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Abstract: The aim of this work is to implement heterogeneous azeotropic distillation schemes in a dividing wall column (DWC) for a feed mixture of water (W), acetic acid (HAC) and an organic component (X). The original design makes use of X to act as an entrainer to facilitate the separation of water and HAC, and we also propose a DWC design based on this idea. This DWC design reduces the capital cost, but the energy usage is almost unchanged. To achieve energy savings and further reductions in capital costs, we need to use a Petlyuk DWC. We introduce isobutyl acetate (IBA) as an additional entrainer for the Petlyuk DWC, and achieve energy savings of about 20%.

Reviewers' comments:

Reviewer #1: The conceptual idea of adding an extra entrainer which cycles in the top column part is very interesting.
However, besides a few editorial mistakes (obsolete words, inconsistent nomenclature HAC vs. ACETI-01 and IBA vs. ISOBU-01) there are some details missing that hinder understanding the complete process.

1. The author does not mention any reason why part of the aqueous phase from decanter D1 is recycled to the column. This recycle stream has to be evaporated and condensed again. The advantages and/or disadvantages should be made clear.

Answer:

Page 5, paragraph 1, beside figure 5: "Part of the aqueous phase needs to be recycled back to the top of C14 to provide the "normal" reflux to prevent the heavy key component (HAC) from entering into the top vapor stream. If the reflux ratio drops much below 0.4, then we get breakthrough of HAC in the top of the column as illustrated in Figure 4b. Actually, there is a range of reflux ratios where we have multiple possible steady state operating points, including one desired without breakthrough of HAC (Figure 4a) and one undesired with breakthrough and no X in the top (see prefractionator in Figure 10a below) "

2. As mentioned in the text, Figure 3 shows a pinch region of below the feed point. This implies that either the feed stage is chosen to high or that the stripping is overdesigned. The additional stages do not allow a further reduction of the amount of water in the bottom product. Instead, it would make sense to remove these stages in order to reduce pressure drop.

Answer:

Changes were made in figure 4a, page 4.

The column was resized. The feed stage cannot be higher (above stage 20), since the process cannot converge

3. Mole fractions are not appropriate for the profile diagrams because heavy components with low weight percentages almost disappear in the mole plot.

Answer:

The mass concentrations of heavy components (HO1 and HO2) are really small (less than 1 wt%) then they almost disappear even in the mass composition profiles.

However, taking into account your comment, I change all the mole plots in mass plots.

4. Figure 5 shows an additional feed stream to column C1 on stage 1. This stream is not mentioned in the text and I do not see any need for it.

Answer:

Page 5, before the last paragraph or paragraph 6: " Note that a small stream with Water-X is added to the main column C1. This additional stream is used to make the simulation converge. This stream is very small (0.12 kg/h) and has almost no effect on the final result."

5. The caption of Figure 6 is misleading: Figure 4 does not contain any column. The reference might be wrong?

Answer:

Page 6, the caption of Figure 7, replace "Figure 4" by "Figure 6"

6. Figure 6 again implies that stages 31 to 46 are not necessary and can be omitted.

Figure 5 page 5 and figure 6 page 6.

The column was resized, and for the same problem in conventional design, the feed stage cannot be higher (above stage 20). The mass plot is used instead of mole plot (figure 6)

7. If IBA+HAC reveal a T-max azeotrope, why is there no IBA in the stripping part of the MAINCOL (above stage 37)? The concentration profile shown in Figure 10 shows no IBA inside the column. At least at stage 1 a concentration > 0.0 % is expected since the distillate contains > 3 wt% IBA. Further, I would expect an IBA concentration peak between stage 1 and 37.

Answer:

Page 9, Figure 10a and Figure 10b, the mass plots are used instead of mole plots.

Page 9, Figure 10c is added. Page 10, the 1st paragraph beside Figure 11: "The concentration of IBA inside the column is very low and in the composition profiles it can be only observed in the vapor composition in the top of MAINCOL (Figure 10c). This implies that the loss of IBA is very small as can been seen from the tiny makeup stream of 10-5 kg/h."

8. The energy consumption of the Petlyuk-DWC is benchmarked against the original process setup. However, in the latter case no additional entrainer is used. There should also be a comparison to the original setup with addition of IBA. How would the additional entrainer influence purities and energy consumption?

Answer:

In the conventional arrangement, there is no water-acetic acid separation so that instead of using entrainer, we use a steam (pure water) heating up a side stripper to remove component X remained in the water product stream.

In the Petlyuk arrangement, we do have water-acetic acid separation.

"This mixture of water and HAC forms a tangent pinch (Figure 2) and cannot be separated easily using a side stripper hence entrainer adding is necessary.", see in page 10, 2nd paragraph, from line 8 to line 13

Moreover, the fresh entrainer makeup is surprisingly small (10-5kg/h), so that there is almost no effect on the product purities.

9. Distillation curves in the ternary diagram and binary VLE plots would add much to understanding the process.
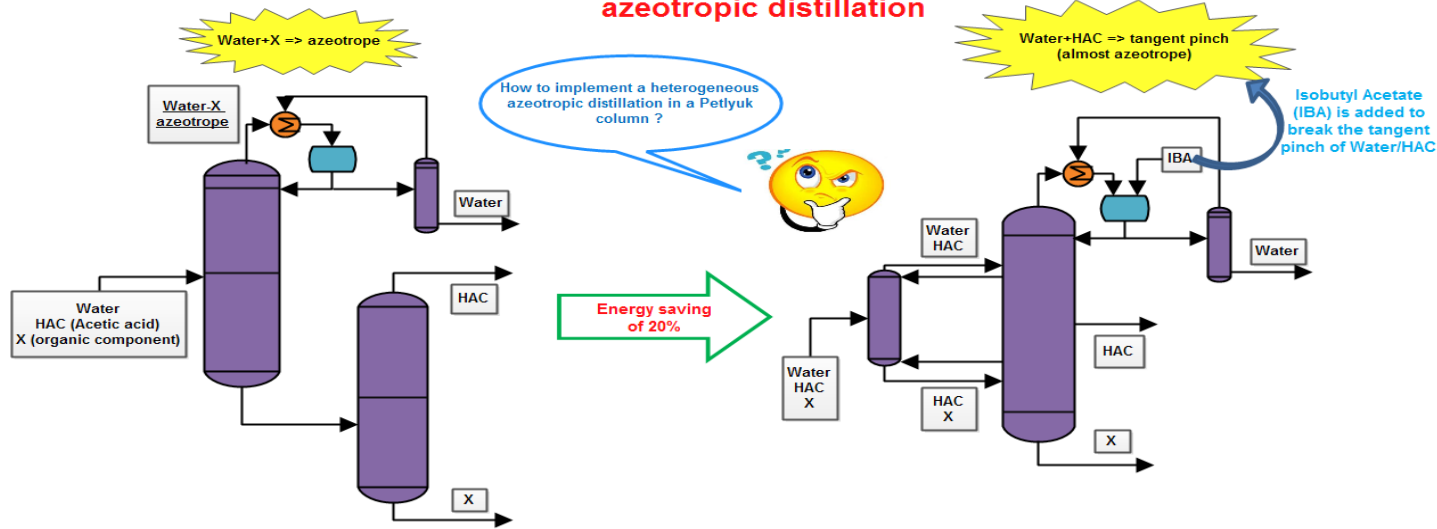
Answer:

A phase diagram for Water-HAC-IBA is added with the material balance lines of the upper part of the main column; see Figure 11, page 10.

An explanation is given in page 10, 2nd paragraph from line 1 to line 8: "To understand better the behavior of the main column (MAINCOL), we note that it can be divided into two "columns", C21 (top) and C22 (see Figure 8a). Figure 11 shows the phase diagram for water-HAC-IBA with the material balance lines of the upper part (C21)."

It would be nice to ass VLE diagrams for Water-X and HAC-X, but this is not possible for condidentiality reasons

VLE diagram for HAC/Water is shown in Figure 2.

Graphical Abstract (for review)

Dividing wall column for heterogeneous azeotropic distillation

Water+X => azeotrope

Water-X azeotrope

How to implement a heterogeneous azeotropic distillation in a Petlyuk column ?

Water

Water
HAC (Acetic acid)
X (organic component)

HAC

Energy saving of 20%

X

Water+HAC => tangent pinch (almost azeotrope)

Isobutyl Acetate (IBA) is added to break the tangent pinch of Water/HAC

IBA

Water
HAC

Water

Water
HAC
X

HAC
X

HAC

X

Highlights :

- Implementing heterogeneous azeotropic distillation in a dividing wall column.
- Two possibilities: distillation column with side-rectifier and Petlyuk column.
- Using isobutyl-acetate (IBA) as entrainer for the separation of water-acetic acid.
- Only with Petlyuk arrangement, we can achieve energy savings of <u>about 20%.</u>

Dividing wall columns for heterogeneous azeotropic distillation

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Abstract

The aim of this work is to implement heterogeneous azeotropic distillation schemes in a dividing wall column (DWC) for a feed mixture of water (W), acetic acid (HAC) and an organic component (X). The original design makes use of X to act as an entrainer to facilitate the separation of water and HAC, and we also propose a DWC design based on this idea. This DWC design reduces the capital cost, but the energy usage is almost unchanged. To achieve energy savings and further reductions in capital costs, we need to use a Petlyuk DWC. We introduce isobutyl acetate (IBA) as an additional entrainer for the Petlyuk DWC, and achieve energy savings of about 20%.

Keywords

Dividing Wall Column (DWC), heterogeneous azeotropic distillation, Petlyuk arrangement, energy saving.

1. Introduction

Distillation is one of the most energy-consuming processes in the chemical industry. Thus, reducing its energy requirement, which also leads to lower operating costs, is a priority target of chemical manufacturers all over the world. One of the most promising technologies is a Petlyuk distillation arrangement implemented in a Dividing Wall Column (DWC), see Figure 1(a). Indeed, for a three-component separation, this arrangement provides a potential energy saving of up to 30% compared to a conventional two-column sequence. The Petlyuk-DWC is also more compact, with only one column shell, one reboiler and one condenser, which typically reduces the capital cost by 30% [3]. The main disadvantages with the DWC arrangements are that they are less flexible and that the operation and control are more difficult. The Petlyuk-DWC was first patented by Wright in 1949 [5], but it was only taken into industrial use in 1985 by the German company BASF [3]. Since then there have been many installations, with more than 100 industrial applications reported in 2006 [3].
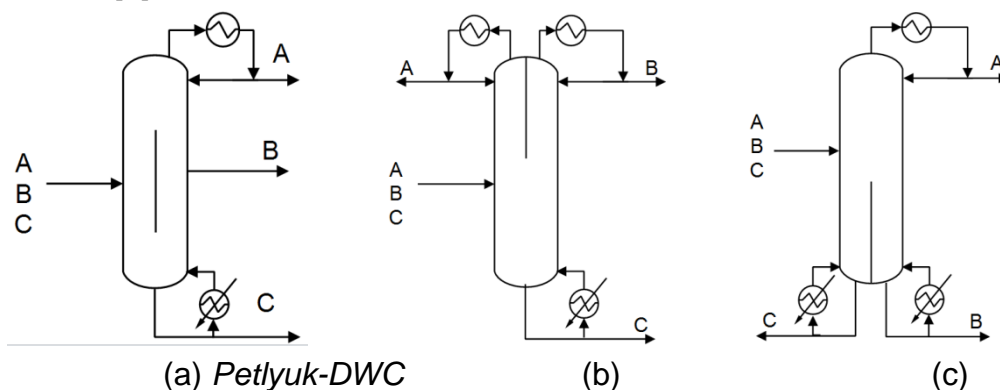

(a) *Petlyuk-DWC*   (b)   (c)

Figure 1: Three alternative Dividing Wall Column (DWC) configurations for ABC-separation

There are also other dividing-wall arrangements for a three-component separation, in which the partition wall is located either at the upper or at the lower part of the column shell, see Figures 1(b) and 1(c), but these require an additional condenser or reboiler. These are equivalent to a side-rectifier and a side-stripper configuration, respectively.

Another approach to make distillation more efficient and compact is to make use of liquid-liquid separation (decanting), whenever applicable. Indeed, *heterogeneous azeotropic distillation* is widely used in the chemical industry to separate azeotropes and close-boiling binary mixtures [1, 4]. The main idea is to "break" the binary azeotrope (A,B) by adding a third component (C), known as the entrainer [4] or solvent [1]. The entrainer (C) is generally a component that does not mix well with at least one of the components (A) in the original binary mixture, thus causing the two components (A,C) to evaporate more easily and to stay in the top part of the column, where they often form another azeotrope. When condensed, the overhead vapor (which usually is close to AC-azeotrope composition) forms two liquid phases which are separated in a decanter. All of the entrainer phase (C) is recycled to the column, while part of the other phase (A) is recycled (refluxed) and the remaining is taken as overhead (distillate) product. Ideally, the overhead product contains no C and also no C leaks out in the bottom, so that C just stays inside the column, with no need to supply "fresh" C.

The resulting overall separation can be counterintuitive, for example, with the lightest of the original binary components ending up as the bottom product. The earliest example of heterogeneous azeotropic distillation is the breaking of the water-ethanol azeotrope using benzene as the entrainer [4]. However, azeotropic distillation arrangements are generally difficult to design and operate, because of distillation boundaries, complex thermodynamics with liquid-liquid phase split, non-linear dynamics, and the existence of multiple steady state solutions [2, 9].

The objective of this paper is to consider heterogeneous azeotropic DWC distillation applied to the separation of water (A=W) and acetic acid (B=HAC). This mixture forms a tangent pinch ("almost azeotrope") at the pure water end, where the liquid and vapor compositions are similar (Figure 2), making separation by conventional distillation difficult. A common industrial way of separating this mixture is to use an entrainer, for example, isobutyl acetate (C=IBA) [7].

However, in our case the original feed mixture actually contains another a third component which can act as an entrainer (C=X) for separating AB. As described above, the non-ideal VLE makes the heavy component C go to the top of the column where it upon condensation forms a separate phase which is recycled. However, since we continuously add component C=X in feed, we need to take out C in the bottom of the column, which is different from the case described above.

In our case, component C=X is an organic component with a boiling point around 150C and with water it form a heterogeneous azeotrope with a boiling point around 98C. In addition, the feed contains small amounts of heavy organic components. In summary, we want to separate 100 kg/h of the following four-component feed mixture into pure components:

A = Water (W)	Bp=100C	8.87 wt%
B = acetic acid (HAC)	Bp=118C	54.55 wt%
C = organic (X)	Bp=150C	35.9 wt%

D = Heavy organics (HO) Bp~200C   0.68 wt%

The heavy organics (D=HO, consisting of HO1 and HO2) have almost no effect on the results in this paper.
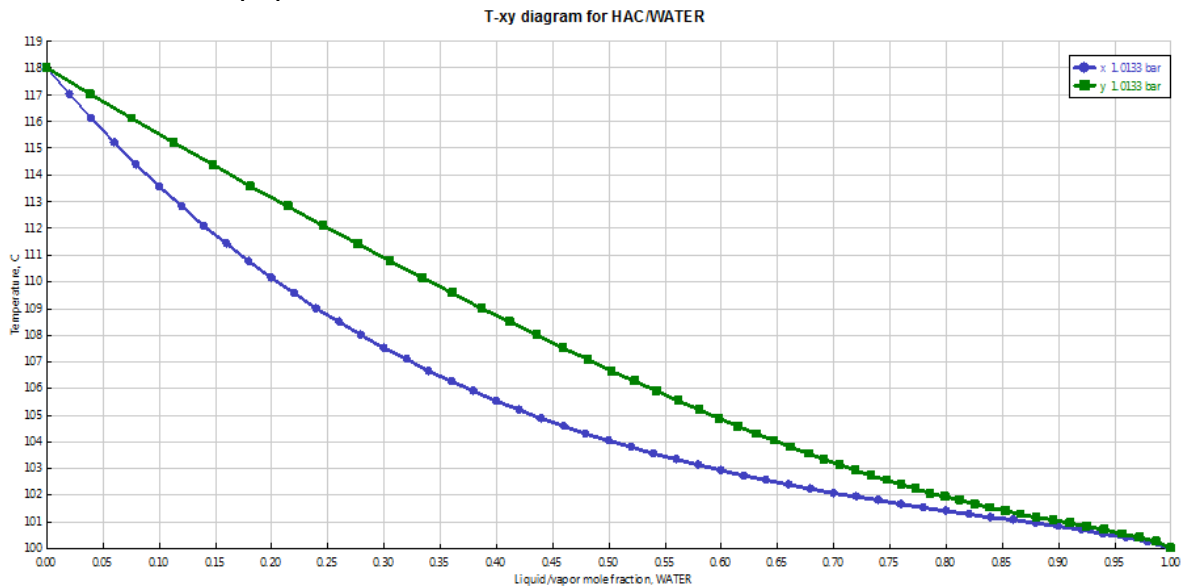

Figure 2: VLE diagram for HAC/Water

The Aspen Plus simulator was used to model the columns. The vapor-liquid-liquid equilibrium was calculated using the NRTL liquid activity coefficient model, with missing binary coefficient estimated from UNIFAC. In addition, the Hayden-O'Connell model [8] is used to represent the dimerization of acetic acid in the vapor phase.

The paper is organized as follows: In Section 2 we give simulation results for the conventional configurations which is presently used in Perstorp (Figure 3). We then consider two different DWC arrangements for integrating the two distillation columns (C14 and C108 in Figure 3). First, we consider the arrangement in Figure 1b, which is quite straightforward to design and simulate (section 3).

Next, we consider the Petlyuk arrangement in Figure 1a, which is much more difficult to simulate (section 4.1), and which actually cannot be applied directly to this feed mixture (section 4.2). To make it work, we need to add a new entrainer (section 4.3), and we choose to use isobutyl acetate (C=IBA).

2. Conventional configuration

Figure 3 shows the flowsheet for the original conventional direct-sequence employed to separate the feed. The stream flows and the reboiler heat duties are also shown. The feed is introduced to the first column, C14. The overhead vapor of C14 (point S17 in Figure 5), which is close to the azeotrope of water and component X, is condensed and separated into two liquid phases in the decanter (D1). The organic phase, rich in X, is totally refluxed back to the top of column C14. The aqueous phase, containing mostly water, is partially refluxed, while the rest is send to the stripper column (C17) where steam (pure water) is used to strip off the remaining X which is recycled to the condenser. The net overhead product of columns C14-C17 is almost pure water which is withdrawn in the bottom of the stripper.
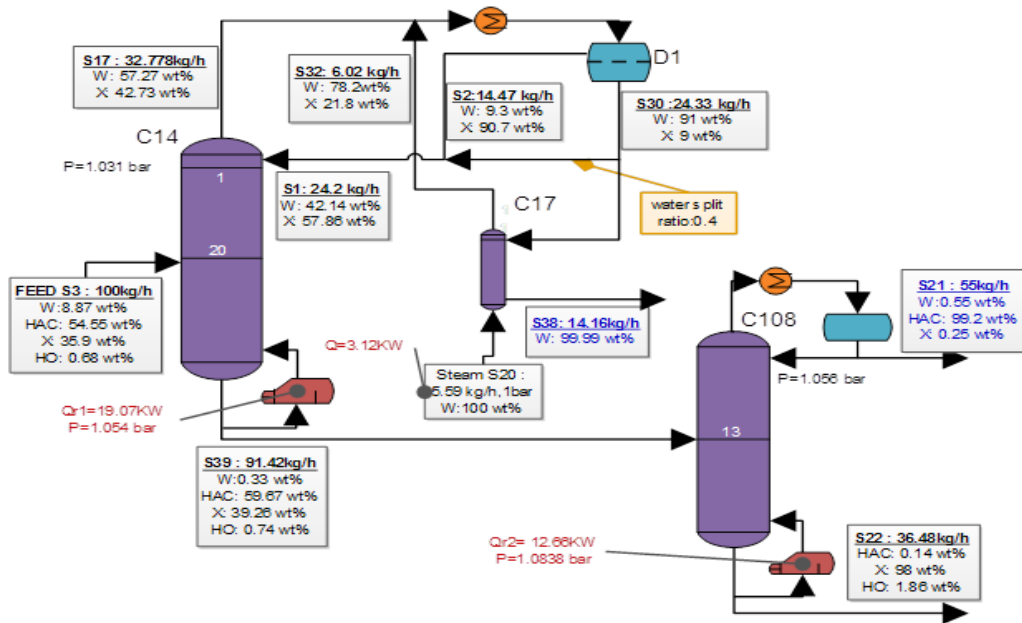
Figure 3: *Original design with two distillation columns (C14, C108), decanter (D1) and stripper (C17). Overall Q=34.85 kW*
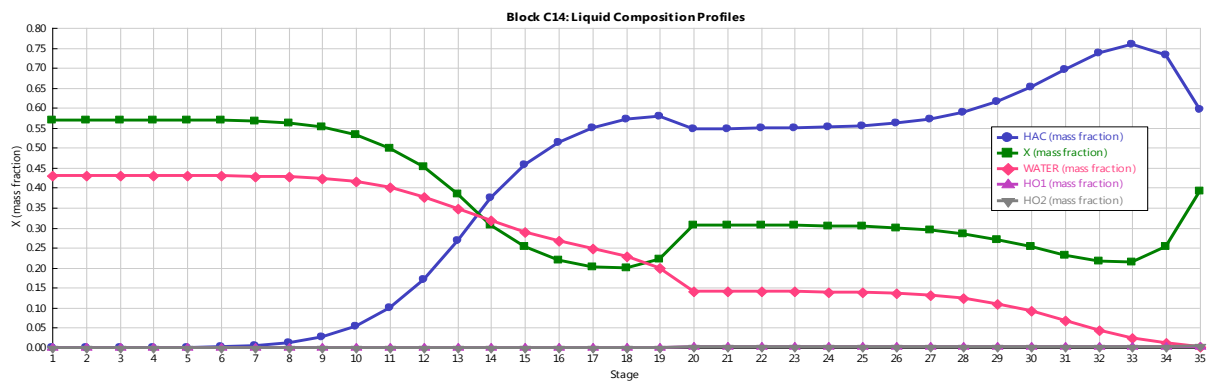

Figure 4a: Liquid composition profiles for column C14 (stage 1=condenser)
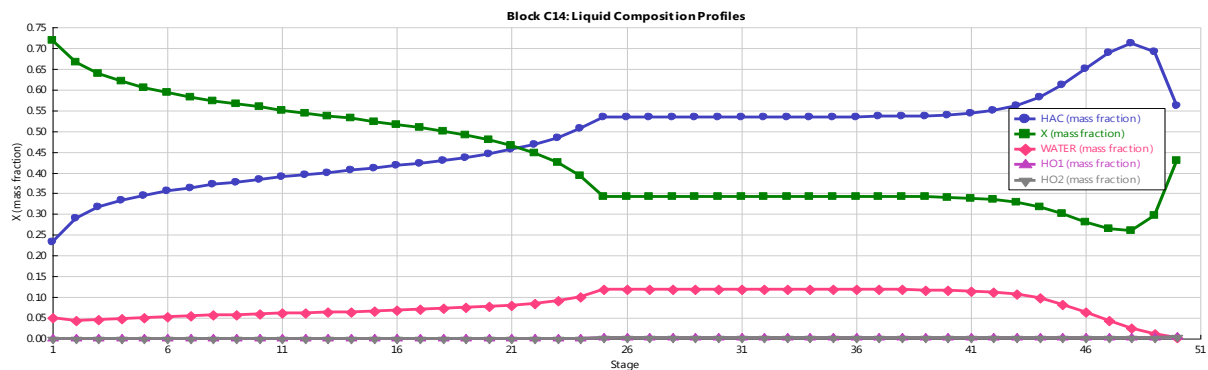

Figure 4b: Undesired liquid composition profiles for column C14 for case with too little reflux of water phase, resulting in breakthrough of HAC in the top.

Part of the aqueous phase needs to be recycled back to the top of C14 to provide the "normal" reflux to prevent the heavy key component (HAC) from entering into the top vapor stream. If the reflux ratio drops much below 0.4, then we get breakthrough of HAC in the top of the column as illustrated in Figure 4b. Actually, there is a range of reflux ratios where we have multiple possible steady state operating points, including one desired without breakthrough of HAC (Figure 4a) and one undesired with breakthrough and no X in the top (see prefractionator in Figure 10a below).
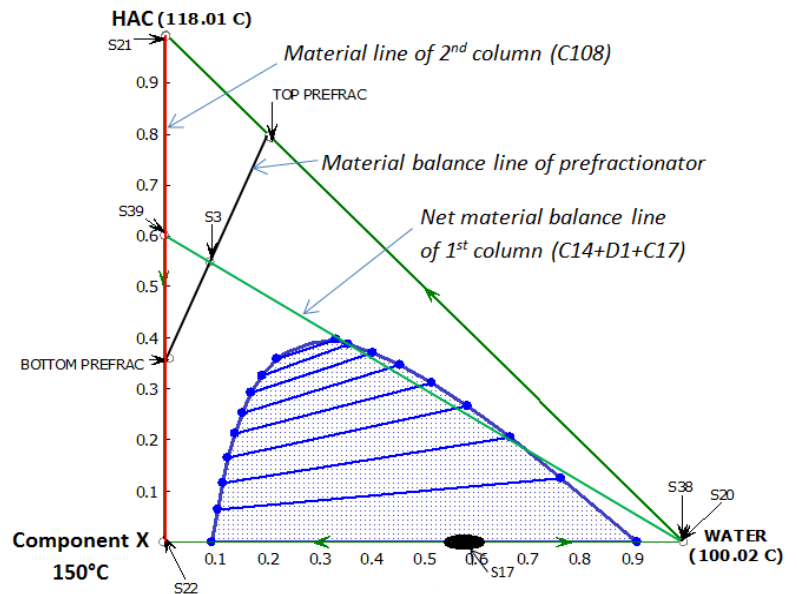
Figure 5: Phase diagram for Water-HAC-X

The bottom product of C14 also contains almost no water and goes to the second column C108. The top product of this column is the HAC-rich product, while the bottom stream is rich in X and HO. The total energy required is 34.85KW.

Figure 4a shows the liquid composition profiles in the first column (C14). Above the feed stage (stage 20), HAC dies out rapidly while water and X approach their azeotropic composition (Figure 4a). Below the feed, there is a pinch region where the composition remains almost constant. This implies that one has extra stages in the bottom, which means that one could probably reduce amount of water in the bottom product, if desired.

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

We first consider the simple DWC solution in Figure 1b with the partition wall placed at the upper part of the column. This arrangement eliminates one reboiler, but still needs two condensers. Assuming negligible heat transfer across the wall, this configuration is equivalent to the simulated flowsheet in Figure 6.

Some observations can be made from the simulation results which are summarized in Figure 6. First, we cannot avoid a slippage of HAC into the bottom stream of C1 (2.90 wt% versus 0.14% in the conventional design in Figure 3). Second, this configuration consumes 33.85 kW which is only slightly lower than the 34.85 kW required for the conventional design. Hence, significant energy savings are not achieved, but the capital costs are expected to be lower.

Note that a small stream with Water-X is added to the main column C1. This additional stream is used to make the simulation converge. This stream is very small (0.12 kg/h) and has almost no effect on the final result.

The liquid composition profiles in the main column C1 (Figure 7) are quite similar to those of C14 (Figure 4b). Note that the HAC composition achieves its maximum

between stages 32 and 34, which is where the vapor sidedraw HAC is taken out and sent to the stripper column C2.
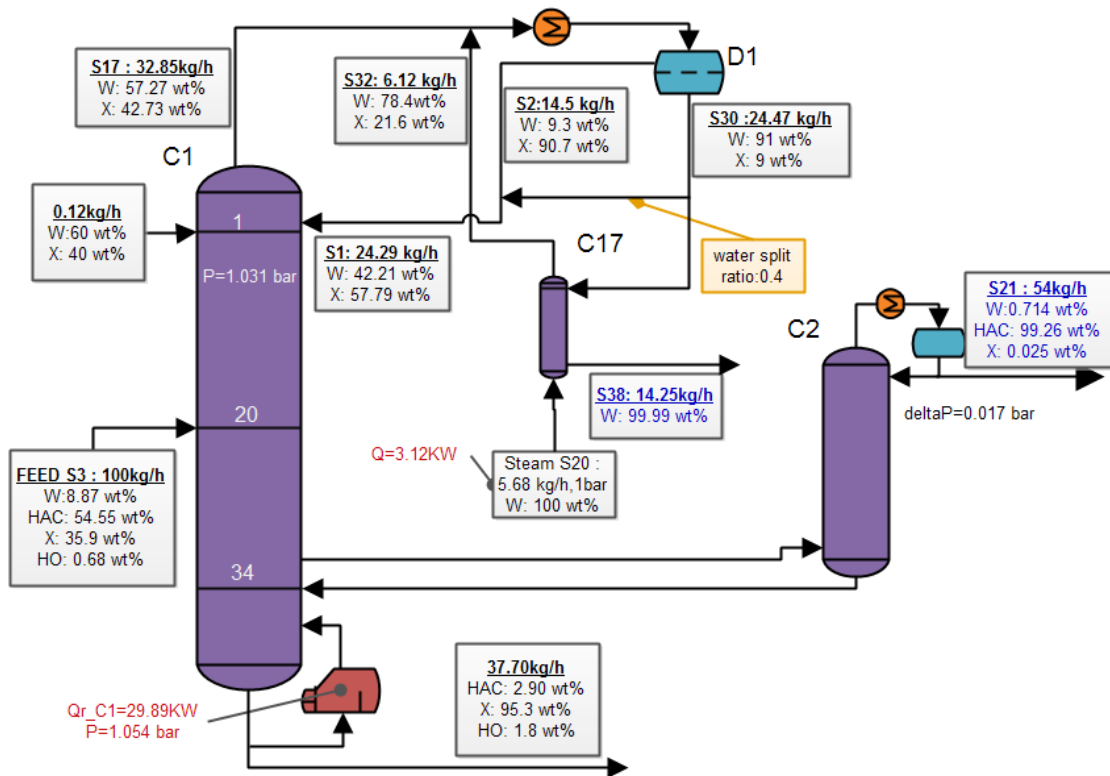

Figure 6: Side rectifier configuration (equivalent to DWC configuration in Fig. 1b with wall in upper part of column). *Overall Q=33.01 kW*
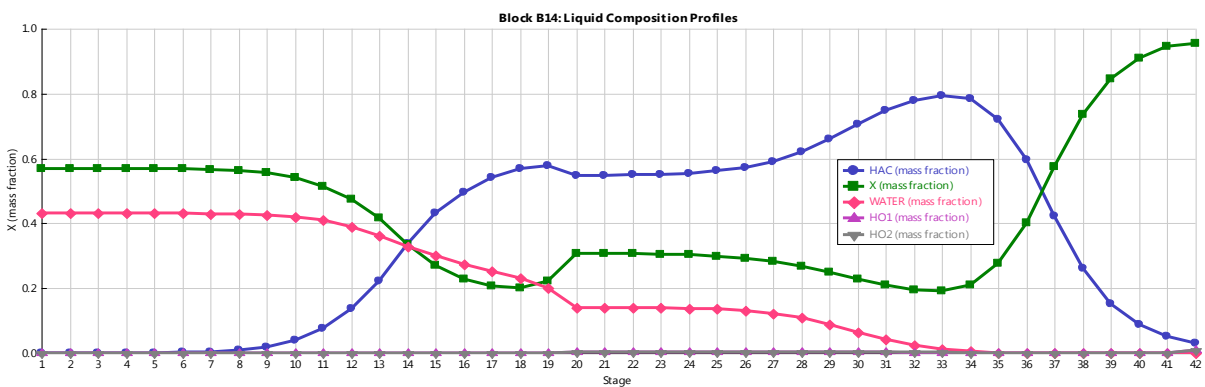

Figure 7: Liquid composition profiles of the main column C1 in figure 6

4.DWC Petlyuk arrangement

4.1 Simulation

Next, consider the three column section arrangement in Figure 8a which is thermodynamically equivalent to the Petlyuk DWC in Figure 1a. As we see from Figure 8a, the Petlyuk arrangement has recycles from column sections C21 and C22 back to C1, which makes it difficult to get numerical convergence for our non-ideal

mixture when using commercial simulators (e.g. Aspen, Hysys or Unisim). Thus, for simulations we use instead the three-column arrangement in Figure 8b with no recycles between the columns. The heat removed in the condenser in C1 in Figure
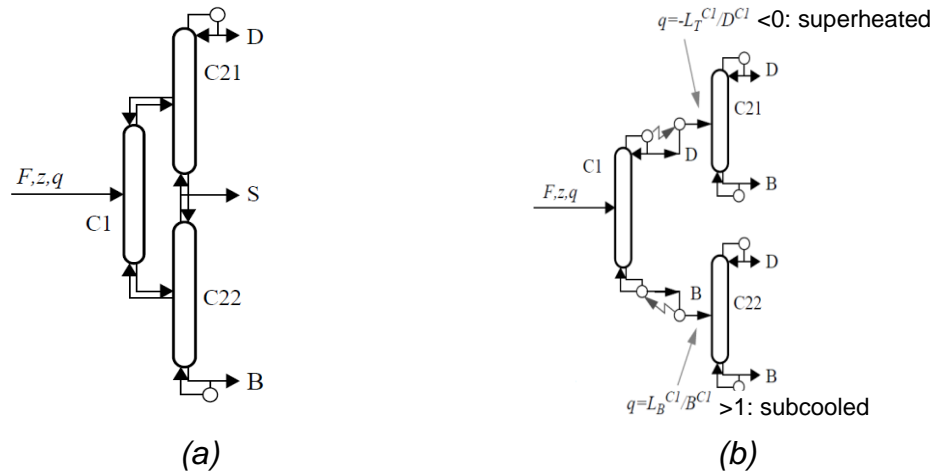

(a) (b)

Figure 8: Petlyuk arrangement (a) and simulation representation (b)

8b, is used to virtually superheat the top product of C1 (or alternatively and maybe simpler, used in a side heater in C21). Similarly, the heat required in C1 is supplied by virtually subcooling the bottom product of C1 (or altenatively, used in a side cooler in C22). The boilup rate in C22 is adjusted until the heat duties in the reboiler of C21 and in the condenser of C22 become equal. More details about this approach are found in Appendix D in the PhD thesis of Halvorsen[6]. The configuration in Figure 8b is equivalent to the configuration in Figure 8a for optimal operation with an infinite number of stages [6], but the two configurations have been found to give almost identical results also with a finite number of stages [6].

4.2 DWC Petlyuk with original feed mixture

A direct application of the Petlyuk idea to integrate the two original columns (C14 and C108 in Figure 3) does not work. The reason is that the nonideal thermodynamics make the heaviest component (X), which eventually must end up in the *bottom* product in C108, appear as an azeotrope with water (W) at the *top part* of column C14. Because of this it is not possible to get an HAC-sidestream in the Petlyuk column with no X.

4.3 DWC Petlyuk with IBA added as entrainer.

However, it is possible to operate the column system such that X does not go to the top, for example, by reducing the amount of water reflux, as discussed when considering the original design in Figure 3. Instead, HAC goes to the top and since the resulting water-HAC mixture is difficult to separate, we need to add another entrainer in the top.

Our first approach was to use X as the entrainer because this avoids adding a new component. We found it to be workable, but X is not an ideal entrainer because the water phase contains about 10 mass% of X (Figure 5) and simulations showed that we need quite a lot of energy to strip off X. There are many better entrainers such as isobutyl acetate (IBA), n-butyl acetate and ethyl acetate [7]. We chose IBA (Bp. 116C) which is almost immiscible with water and forms a low-boiling azeotrope at 88C (so IBA and water don't like each oher) and forms a high-boiling azeotrope with

7

HAC at 123C (so IBA and HAC like each other). The IBA remains in the top in a closed cycle, and only little IBA makeup is needed [7].

The simulation results are summarized in Figure 9. In Figures 10a and 10b we show the liquid composition profiles in the prefractionator (PREFRAC) and main column (MAINCOL) sections, respectively. The temperature profile in the main column is shown in Figure 10d. Note that the number of stages in MAINCOL in Figure 9 is equal to the sum of stages in C21 and C22 in Figure 8b. The amount of IBA needed in the simulations was surprisingly small (only about 3 wt% IBA in the overhead vapor which is far from the azeotrope at 78 wt%). The reason is probably that only a small amount of IBA is needed to "bind" HAC and make it less volatile. To minimize the need for IBA makeup further and make the water product purity comparable with the original design, we added a stripper (C4), similar to that in the original design, but the required amount of steam is quite small and only contributes 0.56 kW.

The total heat input for this Petlyuk arrangement is 28.12 kW, which corresponds to *an energy saving of 19%*, compared to the conventional design. In addition, there will be savings in the capital costs, which are probably more important. The reason for the somewhat low energy savings of 19% is partially because this is a quite easy split (with relative volatilities for W-HAC-X equal to 7.2: 2.8:1 at the feed tray of prefractionator: see Figure 12 which gives the relative volatility on the various stages).
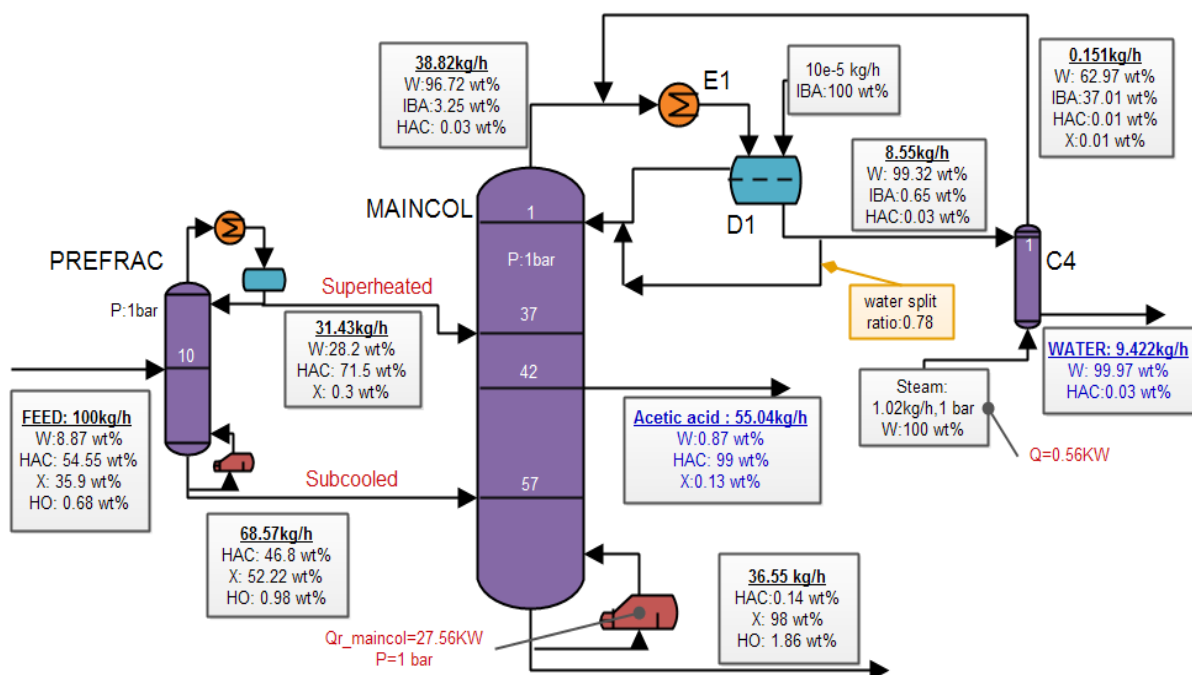

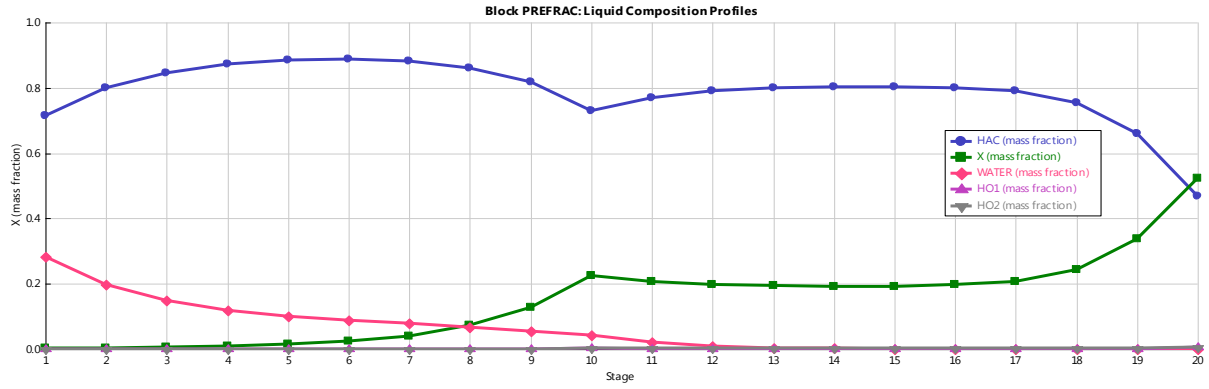*Figure 9:* Simulation of Petlyuk-DWC with IBA as entrainer. *Overall Q=28.12 kW*

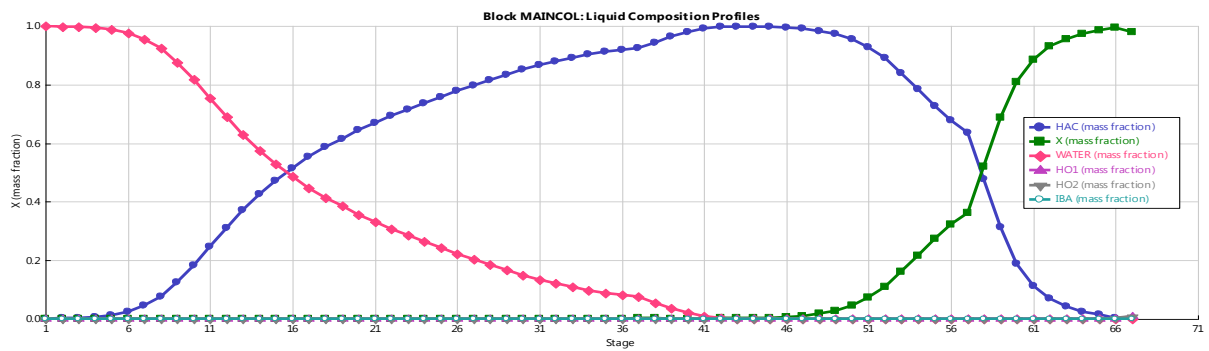*Figure 10a:* Liquid composition profiles of PREFRAC

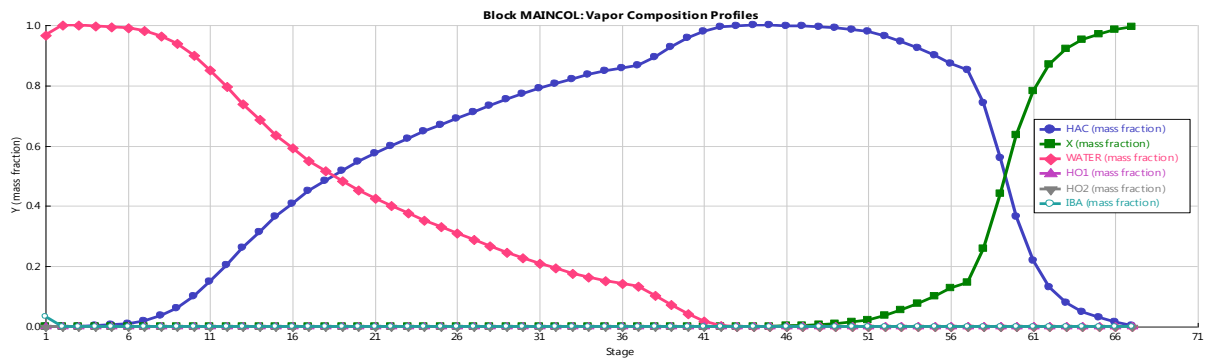*Figure 10b*: Liquid composition profiles of MAINCOL

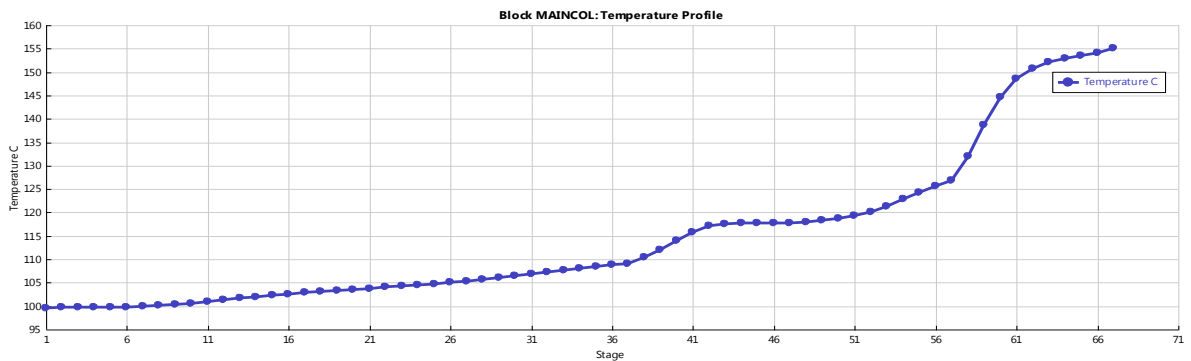*Figure 10c*: Vapor composition profiles of MAINCOL

Figure 10d: Temperature profile of MAINCOL

The concentration of IBA inside the column is very low and in the composition profiles it can be only observed in the vapor composition in the top of MAINCOL (Figure 10c). This implies that the loss of IBA is very small as can been seen from the tiny makeup stream of 10-5 kg/h.

To understand better the behavior of the main column (MAINCOL), we note that it can be divided into two "columns", C21 (top) and C22 (see Figure 8a). Figure 11 shows the phase diagram for water-HAC-IBA with the material balance lines of the upper part (C21). Moreover, this mixture of water and HAC forms a tangent pinch (Figure 2) and cannot be separated easily using a side stripper hence entrainer adding is necessary.
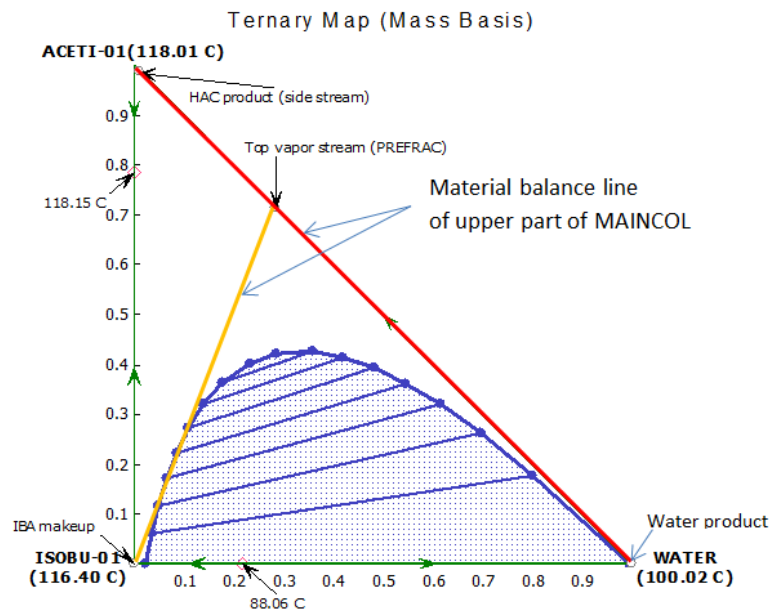

Figure 11: Phase diagram for Water-HAC-IBA
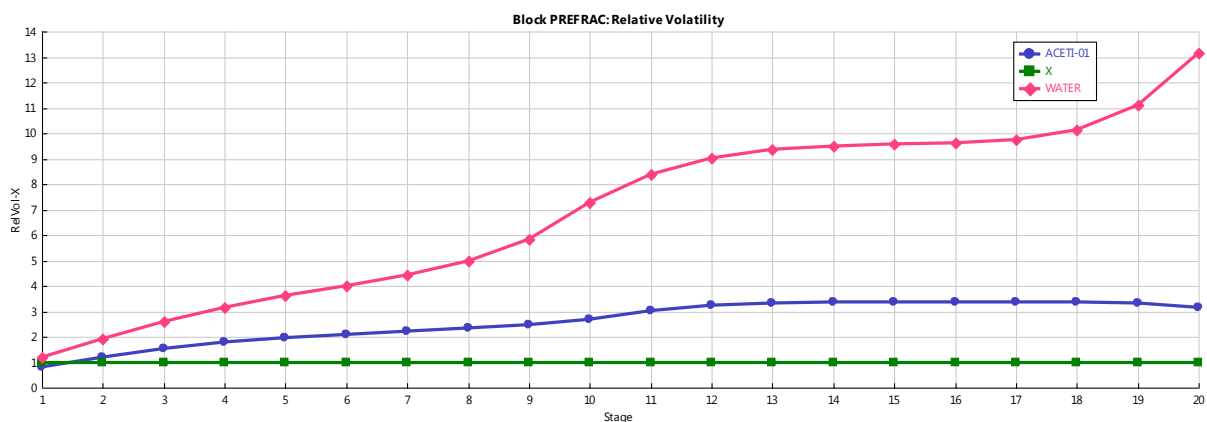
(upper part of MAINCOL)

Figure 12: Relative volatility profiles of PREFRAC

5. Conclusions

This work shows applies dividing wall columns (DWC) to ternary heterogeneous azeotropic distillation. For the feed mixture of water (W), acetic acid (HAC) and an organic component (X), the original design makes use of X to act as an entrainer to facilitate the separation of water and HAC (Figure 3). We propose a DWC design based on this idea (Figure 6). This DWC design reduces the capital cost, but the energy usage is almost unchanged. To achieve energy savings and further reductions in capital costs, we need to use a Petlyuk DWC (Figures 8a and 9). However, because component X is heavier than W and HAC, X cannot be used as the entrainer for this design. Thus, we introduce isobutyl acetate (IBA) as an

additional entrainer and achieve energy savings of about 20%. A challenge for discovering and designing new integrated schemes is to develop systematic methods to supplement the present *ad-hoc* engineering approach.

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