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REACTIVE DIVIDING-WALL COLUMNS: TOWARDS ENHANCED PROCESS INTEGRATION

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Abstract
This work presents an integrated reactive-distillation design based on a dividing-wall column (DWC) applied to an industrial case study within AkzoNobel. Remarkably, it is among the first industrial application of a reactive DWC reported in literature. The benefits of this novel integrated design are the ability to overcome VLE and chemical equilibrium limitations, as well as to separate the main product as high purity side-stream. To solve the problem of a production shift required by market demand changes, we developed an innovative integrated design that combines reaction and separations into one reactive DWC that allows significant savings in capital and operating costs – up to 36% and 15%, respectively. Two scenarios are analyzed and the results of the rigorous simulations are presented.

Keywords: reactive distillation, dividing-wall column, equilibrium restrictions

1. Introduction

One of the most important separation technologies in the chemical processing industry is distillation. Essentially, all of the chemicals produced go through at least one distillation column on their way from crude oil to final product. Even in an economy based on renewable sources of energy such as biomass, the fuel of choice will be bio(m)ethanol or biodiesel – all of these processes requiring separation by distillation. Considering its many well-known advantages, distillation is and it will remain the separation method of choice in the chemical industry – with ten of thousands columns in operation around the world. However, one important drawback is its considerable energy requirements, as distillation can generate more than 50% of plant operating cost. An innovative solution to diminish this energy consumption drawback is using advanced process integration and intensification.[1]

Process integration and intensification aims at significant capital and energy savings, as well as environmental benefits, by integrating different phenomena or operations, as for example: reactive separations, dividing-wall columns, heat integrated reactors or columns. Several successful examples of integrated processes can be found among reactive-separations that combine reaction and separation steps in a single unit, such as reactive distillation, reactive absorption and reactive extraction. For example, reactive distillation has significant economic advantages over conventional reactor-separator-recycle systems,[2] particularly for reversible reactions in which conversion is limited by chemical equilibrium constraints and/or separation is restricted by VLE limitations. However, due to the integration of reaction and separation into a single vessel, reactive distillation is limited to systems in which the reaction and separation conditions are similar – mainly in terms of pressure and temperature. Nevertheless, compared to conventional reactor-distillation sequences, the integrated reactive-distillation design brings several advantages such as:

- increased conversion due to overcoming equilibrium limitations,
- increased selectivity via suppression of secondary reactions,
- reduced energy requirements due to in-situ heat integration,
- avoidance of hot spots by liquid evaporation,
- breaking of azeotropes by chemical reaction and ability to separate close boiling components.

Beside reactive separations, there is also the option to integrate two different separation units together. Conventionally, a ternary mixture can be separated via a direct sequence (lightest first), indirect sequence (heaviest first) or distributed sequence (mid-split) consisting of 2-3 distillation columns. This separation sequence progressed to the Petlyuk column configuration[3] consisting of two fully thermally coupled distillation columns. Eventually, this led to the concept of dividing-wall column (DWC) that integrates in fact the two columns of a Petlyuk system (Figure 1) into one shell.[4,5]

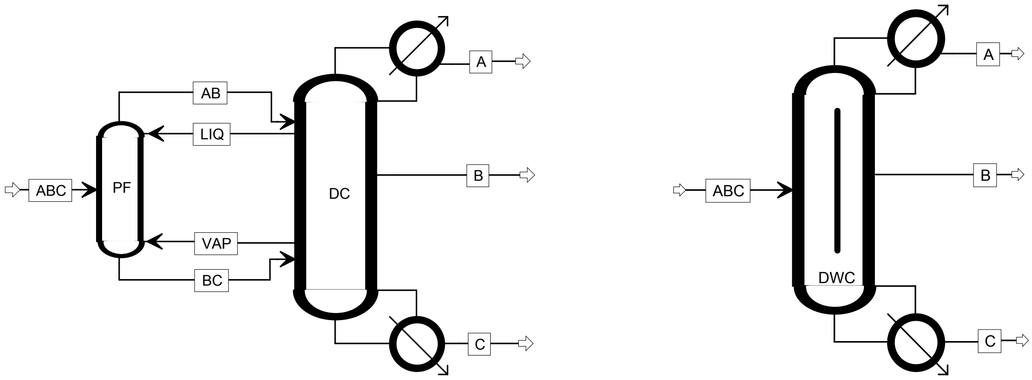

Figure 1. Petlyuk column with prefractionator vs dividing-wall column (DWC).

DWC is very appealing to the chemical industry as it can separate three or more components in a single distillation tower, thereby eliminating the need for a second unit, hence saving the cost of building two columns and cutting operating costs by using a single condenser and reboiler. In fact, using dividing-wall columns can save up to 30% in the capital invested and up to 40% in the energy costs.[2,5-7] Compared to conventional distillation arrangements, DWC offers the following benefits:

- High purity for all three product streams reached in only one column.
- High thermodynamic efficiency due to reduced remixing effects.
- Lower energy consumption compared to conventional (in-)direct separation sequences.
- Small footprint due to reduced number of equipment units.
- Lower capital investment due to the integrated design.

DWC and reactive distillation are both improvements of traditional distillation units but at the same time they correspond to two different ways of integration: separation-separation and reaction-separation, respectively.[8] The incentives of these integrated units could be further enhanced if they are combined via an additional integration step. The resulting unit called reactive dividing-wall column (RDWC) has a highly integrated configuration that consists of one condenser, one reboiler, reactive zones, a pre-fractionator and the main column together in a single-shell distillation setup.

2. Problem statement

The problem and solutions described here relate to a novel integrated design project applicable to one of AkzoNobel plants. The current industrial process involves a relatively complex, fast chemical equilibrium of 10 species – denoted below by letters *A–J*, and sorted in descending order of volatility, with *A* being the most volatile and *J* the heaviest component. Due to the homogeneous catalyst, the reactions may take place everywhere in the system. Therefore, the reactions were modeled as a system of fast equilibrium reactions:

1. $A + J \leftrightarrow C + H$ (main reaction)
2. $B + H \leftrightarrow C + E$ (secondary reaction)
3. $D + H \leftrightarrow C + I$ (secondary reaction)
4. $B + E \leftrightarrow A + F$ (secondary reaction)
5. $F + J \leftrightarrow 2\,G$ (secondary reaction)

Conventionally, the reactor outlet mixture (F1: *ABCDEHI*) is separated in a series of distillation columns. Most of the streams are recycled back to the reactor while component *H* is purified (min. 98.5%) and afterwards put on the market as the main product. However, due to changes in the market demand, the by-product *C* became more economically attractive than the main product *H*. The problem with the existing plant is that no increase of the by-product production rate is possible – at the cost of the main product – although market changes strongly demand it. Moreover, the obvious option of adding another reactor and two distillation columns for this production change was discarded due to the unavailable floor area and the high investment costs involved. To solve this problem we investigated a base case design alternative, namely a two-column configuration that uses a reactive distillation column (RDC), followed by a conventional distillation column (DC). The operating parameters, such as temperature and pressure, are fortunately similar in these two individual columns.

Therefore the design can be further integrated into a reactive DWC setup that combines the two columns of the base case into only one distillation vessel.

3. Results and discussion

The conceptual design of the (reactive) distillation columns was performed using graphical stage composition lines and stage-to-stage methods for RD column design. Note that three binary homogeneous azeotropes are present in the system (C-E, D-E, C-I), as illustrated by the residue curve maps (Figure 2). This drawback can be surmounted in an integrated reactive distillation setup, as these homogeneous azeotropes can be broken by the chemical reactions described previously.

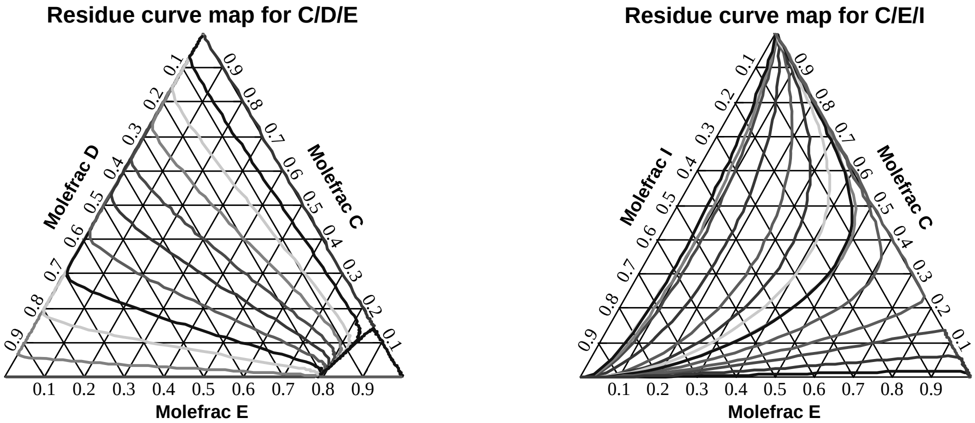

Figure 2. Residue curve map of the ternary systems C-D-E and C-E-I.

The base case design consisting of a reactive distillation column (RDC) and a conventional distillation column (DC) was rigorously simulated in Aspen Plus – flowsheet shown in Figure 3. This sequence has two column shells, two reboilers, two condensers, one extra pump, and it requires a great deal of piping and floor area that are not available in the existing plant. However, the advantage of this setup is its flexibility, as the columns can operate at different pressures – operation that is not possible in an integrated column such as reactive DWC.

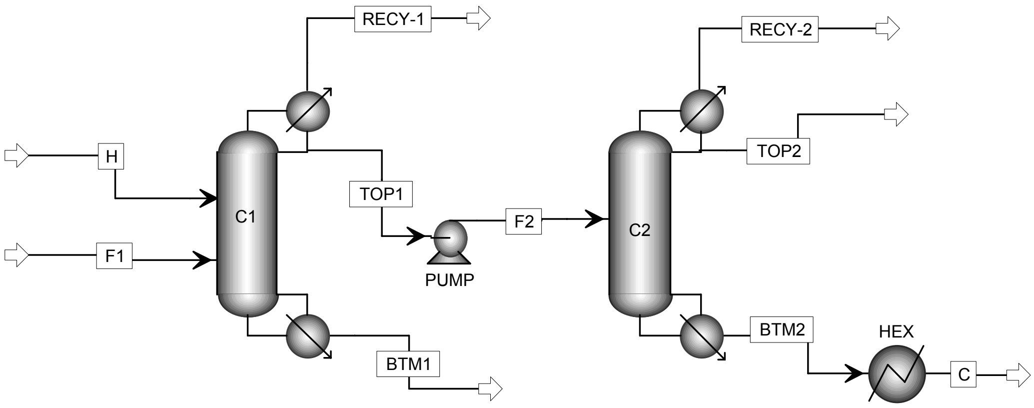

Figure 3. Aspen Plus flowsheet of the two-columns distillation sequence.

The composition and temperature profiles in the RDC (C1) and DC (C2) columns are shown in Figure 4. The top product of the first column is a mixture of the most volatile components *A*, *B*, and *C*. The second column separates *A* and *B* in the top, while component *C* is delivered as a bottom product. The temperature profiles in these columns show small differences, suggesting reactive DWC as a rational choice. Note that the dimensionless temperature used in the following figures, is calculated by dividing the temperature on a specific stage to the maximum temperature of all columns (T_{stage} / T_{max}), namely the reboiler temperature of the reactive DWC – the alternative describe thereafter.

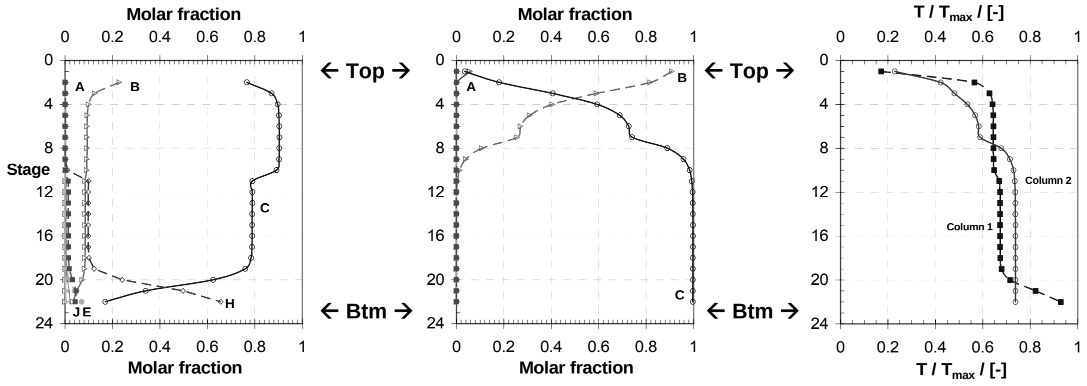

Figure 4. Composition and temperature profiles in the two columns (base case).

In addition to the base case configuration, we considered the more integrated design that combines reaction and separation into one reactive DWC (Figure 5). The key factor that allows such an integration of two columns into one unit is the similar pressure and temperature conditions in the standalone columns. Basically, the reactive DWC setup consists of only one column shell, one reboiler and one condenser and requires significant less piping and floor space compared to the base case design. However, the column diameter is somewhat larger compared to the diameter of the columns presented in the base case. Note that modeling reactive distillation and DWC is nowadays possible using state-of-the-art rate-based models (Mueller and Kenig, 2007). However, due to the absence of a reactive DWC unit in Aspen Plus, this integrated unit was simulated using two coupled rigorous RADFRAC (reactive-) distillation units – the thermodynamic equivalent of reactive DWC (Figure 5).

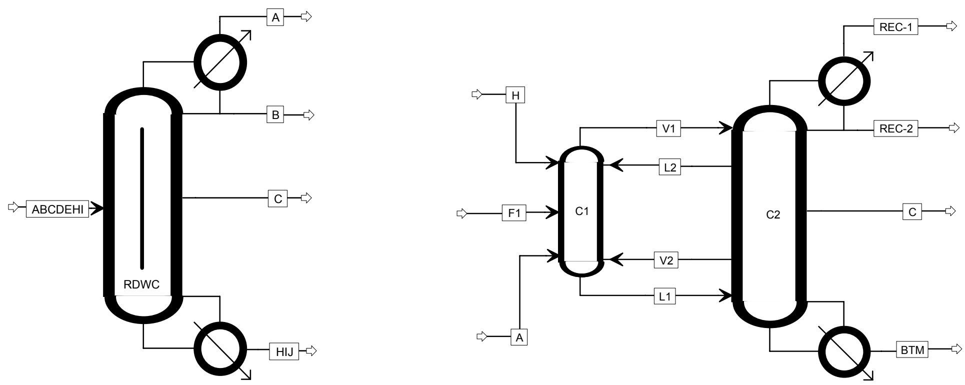

Figure 5. Proposed RDWC alternative (left). AspenPlus flowsheet of DWC (right).

Chemical reactions take place only on the feed side and bottom sections of the column, where the light components are separated from the heavy ones. A small amount of component H is added on top of the feed location, in order to break the azeotropes and to push the mid-boiling and heavy components (*D*-*J*) to the bottom of the column. Moreover, the formation of heavy components *F* and *G* (waste by-products) is avoided by adding an extra feed stream of light component *A* into the bottom of the column. *A* consumes the heavier component *F* and avoids the parallel conversion of *F* into *G*, according to the reactions: $A + F \leftrightarrow B + E$, and $F + J \leftrightarrow 2\ G$.

The reactive DWC column has 22 stages in total, with the feed located on stage 8, and liquid side-draw from stage 12. The location of the feed stage and side-draw has a crucial effect on the side-product purity. Out of all column stages, 3 of them are located above and bellow the dividing-wall, for the common rectifying and stripping sections, respectively. The liquid composition and the temperature profiles in the reactive DWC are shown in Figure 6.

The feed side of the RDWC resembles the RDC of the base case. However, the product side of RDWC performs only the separation of product *C* from *B*, since no chemical reactions take place here – as components *A*, *B*, *C* do not react with each other, according to reactions equations 1-5. Main product *C* is collected as high purity side stream from the product-side of the column, as illustrated by the composition profiles. Note that compared to the base case, the height of the reactive DWC remains the same as of the RDC but the diameter is slightly larger. The temperature differences between the feed- and product-side of the RDWC are reasonable small, the maximum difference being less than 25°C hence it can be easily achieved in practice.

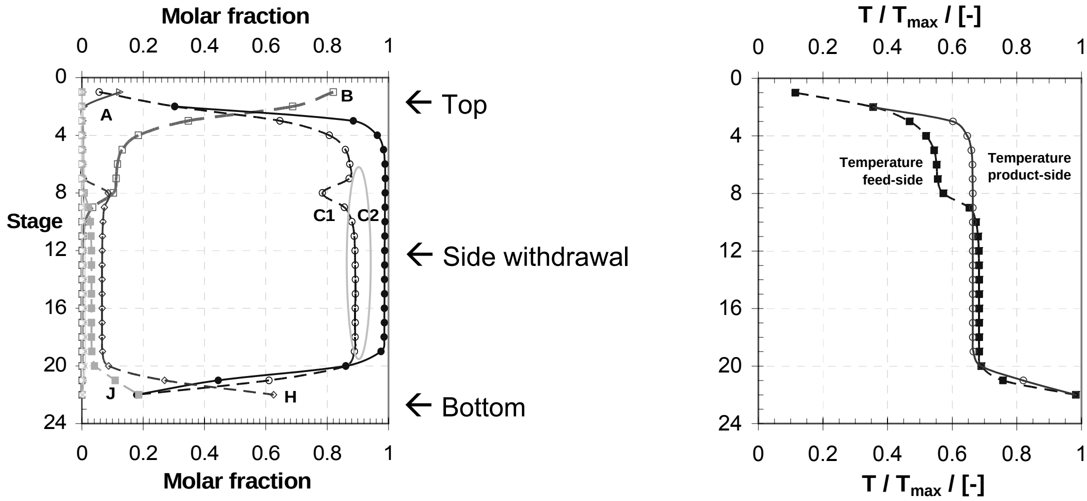

Figure 6. Composition and temperature profiles in the RDWC (C1/C2 – feed/product side).

Figure 7 shows the results of the sensitivity analysis for the side product purity versus column feed stage and side-draw stage, respectively. Remarkably, the product has a high purity on a large range of stages, thus the column is very robust and able to cope well with disturbances in feed flow rate and feed composition. This inherent robustness is the major practical reason to have a relatively large number of stages also on the product removal side of the column – similar to the feed side of the RDWC. Moreover, having some 'useless' stages is an asset during hydraulic design, because it allows dosing the amount of pressure drop required to achieve the required design vapor split.

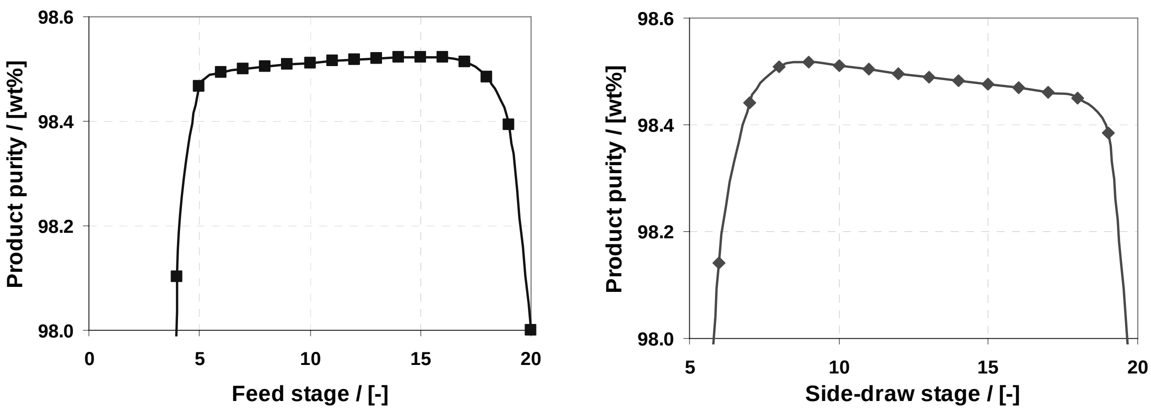

Figure 7. Composition and temperature profiles in RDWC (C1/C2 – feed/product side).

The economics of the reactive DWC alternative was then compared against the base case design. Rigorous calculations of the equipment costs and total investment were performed using AspenTech ICARUS process evaluator (Aspen Technology, 2009). Since the reactive DWC makes use of two columns in one shell (DWC) and only one reboiler and one condenser, the investment costs are significantly lower compared to the base case. Note that the equipment cost includes: equipment and setting, piping, civil and electrical, structural steel, instrumentation, insulation, paint and manpower. For the reactive DWC case the total investment cost is 36% less compared to the base case, due to the need for only one column, condenser and reboiler (Table 1). In addition, about 15% less energy is required mainly because the mid-boiling product *C* is evaporated only once, as no remixing effect is present in the reactive DWC.

Table 1. Equipment and operating cost for the base-case (RD+DC) vs RDWC.

Equipment / Description	Units	Base case	RDWC
Column shell(s)	kEuro	423	**264**
Condenser(s) + Reboiler(s)	kEuro	352	**227**
Total installed equipment cost	kEuro	775	**491**
Steam and electricity	kEuro/year	103	**88**
Cooling water	kEuro/year	4	**3**
Total operating costs	kEuro/year	107	**91**

4. Conclusions

The innovative reactive DWC design proposed in this work is able to overcome the chemical equilibrium limitations by removing the products from the reaction zone – consequently pulling the equilibrium towards products formation – as well as surmount vapor-liquid equilibria (VLE) restrictions by consuming specific components, thus breaking the homogeneous azeotropes present in the system. Moreover, although the main product is not the lightest nor the heaviest component in the system – hence not recoverable as top distillate or bottom product – the reactive DWC can still separate it as high purity side-stream.

The industrial case-study described here proves that the reactive DWC concept is sufficiently developed to become an efficient distillation unit in the chemical industry world-wide. Basically, the reactive DWC unit integrates a reactive distillation (RD) tower with another conventional distillation column (DC). The key factor that allows such integration of reaction + separation + separation is the similar pressure and temperature profiles in the two standalone distillation columns of the base case design (RD+DC).

The reactive DWC setup offers similar or better performance compared to the base case design. Moreover, due to the robust design, the column copes very well with disturbances in both feed flow rate and composition. Compared to the base case design using two standalone distillation columns, the reactive DWC alternative developed for this industrial application allows up to 36% savings in capital costs and 15% savings in energy costs, respectively.

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