Dividing wall columns for heterogeneous azeotropic distillation

Quang-Khoa Le1, Ivar J. Halvorsen2, Oleg Pajalic3, Sigurd Skogestad1\*

1Norwegian University of Science and Technology (NTNU), Trondheim, Norway;

 2SINTEF, Trondheim, Norway; 3Perstorp AB, Perstorp, Sweden. \*skoge@ntnu.no

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 is 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].



1. *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].

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 azetrope”) at the pure water end, where the liquid and vapor compositions are similar, 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.

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 2). We then consider two different DWC arrangements for integrating the two distillation columns (C14 and C108 in Figure 2). 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 2 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 4), 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 2*: *Original design with two distillation columns (C14, C108), decanter (D1) and stripper (C17). Overall Q=34.85 kW*

*Figure 3: Liquid composition profiles for column C14 (stage 1=condenser)*



The bottom product of C14 also contains almost no X 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 3 shows the liquid composition profiles in the first column (C14). Above the feed stage (stage 25), HAC dies out rapidily while water and X approach their azeotropic composition. 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.

*Figure 4: Phase diagram for Water-HAC-X*

 **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 5.

Some observations can be made from the simulation results which are summarized in Figure 5. First, we cannot avoid a slippage of HAC into the bottom stream of C1 (2.89 wt% versus 0.14% in the conventional design in Fig. 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.



**

*Figure 5: Side rectifier configuration (equivalent to DWC configuration in Fig. 1b with wall in upper part of column). Overall Q=33.85 kW*

*Figure 6*: Liquid composition profiles of the main column C1 in figure 4

The liquid composition profiles in the main column C1 (Figure 6) are quite similar to those of C14 (Figure 3). Note that the HAC composition achieves its maximum between stages 57 and 58, which is where the vapor sidedraw HAC is taken out and sent to the stripper column C2.

4.DWC Petlyuk arrangement

**4.1 Simulation**

Next, consider the three column section arrangement in Figure 7a which is thermodynamically equivalent to the Petlyuk DWC in Figure 1a. As we see from Figure 7a, 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 7b with no recycles between the columns. The heat removed in the condenser in C1 in Figure 7b, 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 7b is equivalent to the configuration in Figure 7a 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].

 *(a) (b)*

*Figure 7:* *Petlyuk arrangement (a) and simulation representation (b)*

<0: superheated

>1: subcooled

**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 2) 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 we found out when simulating the original design in Figure 2. 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 4) 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 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 8. In Figures 9 and 10 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 11. Note that the number of stages in MAINCOL in Figure 8 is equal to the sum of stages in C21 and C22 in Figure 7b. 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 8:* *Simulation of Petlyuk-DWC with IBA as entrainer. Overall Q=28.12 kW*



*Figure 9:* Liquid composition profiles of PREFRAC



*Figure 10*: Liquid composition profiles of MAINCOL



*Figure 11*: Temperature profile 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 2). We propose a DWC design based on this idea (Figure 5). 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 7a and 8). 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.

 References

*[1] M. Benedict and D.R. Rubin, Extractive and Azeotropic Distillation. I. Theoretical Aspects, Trans. Am. Inst. Chem. Eng., 41 (1945), 353-370*

*[2] S. Widagdo and W.D. Seider, Azeotropic distillation, AICE J., 42 (1996), 96-130.*

*[3] G.Parkinson, Dividing-wall columns find greater appeal, Chem. Eng. Prog., 103, 5 (May 2007), 8-11*

*[4] H.H. Pham and M.F. Doherty, Design and synthesis of heterogonous azeotropic distillations - III. Column sequences, Chem. Eng. Science, 45 (1990), 1845-1854*

*[5] R.O.Wright, Fractionation apparatus, US Patent No. 2471134 (1949)*

*[6] I.J. Halvorsen, “Minimum Energy requirements in complex distillation arrangements”, PhD thesis, Dept. of Chemical Engineering, NTNU 2001:43 (available from the home page of S. Skogestad).*

*[7] W.L. Luyben and I-L. Chien, “Design and Control of Distillation Systems for Separating Azeotropes “, John Willey & Sons Inc, 2010.*

*[8] Scott P.Christensen, James D.Olson, “Phase equilibria and multiple Azeotropy of the Acetic Acid-isobutyl Acetate system”, Fluid Phase Equilibre, 79 (1992) 187-199, Union Carbide Chemical and plastics Company Inc.
[9] M.A Gaubert, V. Gerbaud, X. Joulia, P.S. Peyrigain, M. Pons, “Analysis and multiple stedy states of an industrial heterogeneous azeotropic distillation“, Ind. Eng. Chem. Res. 2001, 40 (13), pp 2914-2924*