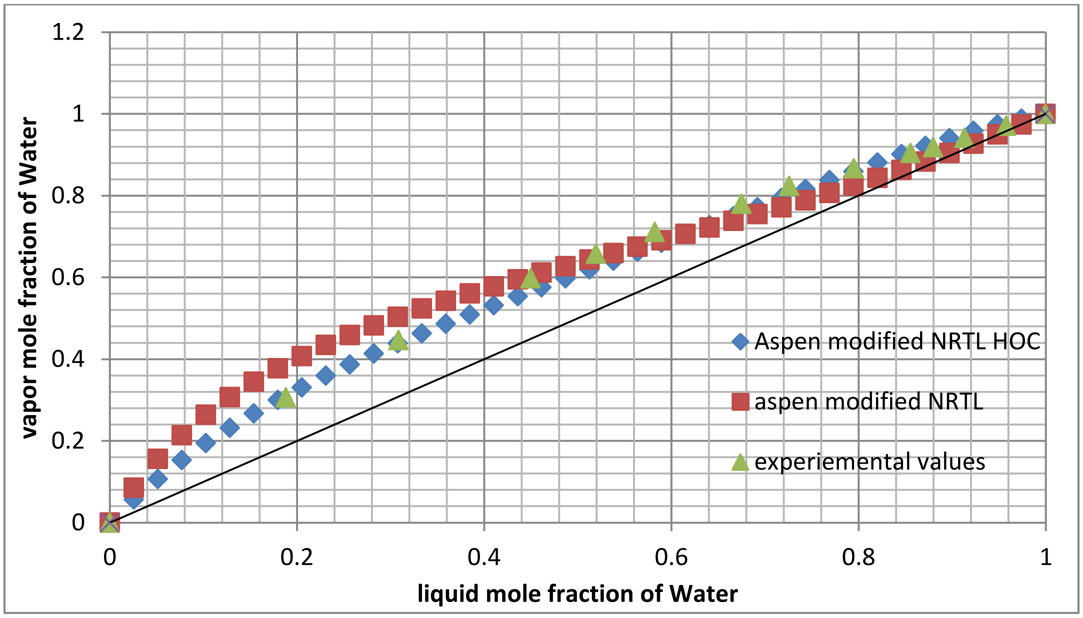

Figure III.1 VLE of system Water/acetic Acid

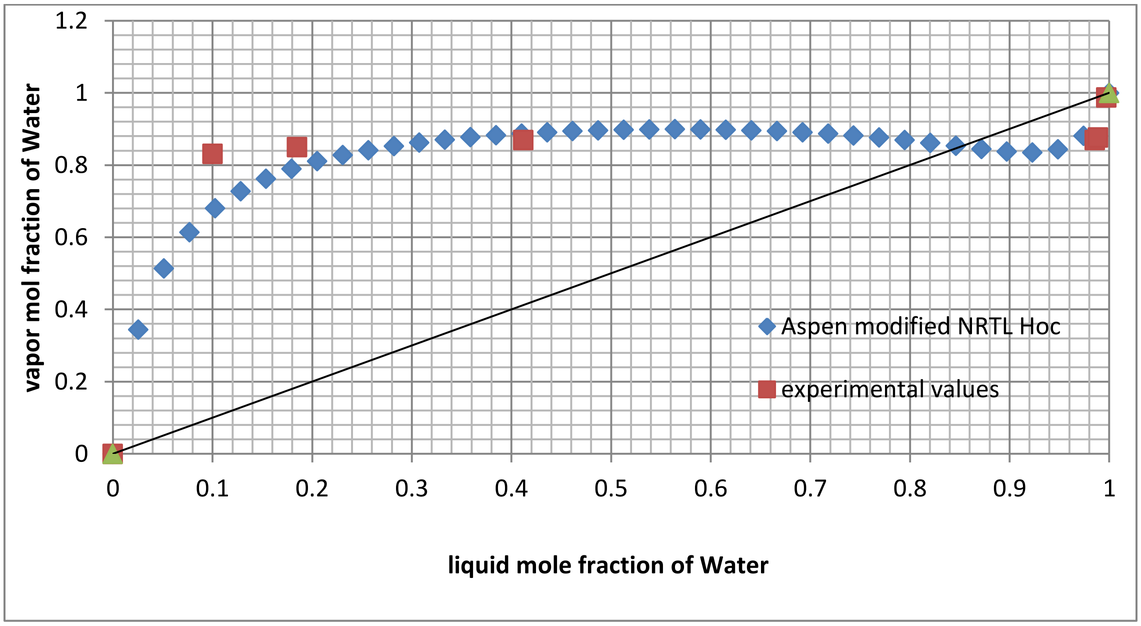

Figure III.2 VLE of system Water/component X

3. Azeotropic research:

Before building and simulating the process, it is important check if the system evaluated contains any azeotrope mixture. An azeotrope report is obtained by Aspen function called "Find Azeotrope", see *table III.1*. This feature helps to locate the azeotropes formed among components of a specific system. In addition, the azeotropic report allows user to visualize the azeotrope properties, such as: boiling point temperature, component composition in a homogeneous or heterogeneous mixture. Three components: water, HAC and X are specified and the property method (NRTL-HOC) is chosen. Moreover, the vapor-liquid-liquid phase is selected because the liquid-liquid splitting occurs in this system.

The table below is a typical azeotropic research report carried out by Aspen Plus.

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**
X	**X**	**Stable node**	**About 150 C**
WATER	**WATER**	**Saddle**	**100.02 C**

The Azeotrope

01	**Number Of Components: 2** **Heterogeneous**	**Temperature around 97 C** **Classification: Unstable node**

	MOLE BASIS	**MASS BASIS**
X	a	c
WATER	b	d

Table III.1 Azeotropic search report

4. Residue Curve Map:

Residue Curve Map (RCM) (12, 13) is routinely used to represent the vapor-liquid equilibrium phase behavior (VLE).

On RCM map:

- A stable node (component X) is the highest boiling point in a distillation region, there are only arrows pointing inward at this point.
- An unstable node (azeotrope) is the lowest boiling point in a distillation region, there are only arrows pointing outward at this point.
- Saddles (water and acetic acid) have both arrows pointing inward and pointing outward.

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

The phenomenon of different distillation regions due to the presence of azeotrope is reported earlier by many researchers (14). Indeed, the distillation boundary line exists if the residue curve runs from the same point and end at different points. An example of different distillation regions is shown in *figure III.3*. The residue curve starts at the azeotrope point and ends at methanol node in distillation region 1, and at methyl ethyl ketone node distillation region 2.

In case there are multiple distillation regions, if the feed composition is located inside a specific region, a residue curve stays in its initial region and cannot cross a boundary line. This means for a distillation column, it is not possible to obtain simultaneously pure components at the bottom and at the top of the column. At least an azeotropic mixture is obtained in one outlet.

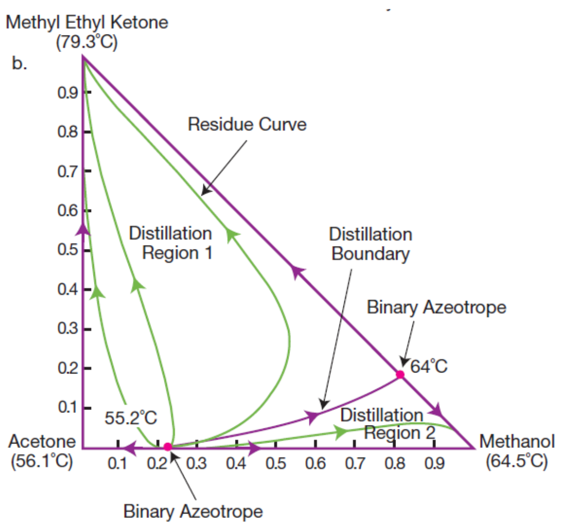

Figure III.3 RCM for acetone/methanol/MEK at 1 atm

Fortunately, although the given system contains one minimum-boiling azeotrope (water-X), but there is only one distillation region observed on the RCM map.

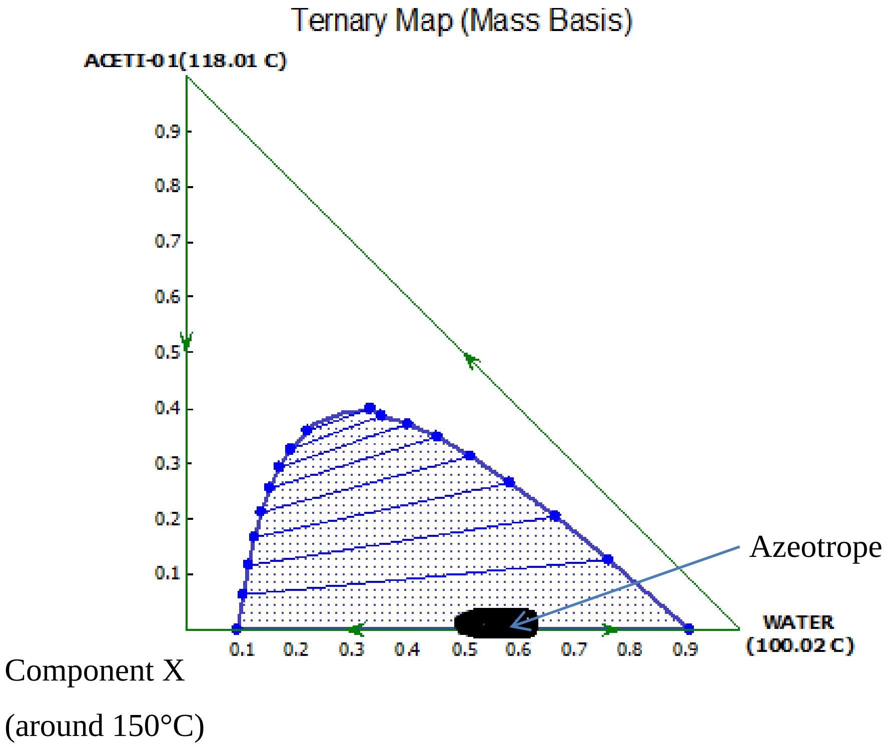

Figure III.4 Ternary map.

It is worth to note from the ternary map above that a high purity of water (99.9 wt%) cannot be achieved by a simple decanter. Thus, we need to use an extra equipment (a small column) if higher purity water product is desired.

The material balance lines that synthesize the separation sequence will be shown on the RCM in the next chapters.

IV. Conventional process:

The flowsheet of conventional process is shown in *figure IV.1*. All the streams and equipment are numbered corresponding to those of the real data produced by Perstorp (15).

The multicomponent feed contains water, acetic acid (HAC), component X and heavy organics (HO).

When specifying component data, we encounter a situation. Specifically, one of the heavy organic components is not available in Aspen Plus databank. Fortunately, Perstorp produces all information about this new component (such as : normal boiling point, molecular weight, molecular structure, Antoine vapor pressure equation…), then the problem is circumvented since Aspen Plus provides a way to add a new non-databank component into the system.

1. Description of the conventional process:

The multicomponent feed (water, HAC, X, HO) is introduced to the first column (or heterogeneous distillation column (C14)) *(figure IV.1)* where water and component X form a minimum-boiling azeotrope and go to the top due to its minimum boiling point. The overhead vapor of this column is sent to a condenser to transform into liquid and afterwards separate into two liquid phases (organic phase and aqueous phase) in the decanter, since the water-X azeotrope is heterogeneous. The organic phase which is rich on component X is totally refluxed back to the top of the first column C14. While the aqueous phase which is rich on water (90 wt%) is partially refluxed to the column C14, and the rest is sent to a small column (C17) which is heated up by a steam. This small column C17 is designed to remove the component X remained in the aqueous phase. The top vapor of column C17 containing mostly water and component X is mixed with the overhead vapor of the first column C14. While a high purity water product (99.99%) can be withdrawn at the bottom of this column

On the other hand, the bottom stream of the first column C14 (containing HAC, component X, HO and some traces of water) is sent to the second distillation column C108. High purity acetic acid can be taken off from the top as a product stream. While component X and heavies can be taken off from the bottom. Afterwards, this bottom stream is sent to the third column C27 where component X product can be obtained at the top and HO can be withdrawn out at the bottom of the column.

Aspen Plus provides the "design specification" feature to control the stream compositions. Indeed, a parameter (so-called output variable) is fixed/controlled at a specific value by adjusting another parameter (called input variable or manipulated variable). The number of manipulated variable depends on the number of degrees of freedom of the process.

2. Degrees of freedom and design specification:

The given process produces totally 7 degrees of freedom (DOF), which are detailed below:

Column C14 has one DOF, since there is only one re-boiler, no condenser. The bottom flow rate is set at 91.26 kg/h. However, this is only initial guess and can be changed later in the design specification to meet the bottom specification (about 0.33 wt% of water).

Column C108 is specified with a total condenser and a kettle re-boiler. Thus, this column has two DOFs, so that two input variables need to be specified. Indeed, the reflux ratio and the bottom rate are initially set at 1.6 and 36.5 kg/h respectively. Two design specifications are set for this column to meet the product purities. Firstly, the distillate specification (99.2 wt% of HAC) is converged first by adjusting the bottom rate. Then with this specification active, we converge the bottom specification (95 wt% of component X) by adjusting the reflux ratio (vary between 0.3 and 5). The reason for this is that the effect of bottom rate on the product specification is much larger than the effect of reflux ratio.

Column C27 has two DOFs: the bottom flow rate and the flow rate of component X fresh stream need to be initialized. Firstly, we control X composition in the bottom product stream (at about 7 wt% of component X) by varying the bottom rate (from 0.67 kg/h to 0.85 kg/h) which is initial set at 0.72 kg/h. Then with this specification active, we control the purity of component X in the distillate stream (at 98.3 wt% of component X) by adjusting the flow rate of component X fresh stream introduced to the top of the column C27.

The small stream C17 has neither condenser nor re-boiler. Water stream is controlled at 99.99 wt% of water by adjusting the steam introduced to the bottom of this column.

Finally, the water splitter provides one DOF: the water reflux ratio. We can set this ratio at 0.5 and run the process. Once the process converges, we can use this ratio to minimize the re-boiler heat input of the first column.

The results obtained on Aspen Plus shown in *figure IV.1* are very close to these of real process data simulated on Chemcad by Perstorp. The minor differences observed are based on the numerical methods and programing's algorithm between Aspen Plus and Chemcad with the same physical properties used.

Note that the vapor-liquid-liquid phase is specified for the first column C14 and azeotropic convergence is specified to have a robust convergence model. While strongly non-ideal liquid convergence is specified for second column C108.

A residue curve map analysis shown below (*figure IV.2*) gives a good synthesis of the process separation

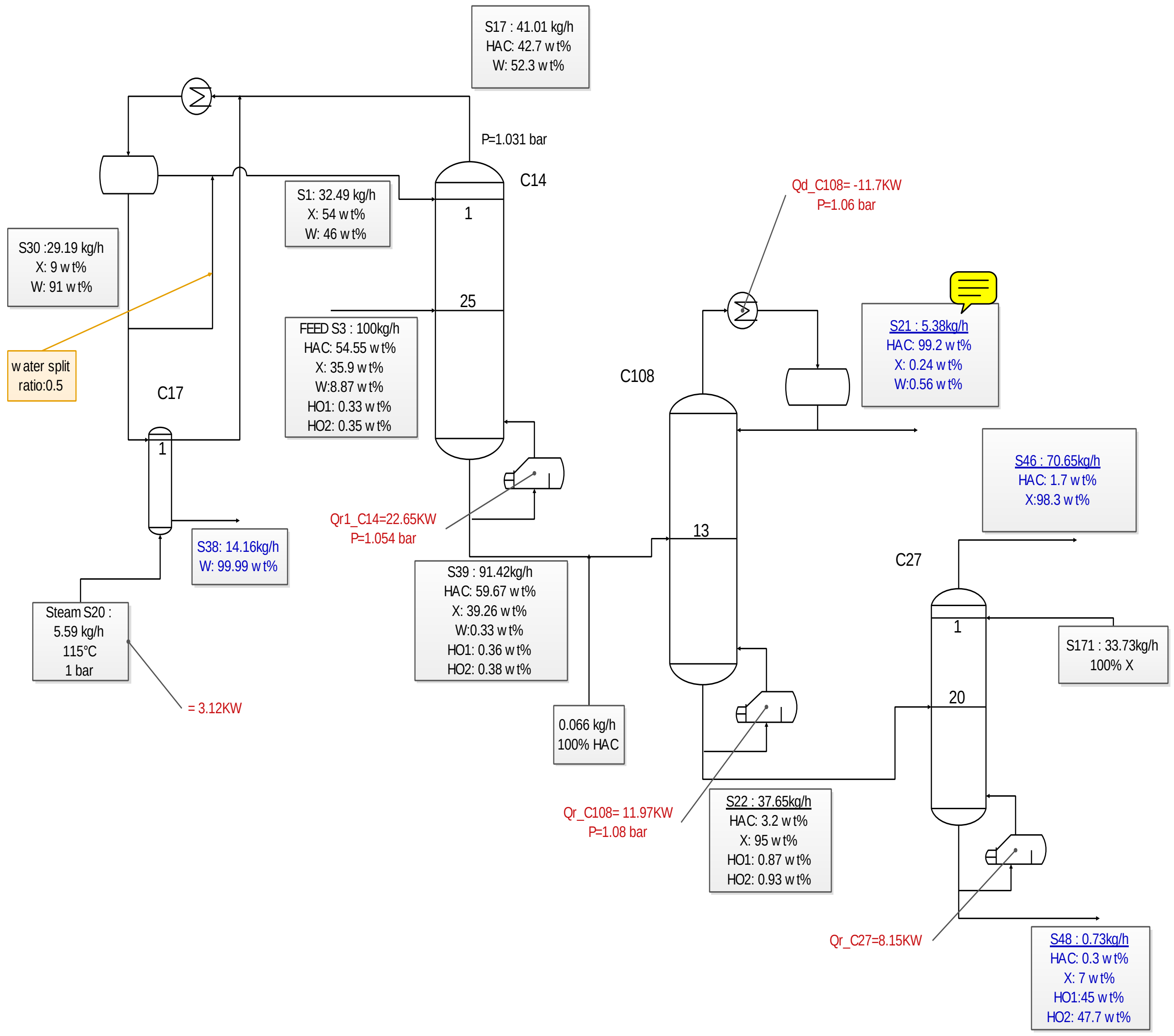

Figure IV.1 Conventional design

3. Residue curve map

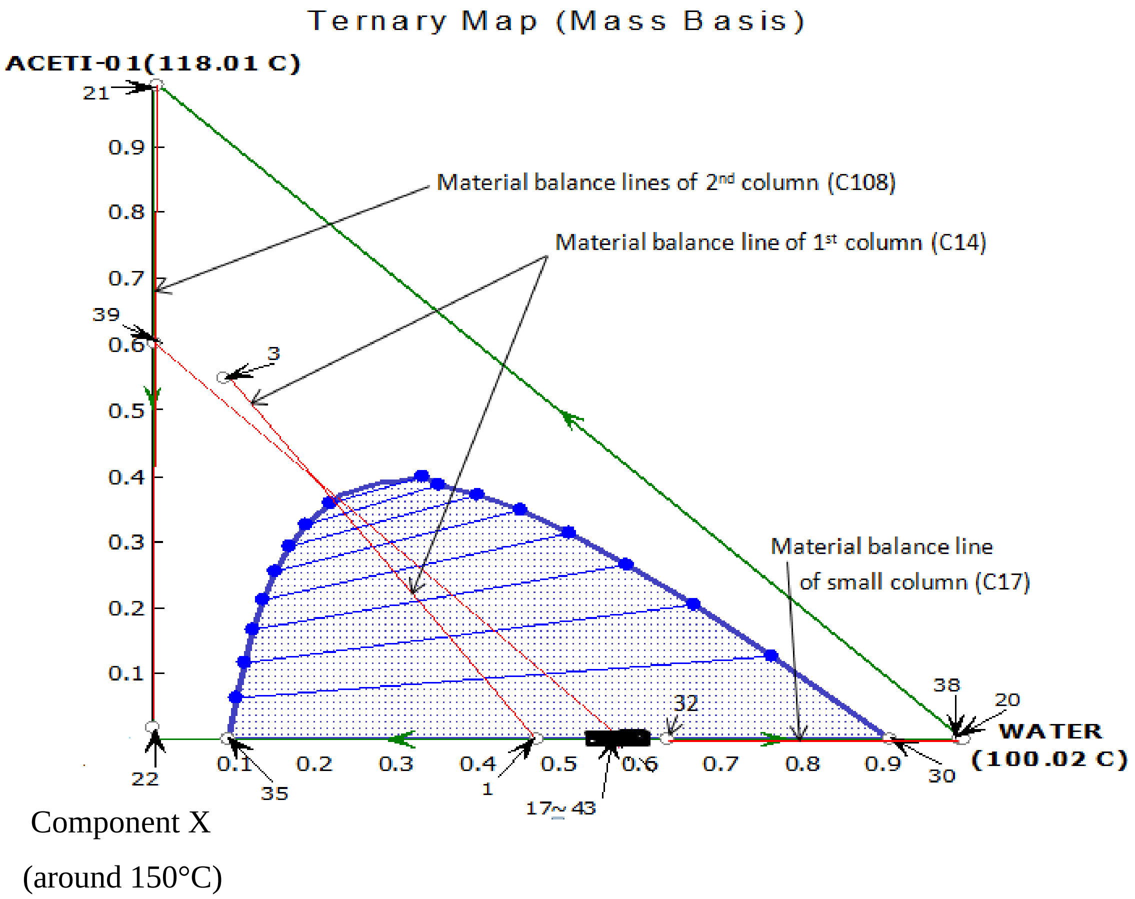

Figure IV.2 Residue curve map

The numbers shown on the residue curve map above correspond to the stream numbers in the process flowsheet shown in *figure IV.1*. The red lines are the material balance lines. The distillate of the 1st column lies in the immiscible region between water and component X. Hence, it is possible to use a simple decantation to carry out the phase separation first, and then a small column can be used to obtain high purity of water product.

Molar liquid composition profiles of the first column C14 (*Figure IV.3)* show that at the lower part of the column C14 (below the feed tray), water and acetic acid form a pinch area first, then water dies out at tray 41, while HAC increases and then lightly decreases at the last tray because of the presence of heavies (component X and HO). At the upper part of the column (above the feed tray), acetic acid dies out rapidly. While the composition of component X decreases lightly in a few trays above the feed tray, and then re-increases until achieve the specific composition of the water-X azeotrope. It is worth to note that if component X dies out suddenly at a few trays above the feed location, the water-X azeotrope formation cannot occur. Therefore, water can form a pinch with acetic acid and together distribute the top of the column C14.

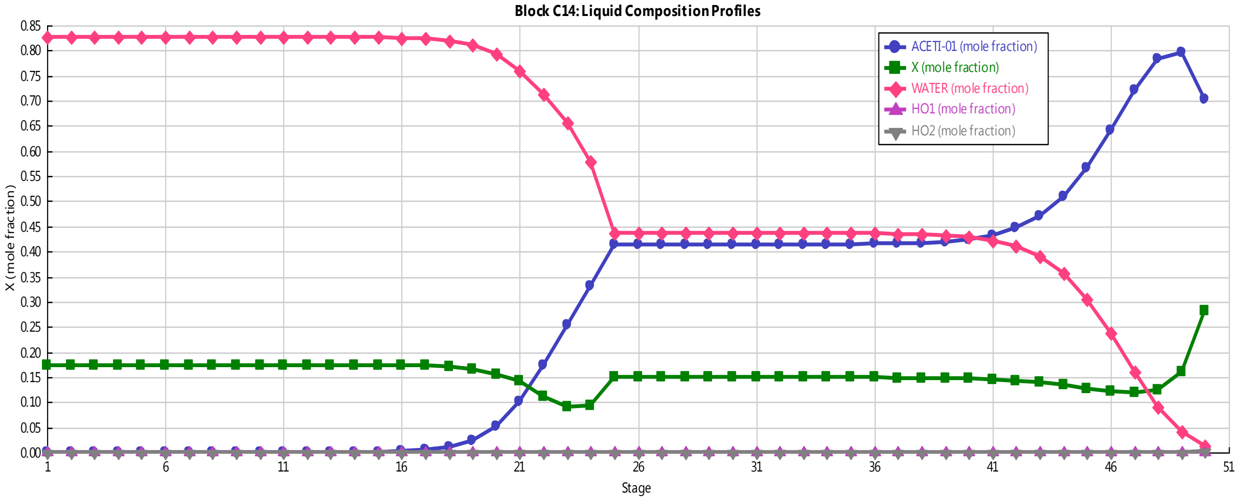

Figure IV.3 Liquid composition profiles of C14

V. Optimization:

The conventional design simulated in the earlier chapter is not optimal, thus it is necessary to optimize this before retrofitting to the dividing wall column. Process optimization is the procedure of adjusting some manipulated variables to optimize some specified parameters without violating the process constraints.

Rangaiah et al. (2006) (16) have worked on optimizing the distillation process. Their paper which is public in 2006 shows that minimizing re-boiler heat duty is minimizing operating cost which directly results in the optimal design of process since the major part of the annual cost is the operating cost. Hence, the objective function needs to be minimized is:

$$f = \sum_{i}^{n} \mathrm{Re}\, b(i)$$

Where: f is the total heat input function.

n is the number of column (C14, C108, C27, C17), n=4.

Reb(i) is the re-boiler heat input of column i.

The first thing to do in this chapter is to identify the design variables that maybe effect on the re-boiler duties:

1-Local feed tray of the columns (C14, C108, and C27)
2-Organic reflux tray
3-Water reflux ratio

The optimization of the conventional design is carried out through three-step procedure detailed below.

<u>Step 1:</u> Optimize the feed location of each column. The feed location varies, and for each chosen feed location, the total re-boiler heat duty is varied to find the configuration that consumes less energy.

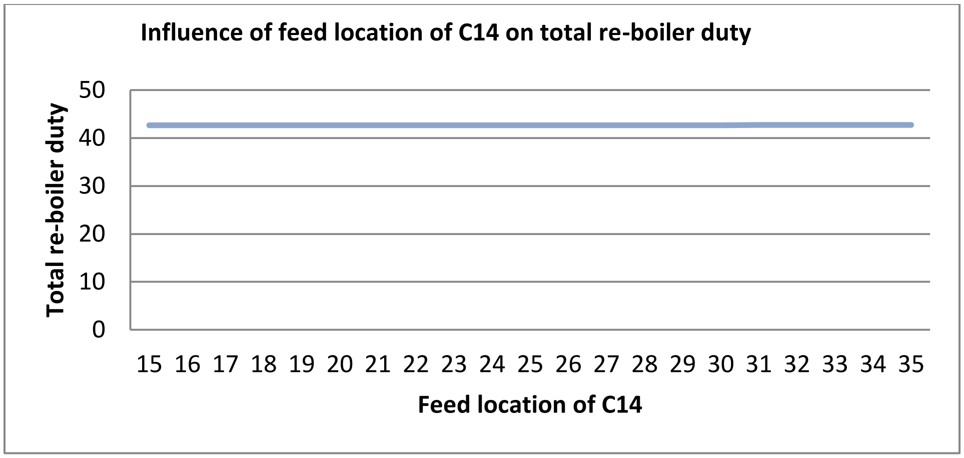

Figure V.1 Influence of feed location of the first column C14 on total re-boiler duty

Figure V.1 shows that the feed location of the first column has no effect on the total re-boiler heat duty. Therefore, the feed location is remained at the current position.

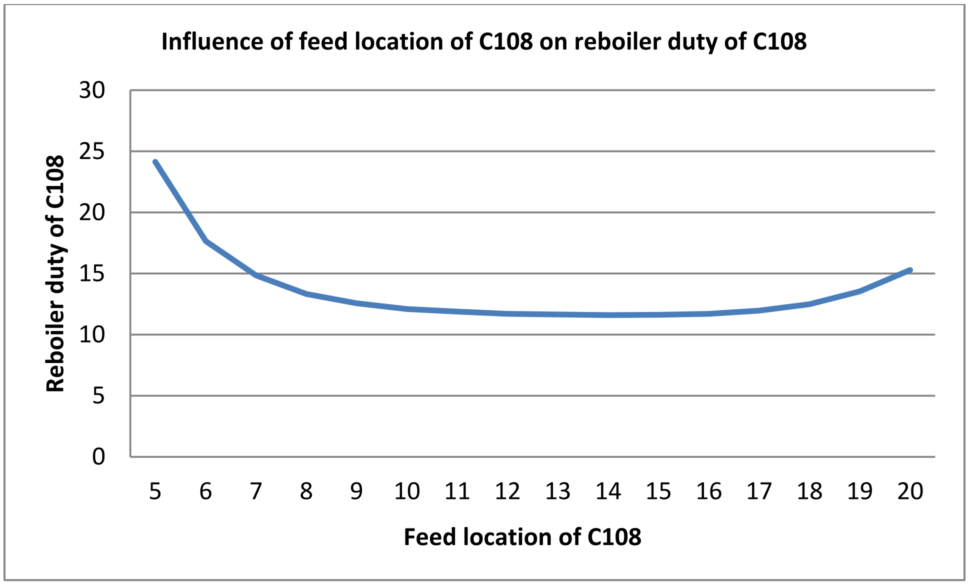

Figure V.2 Influence of feed location of second column C108 on its re-boiler duty

On *figure V.2* the re-boiler heat duty of C108 achieves its minimum when the feed is introduced to the tray number 13th. However, the re-boiler duties curve is quite flat for feed tray from 11th to 16th. Thus there is no need to change the feed position from current position to tray 13th.

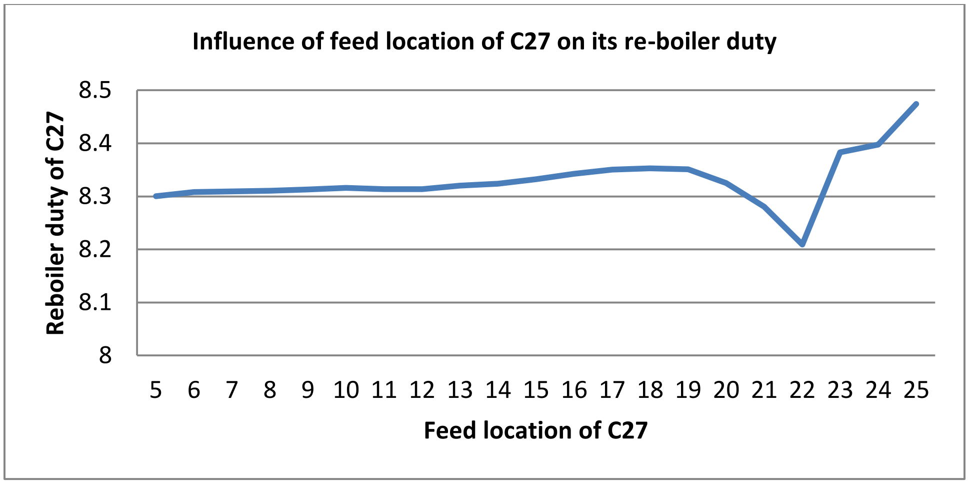

Figure V.3 Influence of feed location of third column on its re-boiler duty

From the figure above, the optimal feed location of the third column is obviously at tray 22nd. Thus, the feed location is now switched to the new position (tray 22nd).

Step 2: Optimize the tray location of organic reflux of the first column C14. The water reflux leaving the decanter is still partially recycled back to the top of the first column, but the organic reflux location varies from tray 1st to tray 20th. The total heat input is calculated for each case to find the configuration which consumes less energy. *Figure V.4* shows that the total re-boiler heat duty almost stays stable when the organic reflux location changes from tray 1st to 20th.

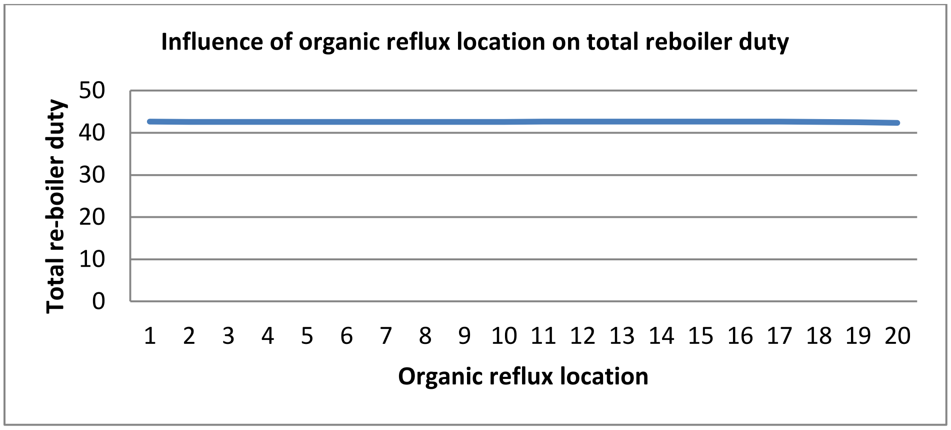

Figure V.4 Influence of organic reflux location on total re-boiler duty

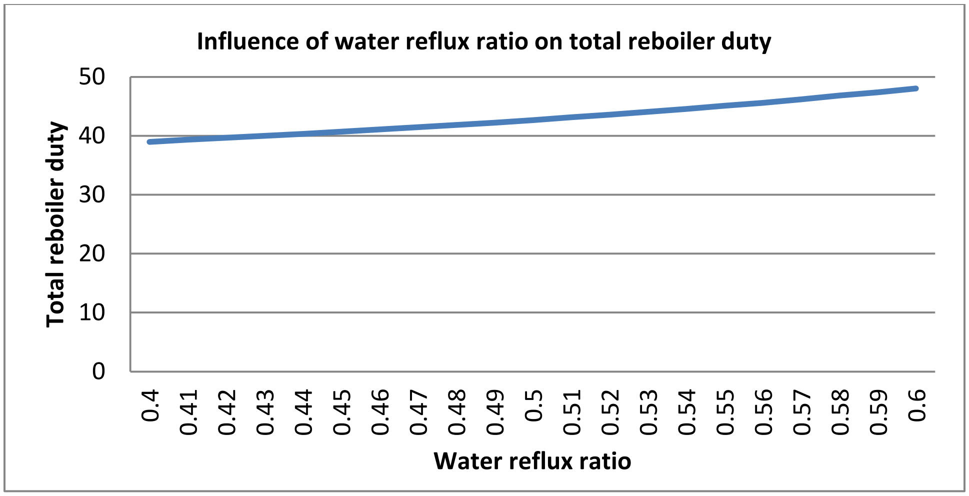

Figure V.5 Influence of water reflux ratio on total re-boiler duty

Step 3: Optimize water reflux ratio. Unlike the other parameters studied in step 1 and step 2, the water reflux ratio has a big influence on the total re-boiler heat input. *Figure V.5* shows that the smaller this ratio is, the less energy input is needed. However, it does not mean that we should set a water reflux ratio nearly 0, since water need to be recycled back to the top of C14 to prevent acetic acid from entering into the top vapor stream of this column. During the simulation, it is worth to notice that the water reflux ratio cannot be smaller than 0.4.

Conclusion, among the parameters studied, only the water reflux ratio has a significant influence on the total energy required function. The process is optimal when the water reflux ratio is set at 0.4. What happen when this ratio is below 0.4? It is noticed that when the water reflux ratio decreases, acetic acid composition increases lightly in the top vapor stream of C14. If water reflux ratio is smaller than 0.4, acetic acid composition becomes too large, and then overhead vapor of C14 may be pulled out of the immiscible zone into the miscible zone in the RCM. If this happens, only one phase is formed in the decanter and totally recycled back to the column. Then the reflux stream becomes too large. The process cannot converge anymore, and never can we pull back to the immiscible zone.

Note that in the previous simulations, a large fresh stream of component X (about 33.73 kg/h) (*figure IV.1*) is introduced to the top of the third column C27 in order to prevent heavy components (HO1 and HO2) from contaminating the top product stream (mainly containing component X). Unfortunately, this leads to a high re-boiler duty required. However, this undesired situation can be avoided if we increase the composition of component X in the feed sent to the third column (from 95 wt% to 98 wt%) .Then the re-boiler heat duty of the second column C108 increases from 11.73 KW to 12.66 KW to meet the new specifications. However, the re-boiler heat duty of the third column decreases significantly from 8.16 KW to 3.11 KW. Moreover, a high purity of component X (99.8% wt of X) can be achieved in the top stream by introducing a much smaller fresh stream of component X (100kg/h) to the top of this column. The re-boiler heat duty of these three columns reduces from 39.51 KW to 34.84 KW.

The process optimized is shown in *figure V.6*

The small column C17 does not have any re-boiler, but a steam is introduced into the bottom of this column. Then the energy required to evaporate this steam has to be added to the total heat duty:

We know that 2 000 kJ of energy are required to evaporate 1 kg of water at 115°C into 1 kg of steam at 115°C, at 1 bar. Then to evaporate 5.6kg/h of water, we need 3.12KW of energy. This sum of energy has to be added to the total heat input of process. Then the total heat input is: 34.84+3.12 = 37.96 KW.

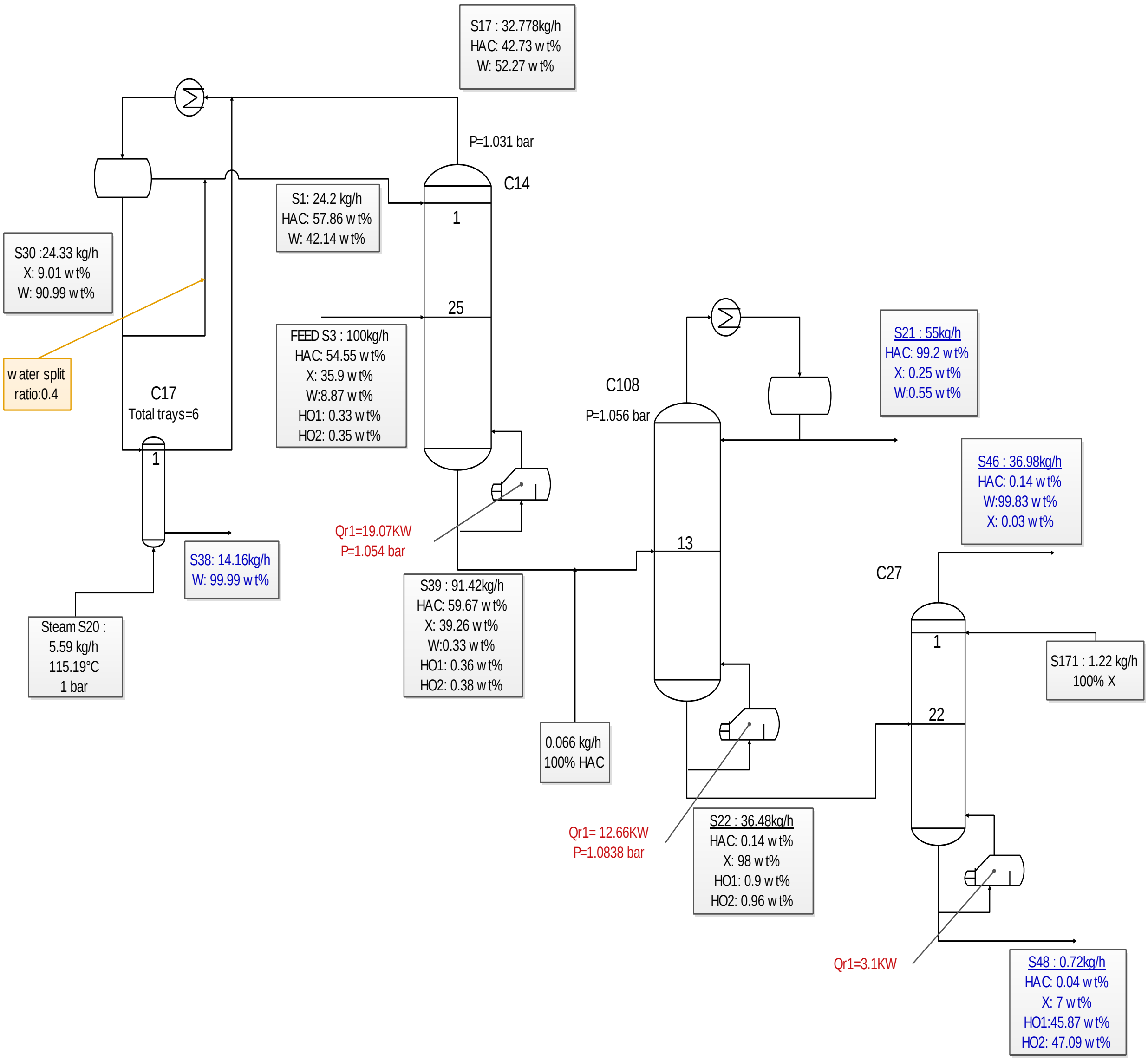

Figure V.6 Conventional process optimized

VI. Dividing wall column (DWC):

1. Introduction:

For a multicomponent separation using conventional columns, there are different sequences to achieve the final goal. Among them, the direct sequence and indirect sequence are routinely employed. In the direct sequence (*figure VI.1*), the light components (A) are removed first, while in the indirect sequence (*figure VI.2*), the heavy components (C) are removed first. It is important to understand and be able to apply the general heuristics for a good choice of distillation sequence in term of energy consuming (11). For the direct and indirect sequence, the methodology is easy to understand and the process is simple to simulate and operate. However, this requires a high capital cost to build a series of columns (at least two columns, it depends on how many components in the feed and the product purity requirement). Facing with this problem, during the last decades, several researchers have been working on devising a new optimal distillation sequence for multicomponent separation to reduce significantly energy requirement. They finally arrived to the new complex separation configuration which is called dividing wall column (DWC) (12, 13). The selection of optimum sequence, from energy point of view, usually requires considering all aspects, such as: composition of the components in the feed, the relative volatility of one component to another, steam temperature level….

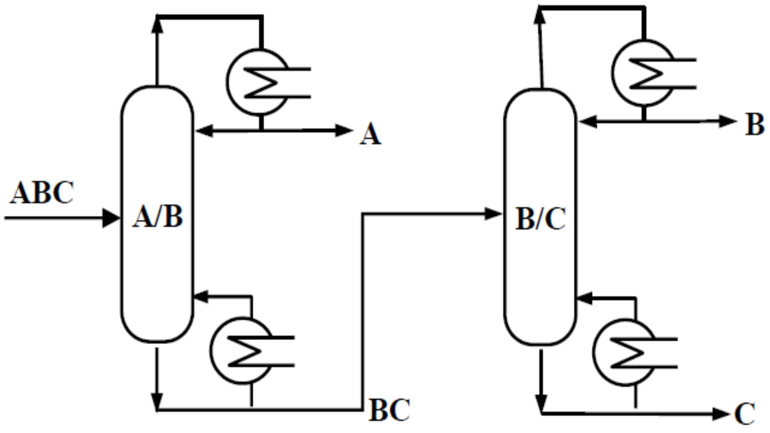

Figure VI.1 Direct sequence

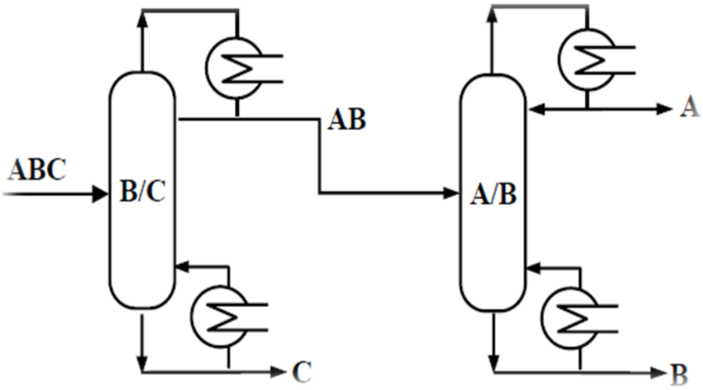

Figure VI.2 Indirect sequence

For three-component separation, there are two different types of normal dividing wall columns. Both of them are equipped with a fixed dividing wall inside the column. However, the column with the wall placed in the middle is more common and has another name: Petlyuk column (*figure 1.2a*). This column is able to carry out the multicomponent separation using one re-boiler and one condenser. The second type of DWC is the column with the dividing wall placed either at the upper or the lower end of the column (*figure 1.2b and c*). Both configurations are designed to enable to save investment cost, since the cost of the second column in the conventional design (with or without a condenser and a re-boiler) is avoided.

The aim of this work is to figure out a novel approach to apply the dividing wall column in heterogeneous azeotropic distillation as well as minimize energy required. Two alternatives are proposed in the next chapter to achieve this goal. However, unlike the first configuration (dividing wall is placed the middle of the column, Petlyuk column), energy saving cannot be achieved for the second configuration (dividing wall is placed either at the top or at the bottom of the column).

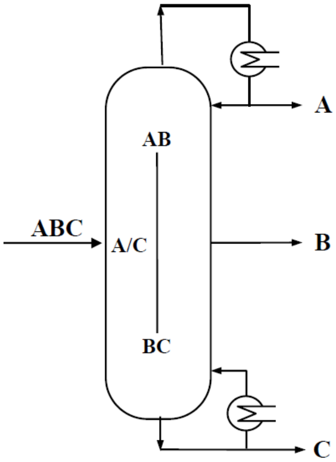

Figure VI.3 Petlyuk DWC column

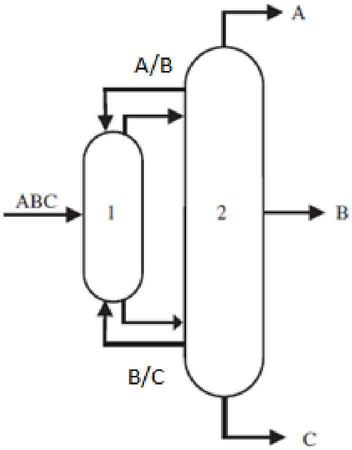

Figure VI.4 Equivalent Petlyuk arrangement

Assume that the multicomponent feed introduced to the DWC contains three main components: low boiling point component (A) or light component (LK), high boiling point component (C) or heavy component (HK), and medium boiling point component or middle component (MK). LK and HK can be withdrawn at the top and the bottom of the column, respectively. While MK can be drawn off by the side of the column (*figure VI.3*).

The Petlyuk dividing wall column has a vertical wall, which separates the column into two parts of its length: a "pre-fractionator" and a "main column". The liquid reflux from the top is divided and sent to two parts of the column. While the boil-up vapor from the re-boiler also splits, in the lower part of the column, on both side of the wall. Assuming that the heat transfer through the wall is insignificant, then dividing wall column is thermodynamically equivalent to the Petlyuk configuration.

It is desirable to transform the Petlyuk configuration into another configuration which is easier to operate and investigate. To achieve this goal, the main (second) column is divided into two parts at the side stream tray. This new design is shown in *figure VI.5*. A side stripper (named C21) and a side enricher (named C22) are thermally coupled with the pre-fractionator (the first column).

The distillate stream of the side enricher (C22) and the bottom stream of the side stripper (C21) together constitute the side stream product (S).

In this configuration, column C22 operates at higher condenser temperature due to the higher boiling point components and can be coupled with the re-boiler of column C21 with lower re-boiler temperature. Therefore, the cooling and heating requirements can be met due to the process stream without any internal utilities.

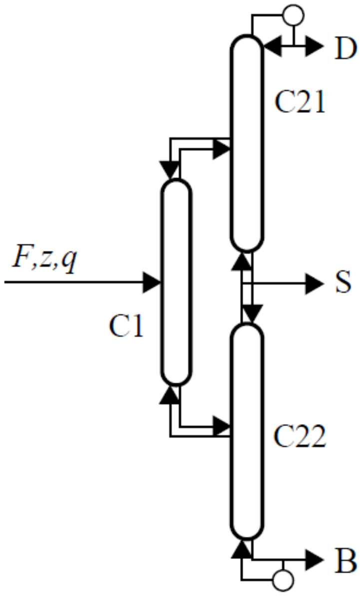

Figure VI.5 Implementation with three conventional columns

2. Advantages and disadvantages of DWC:

Like the other technologies, Petlyuk arrangement also has advantages and disavantages:

a) Advantages:

- Lower energy consumption:

Lower energy consumption may be achieved with Petlyuk arrangement. Each column performs only the easiest split between lightest and heaviest components, which reduces mixing losses and is more advantageous than the conventional design in term of energy consumption. Some configurations for Petlyuk column have been reported energy reductions of up to 30%.

- Less capital cost:

This is one of the main advantages of the Petlyuk DWC. The conventional design has two columns with one re-boiler and one condenser each. While in the Petlyuk arrangement (see *figure VI.3*), thanks to the dividing wall, two conventional columns are combined into one column system which has only one condenser and one re-boiler.

Since some pieces of equipment are eliminated using the DWC technology, we can not only reduce the capital cost, but also reduce the maintenance cost associated with the factory and size of the plant.

- Product purity:

The high purity of the middle product (B) can be achieved in the side stream. If the middle product is valuable and needs to be over purified, DWC is recommended.

b) Disadvantages:

Despite all the advantages mentioned above, there are still some restrictions limiting the industrial application of DWC. The dividing wall columns are usually tall and complicated to operate. Moreover, the Petlyuk column has more degree of freedom compared to the ordinary distillation column due to the side stream. That makes the design and the control of the column more complicated.

3. Rigorous simulation of standard distillation column equivalent to Petlyuk arrangement:

As discussed above, Petlyuk arrangement can be simplified and thermodynamically equivalent to the three columns fully thermally coupled shown in *figure VI.5*. However, it can be a bit complicated to simulate these three columns on simulator program (e.g. Aspen, Hysys) due to the large number of degrees of freedom related to the side streams between the two columns C21, C22 and the pre-fractionator C1.

The problem can be circumvented using another configuration proposed by Ivar Halvorsen (17), *figure VI.6*. This design using standard distillation columns is computationally equivalent to the ternary Petlyuk arrangement. All the heat duty removed from the condensation (C1) is used to superheat the top product and all re-boiler duty required (C1) is supplied from sub cooling the bottom product (*figure VI.6*). The Petlyuk column concept is still respected. Indeed, there is no external heat exchange between the pre-fractionator and the two succeeding columns. In addition, the thermal conditions at the feed tray of two succeeding columns (C21 and C22) are identical to those of the fully thermo coupled configuration (*figure VI.5*).

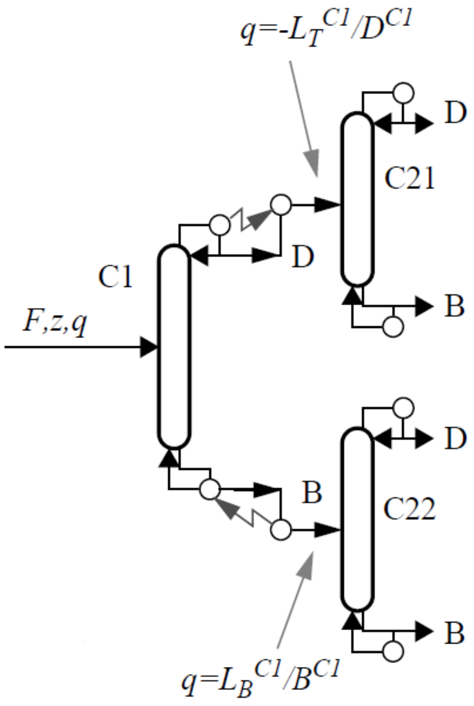

Figure VI.6 Configuration computational equivalent to the Petlyuk arrangement

A Petlyuk arrangement is working at optimum condition if each column operates at its local preferred split, in which the recoveries of light component in the bottom and of the heavy component in the top are small. These recoveries are maintained by using the two design specifications available in each column of the configuration shown in *figure VI.6.* Moreover, there are no recycle streams between the columns that may make the column extremely difficult to operate and simulate.

The boil-up rate throughout the Petlyuk arrangement can be easily determined by comparing the heat duties in the re-boiler of C22 and in the condenser of C21. If the condenser duty of C22 is larger, the heat duty of column C22 is also the required heat duty in the re-boiler of the Petlyuk column. Otherwise, we have to increase the boil-up in C22 until the condenser duty of C22 meets the re-boiler duty of C21.

VII. Application of DWC for a ternary heterogeneous distillation:

In our system, water does not only form a minimum boiling point azeotrope with component X, but also form a pinch with acetic acid at the pure water end which is not easy to be separated. This complexity may cause the multiple steady states in the first column: either water-X azeotrope or water-acetic acid mixture can be found at the top of the first column.

1. Water-X azetrope at the top of the first column:

Assume that a Petlyuk arrangement is feasible for this case. Firstly, we identify the three key components A, B and C of this system for the Petluyk arrangement.

Light component (A): water-X azeotrope
Middle component (B): HAC
Heavy component (C): X+HO

A simplified three separate columns computationally equivalent to Petlyuk arrangement is built up and shown in *figure VII.1*. The heavy components (X+HO) as well as one part of HAC (middle component) go to the bottom of the pre-fractionator column (C1) and head to the side enricher column (C22), while water –X azeotrope as well as one part of HAC go to the top of C1 and head to the side stripper column (C21). Inside the column C21, water-X azeotrope goes to the top due to its lower boiling point, and acetic acid goes to the bottom. The top vapor stream passes through some pieces of equipment to separate water and organic phase. Then organic phase rich on component X is totally recycle back to the column C21, while pure water product (about 99.9 wt%) is withdrawn out as a product stream. We can immediately remark that component X in column C21 is not in mass balance. Petlyuk configuration is not feasible for this case.

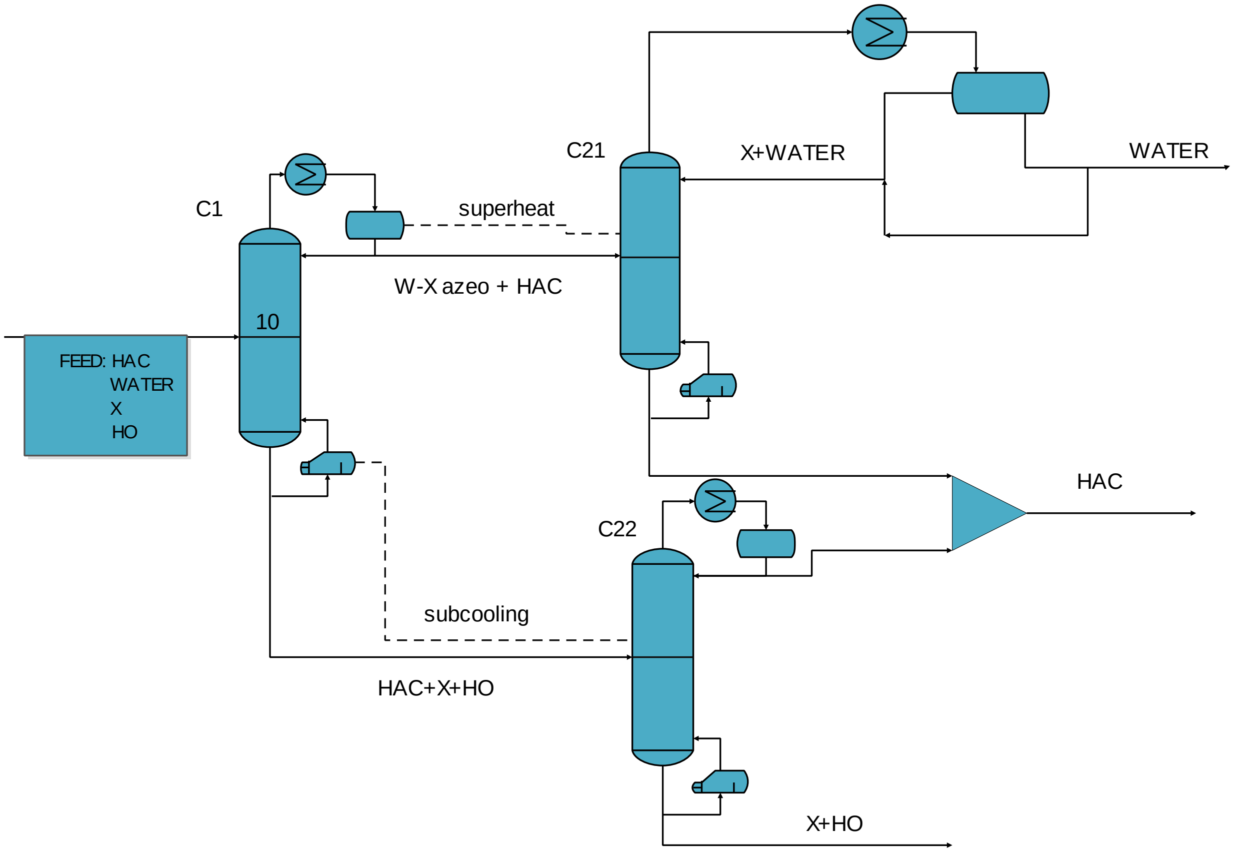

Figure VII.1: Petlyuk arrangement with W-X azeotrope at the top of pre-fractionator

However, the DWC configuration with the dividing wall placed at the upper part of the column may be applicable for this case (*figure VII.3*) The way to thermally couple the two columns is to eliminate the re-boiler of the second column (C2) by sending the vapor directly from the stripping section of the first column (C1) to the bottom of the second column. The liquid from the bottom of the second column is sent back to the main column C1 at the same tray where the vapor is drawn out. HAC liquid product can be withdrawn at the top of the second column. The heavy components (X+HO) at the bottom of C1 are sent to the third column where component X can be separated from heavy organics (HO). The overhead vapor of the first column C1 is treated exactly the same way in the conventional design (*figure VII.3*)

The operating condition and design parameters of this DWC configuration are shown in the table below.

	C1	C2
Total trays	65	30
Feed tray	Main feed: 30th Liquid back from C2: 59th	Vapor stream: 30th
Side stream	Vapor side stream: 59th	
Top pressure	1.031	1.031
Pressure drop	0.023	0.017
Condenser	0	1
Re-boiler	1	0

Table VII.1: Column design parameters

The operating and design condition of column C3 are identical to the column C27 in the conventional design.

Azeotropic convergence and three phase vapor-liquid-liquid are specified for the main column C1 since the liquid-liquid splitting may occur. While strongly non-ideal liquid convergence is specified for the side column C2.

The top vapor of C1 is set at 32.85 kg/h and expected to contain only the water-X azeotrope. A small stream (0.12 kg/h) containing water (60%) and CH (40%) is introduced to the top of column C1 to prevent the top stage from being dry. The vapor side stream is withdrawn out of the main column at tray 59th and initially set at 58.4 kg/h. The reflux ratio of the side column C2 is set at 0.75. These initial guess will be changed later by using the column design specification. The water reflux ratio is set at 0.4.

Running the process with these initial guesses, when it converges, we set the design specifications of the columns to meet the product purities. More specifically, the flow rate of vapor side stream is adjusted to meet the bottom product purity of column C1 (95.3 wt% of component X). Then, with this specification active, we control the top product purity of column C2 (99 wt% of HAC) by adjusting the reflux ratio of column C2. Finally, the bottom product purity of column C3 is fixed (7 wt% of water) by varying the bottom flow rate, and the component X fresh stream is adjusted to achieve the requirement of the component X purity product at the top.

Some observations can be made from the simulation. Firstly, a slippage of acetic acid into the bottom of the column C1 cannot be avoided. For this reason, the composition of component X in this bottom stream cannot surpass 95 wt%. Then, a large fresh stream of component X (about 26.77kg/h) is needed to meet the product purity. Secondly, this configuration consumes 3345KW which is lightly higher than the energy requirement for the conventional design. Hence, saving energy is not achieved, but maybe capital cost and maintenance cost can be reduced.

Liquid composition profiles of the main column C1 is shown in *figure VII.2*. Above the feed location, the figure is quite similar to that of the first column in the conventional design. In contrast, below the feed location, a maximum concentration of acetic acid is observed at tray 57th. The side vapor location switches to this position, since we expect to obtain high purity acetic acid in the side stripper C2. The re-boiler heat duty of the main column is reduced insignificantly, and still higher than that of the conventional design

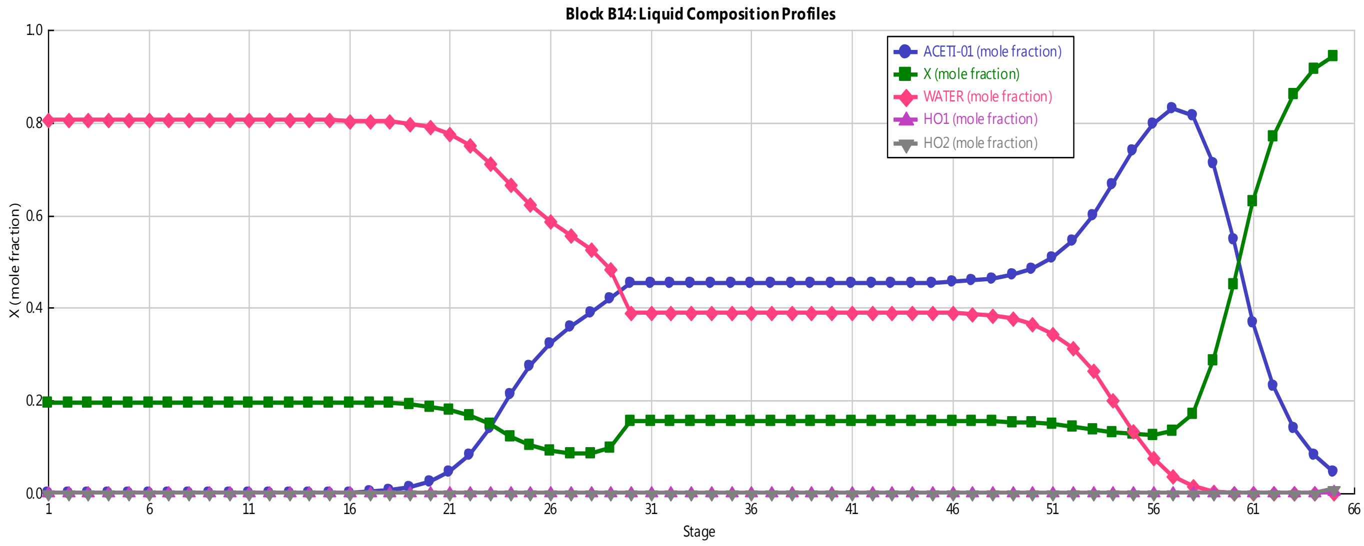

Figure VII.2 Liquid composition profiles of main column C1

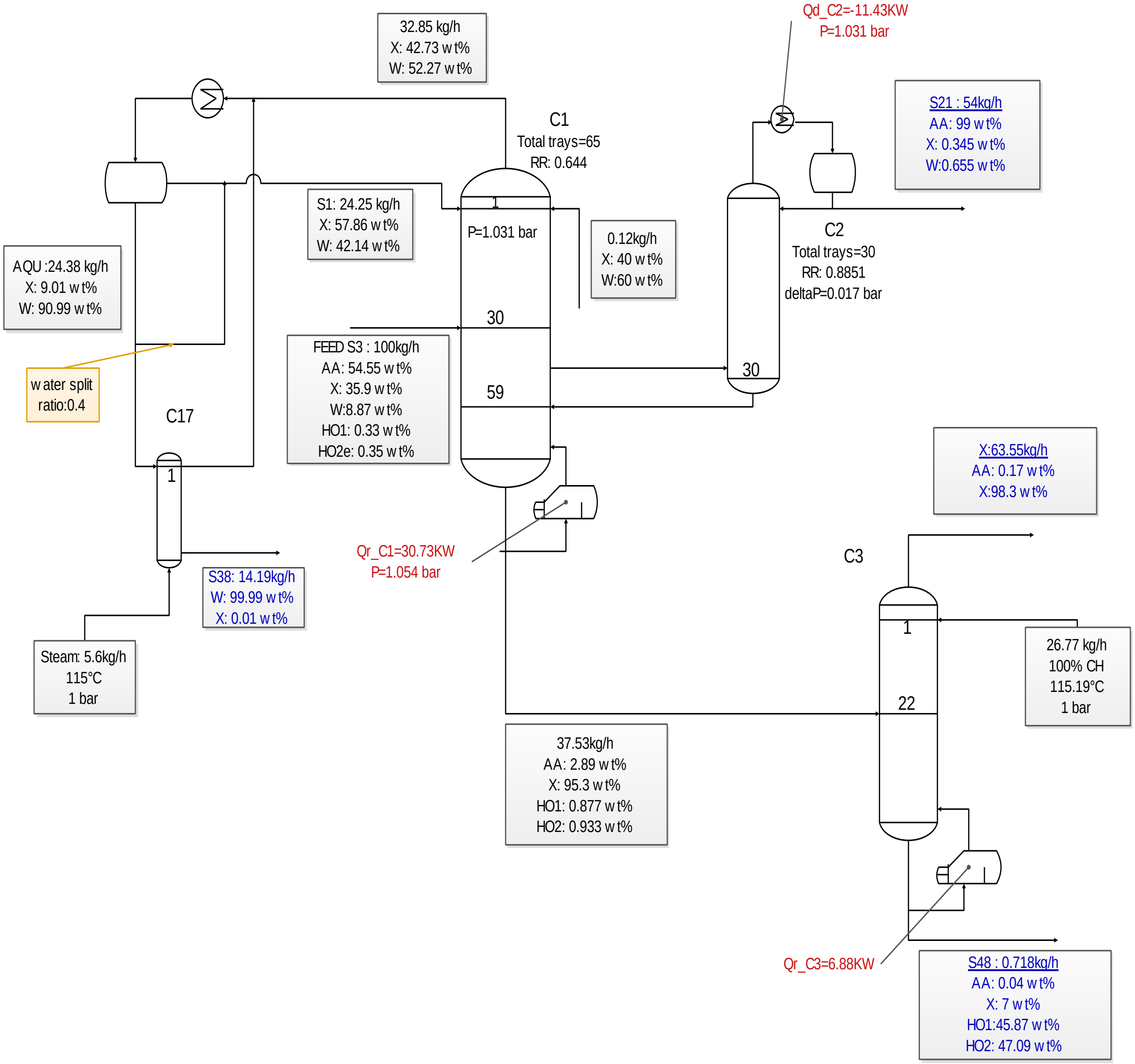

Figure VII.3 DWC with the wall placed at the upper part of the column

2. Water and acetic acid form a pinch at the pure water end

The mixture of water-HAC is now the light component (A). Acetic acid is the middle component (B). Heavy organic and X are heavy component (C). Water-HAC (and some traces of component X) distributes to the top of pre-fractionator and then goes to side stripper column C21. High purity of HAC product can be withdrawn at the bottom of C21, while water product can be obtained from the top due to its lowest boiling point. The Petlyuk arrangement could be applicable for this case.

Nevertheless, as discussed previously, using a conventional column to carry out the separation of water-HAC may require a large number of trays and a large boil-up flow rate that leads to the high operating cost. Fortunately, this problem could be circumvented by the heterogeneous azeotropic distillation technology. A third component called entrainer is added to the system to make the separation easier by creating a new lower boiling point azeotrope. However, adding a new component makes the column extremely difficult to operate and simulate. The Petlyuk arrangement analysis is carried out in the next chapter.

VIII. Petlyuk arrangement:

1. Entrainer analysis:

Different entrainers can be used to carry out this separation, such as: isobutyl acetate (IBA), n-butyl acetate (n-IBA), ethyl acetate …. Each of them has pros and cons. William L.Luyben and I-Lung Chien (18) have worked on these entrainers and they have found that IBA is the best from the annual operating cost point of view. Therefore, IBA is added to our system as entrainer.

Figure VIII.1 shows that NRTL-HOC model still gives a good match between predicted and experimental data.

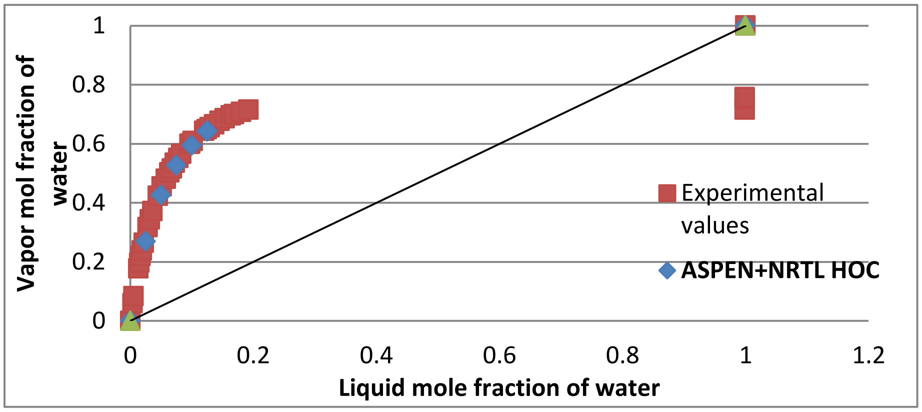

Figure VIII.1 *VLE of system water/IBA*

The ternary map (*figure VIII.2*) shows that IBA form a maximum boiling azeotrope (118.15°C) with HAC and a minimum boiling azeotrope (88.06°C) with water. The presence of these azeotropes may cause the phenomenon multiple steady states when running a heterogeneous azeotropic distillation. For the system of water-HAC-IBA, the existence of this phenomenon has been proved experimentally by several researchers (19, 20).

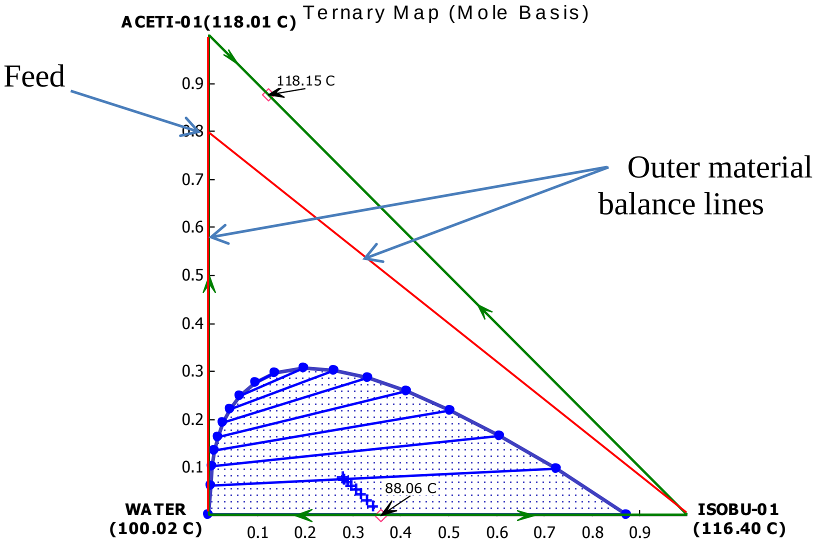

Figure VIII.2 Ternary map of HAC/W/IBA

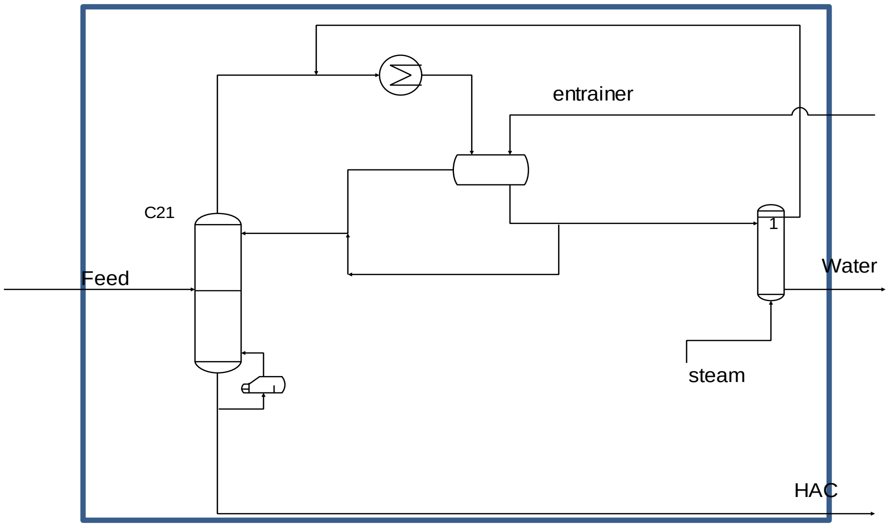

Figure VIII.3 Acetic acid dehydration process

Acetic acid dehydration process is shown in *figure VIII.3*. The feed containing water (20%) and HAC (20%) is introduced to the column. High purity of acetic acid product can be obtained in the bottom of column due to its highest boiling point, while the water-IBA azeotrope distributes to the top. From the ternary map above, water-IBA azeotrope is laid on the immiscible region between IBA and water. Thus, a decanter can be used to carry out the two liquid phase separation. Organic phase rich on entrainer is totally refluxed back to the top of the column, while the aqueous phase rich on water is sent to a recovery column. Water product can be withdrawn out from the bottom of this column. An IBA makeup stream is needed to compensate the loss of entrainer through the water outlet.

The outer material balance envelope of the acetic acid dehydration process is shown on the RCM (*figure VIII.2*). The two inlet streams are at the points of pure IBA and feed composition. The two outlets are at the points of pure water and pure acetic acid. The distance between the intersection point of the two material balance lines and the feed composition point can be used to determine the entrainer makeup flow rate. If this distance is very small, the entrainer makeup will be very small.

Moreover, a large difference of temperature between the two desired products at the bottom (118°C) and at the top (88°C, azeotrope) of the column makes the separation be easier and the slippage of the light component into the bottom product is excluded.

The simulation of three columns computationally equivalent to the Petlyuk arrangement is carried out first, and then based on these results; we combine two succeeding columns (C21 and C22) into one column called main column in Petlyuk arrangement.

2. Three columns computationally equivalent to the Petlyuk arrangement:

a. Process description:

The process flowsheet is shown in *figure VIII.4*. Multicomponent feed is introduced to the pre-fractionator (C1), water and acetic acid distribute to the top of the column while the rest of acetic acid along with component X and HO goes to the bottom:

The overhead vapor containing water-HAC mixture is sent to the side stripper column (C21). This column is designed to perform the azeotropic ditillation and its operation condition is given in the *table VIII.1*. IBA entrainer is introduced to the decanter. High purity acetic acid can be obtained in the bottom while most water and IBA go to the top of the column. The top vapor stream of column C21 passes through a heat exchanger to decrease its temperature to 40°C. The vapor is condensed into liquid and then forms two liquid phases in the decanter, since the water-IBA azeotrope is heterogeneous. The organic phase containing almost entrainer is totally refluxed back to the heterogeneous column C21, and the aqueous phase is also partially refluxed back to the top of this column in order to avoid the loss of HAC through the water outlet. The rest of water is headed to a small column C4 (no re-boiler, no condenser) heated by a steam. High-purity water product (99.99 wt%) is obtained at the bottom while the water-IBA mixture at the top of the column C4 is mixed with the overhead vapor of column C21. A very small entrainer IBA is lost through the water product stream. Therefore, a small stream of IBA fresh is introduced into the decanter to compensate this loss.

The bottom mixture from the pre-fractionator is dispatched to the side enricher column (C22). Acetic acid becomes the light component and can be withdrawn from the top of this column, while the heavy components (containing component X and HO) collected at the bottom are headed to the third column (C3). This column perform a separation between X and HO.

Assuming that column C1, C21 and C22 operate at atmospheric pressure (1bar).

Azeotropic convergence is specified for the pre-fractionator C1 and side stripper C21. Three phase vapor-liquid-liquid is chosen for the pre-fractionator since the liquid-liquid splitting may occur in this system. The super heating stream is introduced to the tray 30th of column C21, and the sub cooling stream is taken off from the tray 16th of column C22.

Column C3 is specified like column C27 in the conventional design.

The table below resumes the operating conditions of all columns:

	C1	C21	C22	C4

Number of stage	20	41	26	10
Condenser	1	0	1	0
Re-boiler	1	1	1	0
Pressure (bar)	1	1	1	1
Feed stage	10	37	16	Aqueous stream: 1st Steam: 10th

Table VIII.1: Column design parameters

b. Process simulation:

Pre-fractionator C1: The distillate to feed ratio is set at 0.6. This is an initial guess; the ratio will be changed later to keep X composition in the overhead stream of the pre-fractionator at 0.001(molar fraction). The reflux ratio is specified at 1. The feed is introduced at stage 10th.

Side stripper column C21: The bottom to feed ratio (mole fraction) is set at initial value at 0.3. The feed is introduced at stage 37th.

Side enricher column C22: The bottom to feed ratio (mole fraction) is set at initial value at 0.6 and the reflux ratio is set at 3. These initial values will be changed later by the design specification. The feed is introduced at stage 16th.

The column C3: we set the bottom rate at around 0.73 kg/h;

The column C4 has only one DOF: the steam introduced to the bottom is initially set at 0.85 kg/h. The column is heated up by this steam instead of re-boiler.

Water reflux ratio is set at 0.82. This ratio will be changed later to meet the desired purity of water product and to reduce the boil-up flow rate through the column C21.

The decanter is working at 1 bar and 40°C.

CH fresh stream is initially set at 1.22 kg/h.

The product specification is supposed to be in the table below:

Product name	HAC	X	Water	HO (HO1+HO2)
Purity	99%	99%	99.99%	93%

Table VIII.2: Product specification

A small IBA fresh stream is introduced to the decanter to compensate the IBA loss through the water product outlet.

Firstly, the process runs with the design specification of the pre-fractionator and the initial guess of the other columns. For the first running, IBA makeup stream is set at 1 kg/h, since if the IBA makeup flow rate is smaller than this value, there is not enough IBA in the decanter to form two-liquid phase. Afterwards, the IBA makeup flow rate is changed from 1 kg/h to 0.001 kg/h, while keeping the results from the last running and running the process again.

The process converges and the product stream is shown in the *table VIII.2*. The distillate stream of the column C22 (named HAC2) and the bottom stream of the column C21 (named HAC1) together constitute the HAC product stream.

	WATER	CH	HO	HAC
Mass Frac				
ACETI-01	0.0000	0.0000	0.0000	0.8215
CYCLO-01	0.0007	0.9993	0.1015	0.1277
WATER	0.9993	0.0000	0.0000	0.0507
POLYCAPA	0.0000	0.0000	0.4496	0.0000
CAPRO-01	0.0000	0.0007	0.4489	0.0000
ISOBU-01	0.0000	0.0000	0.0000	0.0000
Total Flow kmol/hr	0.353	0.292	0	1.18

Total Flow kg/hr	6.364	28.58	0.73	66.39
Temperature C	100	82	136	112
Pressure bar	1	0	0	1
Vapor Frac	0	1	0	0
Liquid Frac	1	0	1	1

Table VIII.3: Column desin parameters

Only water product purity is satisfied. We set the design specifications to meet all the product purity required:

Column C21: the composition of HAC in the bottom product is set at 98.7% by varying the bottom to feed ratio.

Column C22: the composition of HAC in the top product is set at 99.2% by varying the bottom to feed ratio, while the composition of component X is set at 98% by varying the reflux ratio from 0.1 to 2

Column C3: the composition of HO in the bottom product is fixed at 7% by varying the bottom rate from 0.67 kg/h to 0.79 kg/h.

Column C4: steam flow rate is varied from 0.12 to 1.2 kmol/h to meet the high purity of water 99.99 wt%

	WATER	CH	HO	HAC1	HAC2	HAC
Mass Frac						
ACETI-01	0.0000	0.0012	0.0074	0.9870	0.9920	0.9889
CYCLO-01	0.0001	0.9982	0.0700	0.0030	0.0080	0.0049
WATER	0.9999	0.0000	0.0000	0.0100	0.0000	0.0063
POLYCAPA	0.0000	0.0000	0.4640	0.0000	0.0000	0.0000

CAPRO-01	0.0000	0.0007	0.4586	0.0000	0.0000	0.0000
ISOBU-01	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total Flow kg/hr	0.956	36.87	0.7	34.6	20.5	55.11
Temperature C	100	82	141	116	118	116
Pressure bar	1.0000	0.0930	0.1285	1.0000	1.0000	1.0000
Vapor Frac	0.0000	1.0000	0.0000	0.0000	0.0000	0.0003
Liquid Frac	1.0000	0.0000	1.0000	1.0000	1.0000	0.9997

Table VIII.4: stream table

	C21	C22	C3
Condenser (KW)		-2.31	
Re-boiler (KW)	13.69	22.97	3.02

Table VIII.5: heat duty

All the product purity are achieved but the condenser heat duty of column C22 is much smaller the re-boiler heat duty of column C21 (*table VIII.5*). Then we need to increase the re-boiler heat duty of C22 and decrease the heat duty of column C21. To achieve this goal, the HAC composition in the distillate stream of C22 is now increased to 99.9 wt%. While the HAC composition in the bottom product of C21 is reduced to 98 wt% . The purity of HAC stream increases to 98.7%. The water reflux ratio is also reduced to 0.78. The heat duties are shown in *table VIII.6*:

	C21	C22	C3	TOT
Condenser (KW)		-3.15		-3.15
Re-boiler (KW)	6.86	23.8	2.88	33.55

Table VIII.6: heat duty

The condenser temperature of C22 is 117.5°C, while the re-boiler temperature of C21 is 114.5°C. Then the column C22 and C21 can be combined into one column called main column. The re-boiler heat duty of C21 is still higher than the condenser heat duty C22. Therefore, we need to add this difference of energy to the total heat duty of main column.

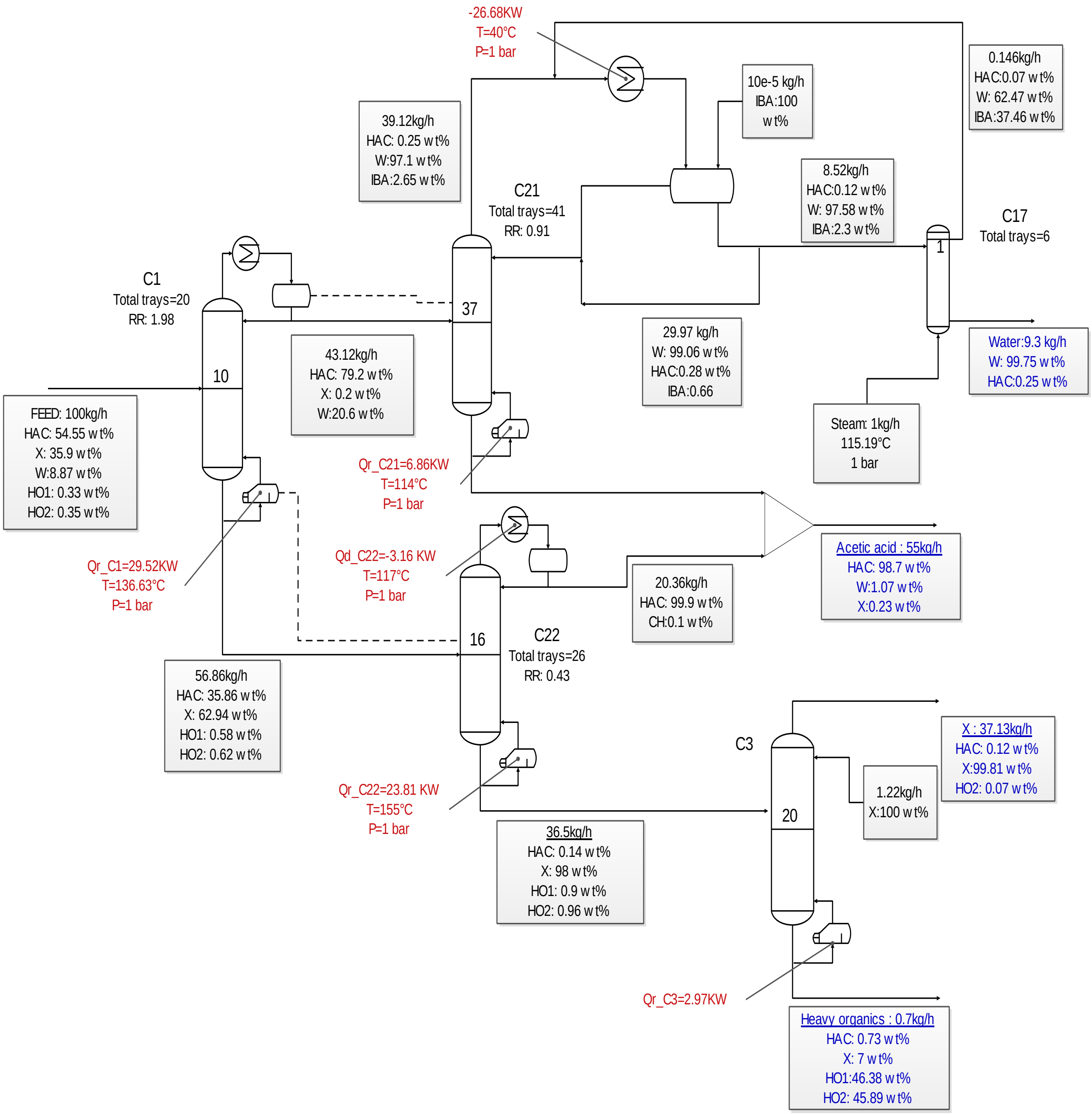

Figure VIII.4: Three columns computationally equivalent to the Petlyuk arrangement

The RCM map below synthesize the separation of three columns computationally equivalent to the Petluyk arrangement

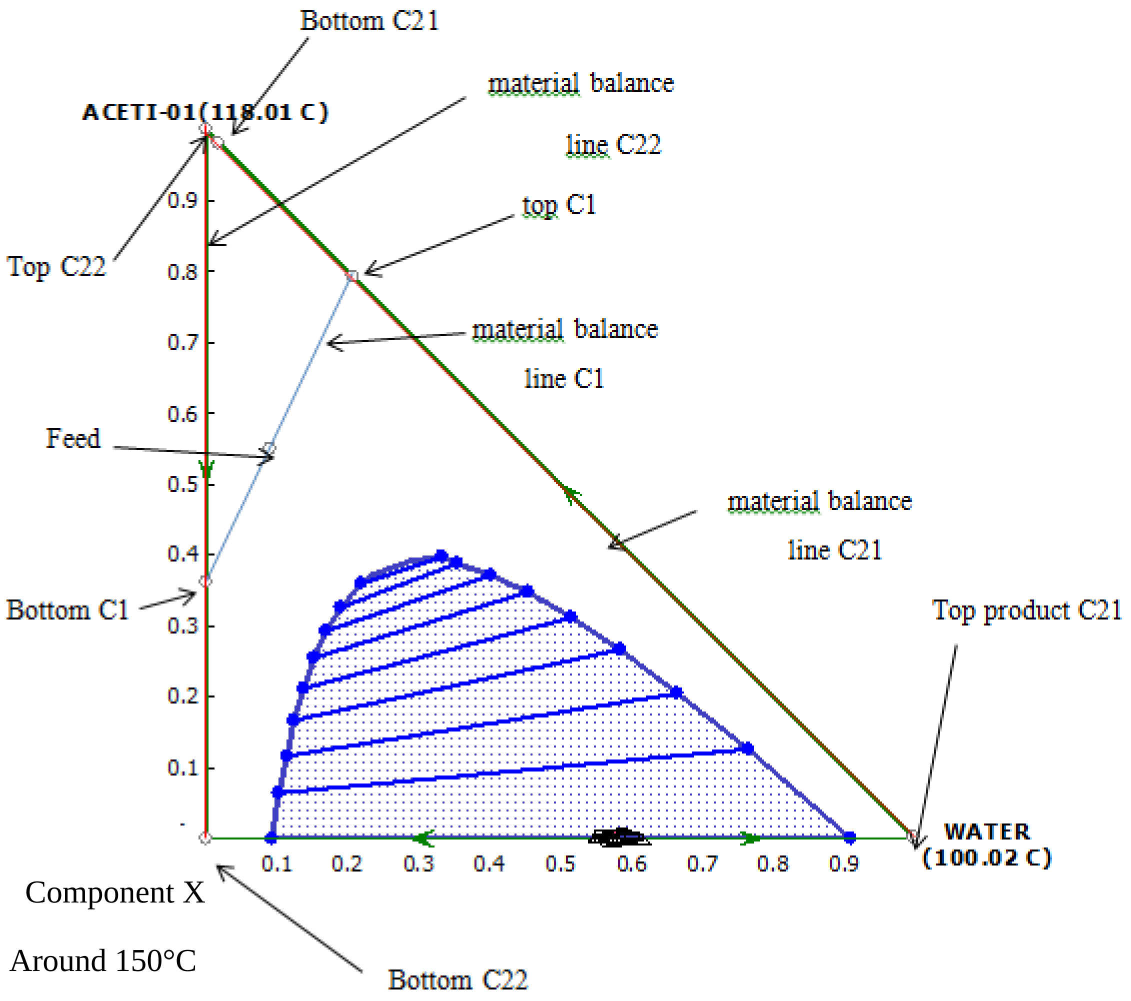

Figure VIII.5: Residue curve map

3. Petlyuk arrangement:

To build the Petlyuk arrangement, we remain the column C1 (call pre-fractionator) and combine the two succeeding columns (C21 and C22) into one column called main column. This main column has three outlet streams (bottom stream, top stream and side stream) (figure VIII.6). This column is difficult to simulate since there are too many DOFs compared to a normal column. Thus, we need to provide a very good initial guess. The initial guess is based on the results obtained from the simulation of three thermally coupled columns. Indeed, the bottom stream contains mainly component X and heavy organic (HO1 and HO2), the side stream contains 99 wt% of HAC. While the top stream contains mostly water, entrainer IBA and some traces of HAC. The top mixture is sent to a recovery column (C4) to obtain high water product (99.99 wt%). The operating conditions of the columns are detailed in the table below:

	PREFRAC	MAINCOL	C4
Number of stage	20	67	10
Condenser	1	0	0
Re-boiler	1	1	0
Pressure (bar)	1	1	1
Feed stage	10	37 and 57	Aqueous stream: 1st Steam: 10th

Table VIII.7: Column design parameters

The number of trays for main column is equal to sum of number of trays for the two side columns (C21 and C22) in the previous arrangement. Note that in Aspen Plus, re-boiler and condenser are included in the number of trays for the column. The main column has 2 feed streams: one feed is introduced to the upper part of the column at tray 37th (exactly the same feed tray of column C21), the other one is introduced to the lower part of the column at tray 57th (= feed tray of column C21 +number of trays for pre-fractionator). The main column has one re-boiler and no condenser while the pre-fractionator has one condenser and one re-boiler. All heat duty from the condenser of pre-fractionator is used for superheating of the feed to the upper part of the main column, while all re-boiler heat duty required of pre-fractionator is from sub cooling of the feed to the lower part of the main column.

A small IBA makeup stream is introduced to the decanter to compensate the loss of this entrainer during the separation.

Column C3 has no change.

Steam flow rate is initially set at 0.85 kg/h

Main column MAINCOL has two DOFs. Two parameters need to be specified: re-boiler duty is set at 0.34 kW, and the side stream flow rate is set at 55kg/h. These initial values can be changed later with design specification.

Water reflux ratio is kept at 0.81 which might be changed to minimize the boil-up flow rate.

The process is now ready to run. At the first running, the IBA makeup stream is set at 1 kg/h, and then we change this value to 0.001 kg/h (like the start-up procedure with three columns computationally equivalent to the Petlyuk column). The process is now converging.

Afterwards, the process is running with all the design specifications. More specifically, we control the purity of component X at 98 wt% in the bottom product of main column by adjusting the re-boiler duty and control the purity of acetic acid product at 99 wt% by adjusting the side stream flow rate. The water product purity is controlled at 99.9 wt% by varying the steam supplied to the column C4.

We run the process again and the product streams are given in the tables below:

	W	HAC	X	HO
Mass Frac				
ACETI-01	0.0000	0.9900	0.0013	0.0034
X	0.0001	0.0010	0.9981	0.0700
WATER	0.9999	0.0090	0.0000	0.0000
HO1	0.0000	0.0000	0.0000	0.4625
HO2	0.0000	0.0000	0.0005	0.4641

ISOBU-01	0.0000	0.0000	0.0000	0.0000
Total Flow kmol/hr	0.523	0.937	0.377	0
Total Flow kg/hr	9.41	55.05	37.08	0.71
Temperature C	100	116	82	142
Pressure bar	1.0000	1.0000	0.0930	0.1285
Vapor Frac	0.0000	0.0000	1.0000	0.0000
Liquid Frac	1.0000	1.0000	0.0000	1.0000

Table VIII.8: product stream

	MAINCOL	C3
Re-boiler (KW)	27.56	2.9

Table VIII.9: re-boiler duty

In the conventional design, it is concluded that water reflux ratio has a big influence on water product purity and on the total re-boiler heat duty. *Figure VIII.6* and *figure VIII.7* show the influence of water reflux ratio on the water purity and on the re-boiler of main column, respectively. By decreasing slowly and keeping constant water product purity, we achieve to ratio of 0.78, re-boiler duty of MAINCOL is 27.56 KW, and the water product purity is still 99.9%.2 000 kJ of energy are required to evaporate 1 kg of water at 115°C into 1 kg of steam at 115°C, at 1 bar. Then to evaporate 1.02 kg/h of water, we need 2.9 KW of energy. This sum of energy has to be added to the total heat input of process. Then the total heat input equals to 27.56+2.9+0.56 = 31.02 KW. That leads to an **energy saving of 18.3%.**

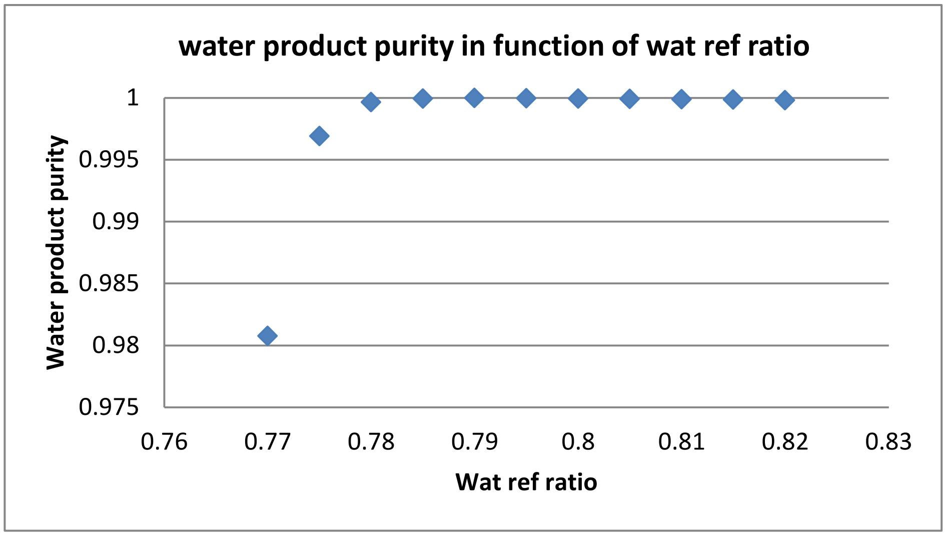

Figure VIII.6: Water product purity in function of water reflux ratio

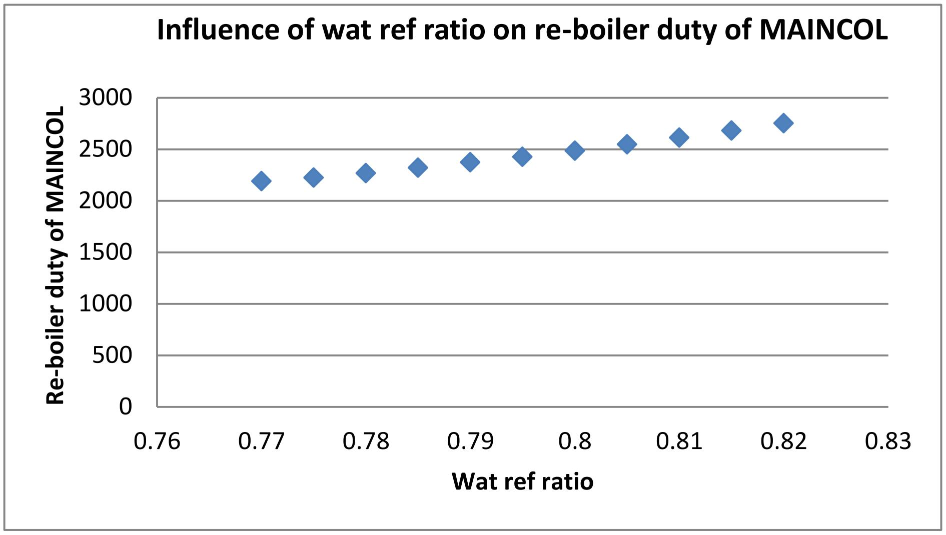

Figure VIII.7: Re-boiler duty of MAINCOL in function of water reflux ratio

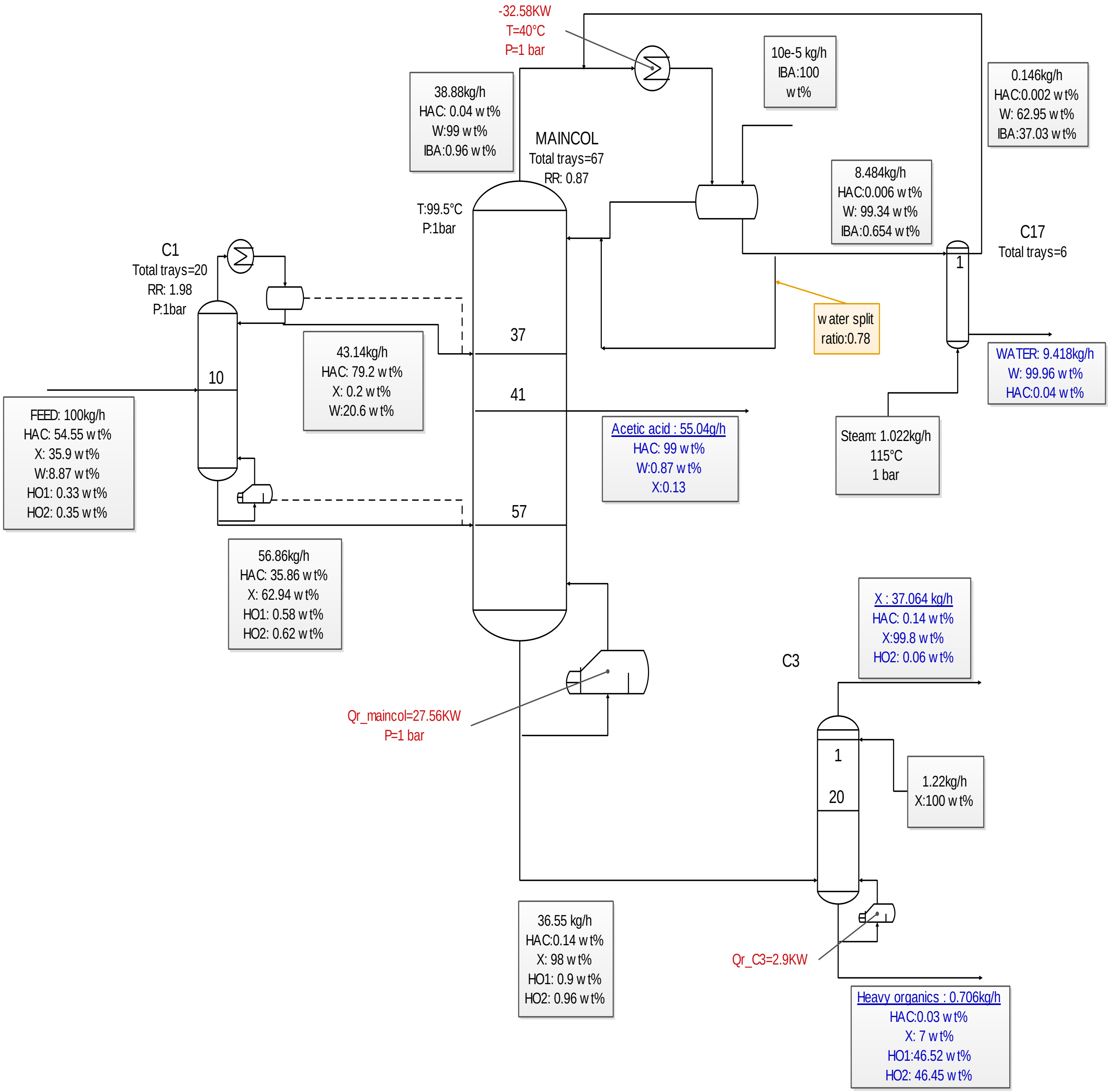

Figure VIII.8: Petlyuk arrangement

4. Discussion and perspective:

Some observations can be made by looking at the Petlyuk arrangement simulation. It is noticed that water can be easily separated from the bottom of pre-fractinonator (PREFRAC or C1) due to its high relative volatility with acetic acid (middle component), see *figure VIII.9*:

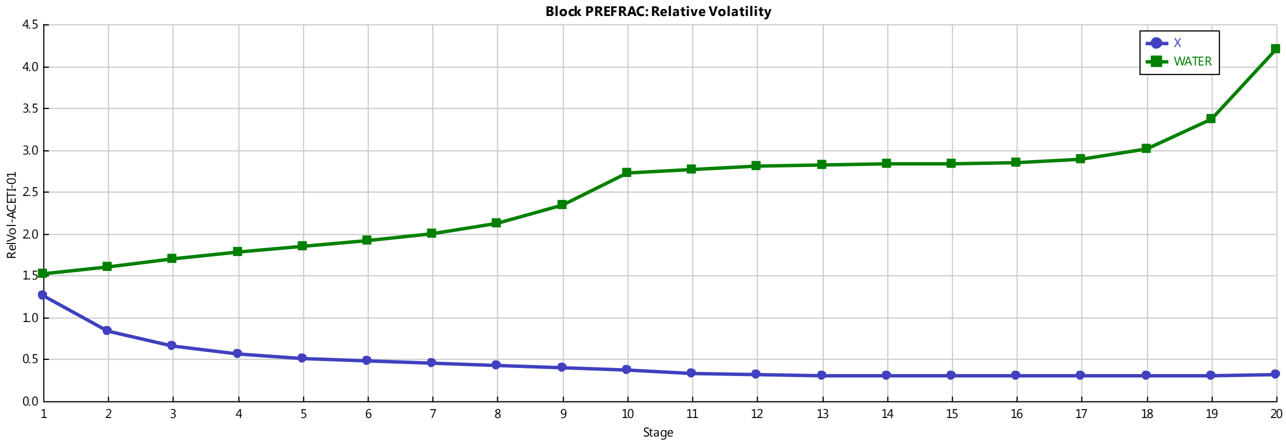

Figure VIII.9: Relative volatility profiles of pre-fractionator (base component: HAC)

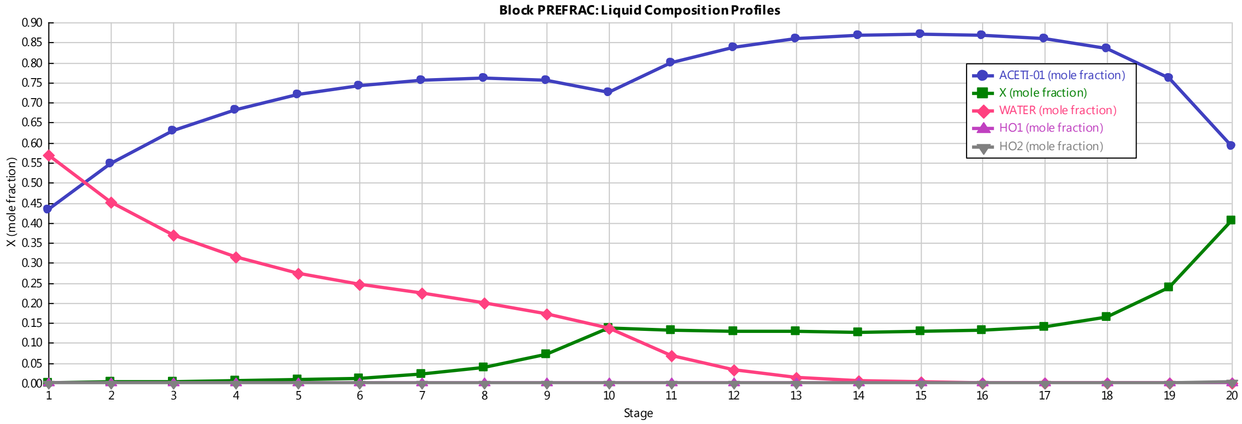

Figure VIII.10: Liquid composition profiles of pre-fractionator

Figure VIII.10 shows the liquid composition of pre-fractionator, acetic acid composition reaches its maximum when component X dies out in the top section, and when water dies out in the bottom section.

Figure below shows the liquid composition profiles of the main column. Acetic acid liquid composition reachs its maximum and withdrawn out as a side stream at tray 41th.

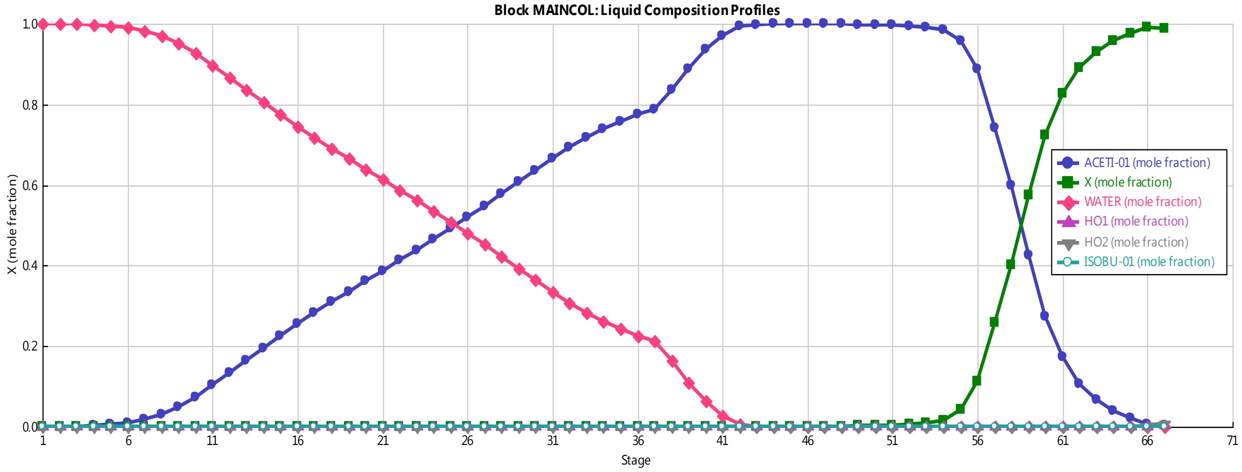

Figure VIII.11: Liquid composition profiles of MAINCOL

Heterogeneous distillation is a complex system and difficult to operate due to distillation boundaries, phase split, non-linear dynamics, and the possible existence of multiple steady states. Dividing wall column is also difficult to operate and simulate since it has more degree of freedom compared to the ordinary distillation column due to the side stream. Thus, applying DWC to heterogeneous distillation could make the design and the control of the whole system extremely difficult.

In many papers, the reducing of heat input up to more than 30% is recorded with DWCs (21, 22). Energy saving achieved in this work (18.3%) is not as much as expected, since the heterogeneous azeotropic distillation column usually consumes more energy than a normal distillation column does, due to the recycle at the top of the column. Nevertheless, this work shows the significant potential for the combination of Petlyuk arrangement and ternary heterogeneous distillation. The result from this retrofitting to DWC is very promising.

5. Future work:

There are several possibilities of improvement for future works

- For the pre-fractionator, the water composition was over-purified in the bottom stream (about 10e-6 molar fraction) which leads to a penalty in term of increased energy. Applying the "Vmin" diagram developed by Halvorsen and Skogestad to the pre-fractionator should estimate the minimum vapor requirement for this part of Petlyuk column.
- Adding a new component to the given system can make the process more difficult to operate. Therefore, instead of adding IBA, we can use component X which can also form a minimum boiling azeotrope with water.

IX. Conclusion:

The aims of this work were achieved. Firstly, a conventional design was build and successfully optimized based on the real data produced by Perstorp (15). Secondly, the combination of dividing wall column and ternary heterogeneous distillation has been successfully studied, to reduce the heat input and hence the operating cost of process.

Two alternatives were investigated. Both of them allow downsizing the chemical plant but only with the Petlyuk arrangement we can achieve an energy saving up to 18.3% compared to the conventional design. Energy saving achieved in this work is not as much as expected, but at least it shows the significant potential for the combination of Petlyuk arrangement and ternary heterogeneous distillation.

In general, the reduction of energy consumption achieved by retrofitting to a dividing wall column results in the reduction of the fossil fuels requirement and consequently contribute to sustainability of chemical processes.

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