

## Overcoming Equilibrium Limitations in Reactive Dividing-Wall Columns

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### Abstract

This work presents an industrial case study within Akzo Nobel Chemicals. Due to the market demand changes, one of the by-products became more expensive, hence more attractive than the main product. However, the current plant design does not allow an increase of the by-product production rate at the cost of the main product. To solve this problem we propose an integrated design that combines reaction and separation into one reactive divided-wall column (RDWC) that allows 35% savings in capital and 15% savings in energy costs.

**Keywords:** reactive distillation, dividing-wall column, equilibrium reactions.

### 1. Introduction

Due to its many advantages, distillation is still the major separation process used in the chemical processing industry. However, one important drawback is its considerable energy requirements – distillation can generate more than 50% of plant operating cost. Process intensification aims at significant capital and energy savings, as well as environmental benefits, by integrating different phenomena or operations (e.g. 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 (e.g. reactive distillation). Note that such an integration requires a match of the reaction and separation conditions.

Compared to traditional 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 consumption via in-situ heat integration,
- ✓ avoidance of hot spots,
- ✓ ability to separate close boiling components.

Along with reactive separations, there is also the possibility to integrate different separation units together. The direct or indirect sequence of two distillation columns evolved via the Petlyuk column to the concept of dividing-wall column (DWC). This is a very attractive design alternative as it saves the cost of building two columns and cuts operating costs by using a single condenser and reboiler. Compared to the conventional distillation design arrangements, the DWC offers the following advantages:

- ✓ reduced number of equipment units,
- ✓ lower energy consumption compared to (in-)direct separation sequences,
- ✓ high thermodynamic efficiency due to reduced remixing effects,
- ✓ high purity for all three product streams reached in only one column.

In fact, using DWC can save up to 30% in capital invested and energy costs.<sup>2</sup> Note however that using DWC requires a match between the operating conditions of the two stand-alone columns. Due to its design limitations, the main weakness of DWC is its inflexibility to changes in the nature of the feed.

Both reactive distillation and dividing-wall columns are developments of a conventional distillation column. However, at the same time they are two different ways of integration. The advantages of both 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, the reactive zones, the prefractionator and the main column together in a single-shell column. RDWC offers an alternative to conventional reactive distillation towers or multicolumn arrangements, with potential significant cost savings.

## 2. Problem Statement

One of the processes within Akzo Nobel Chemicals involves a relatively complex, fast equilibrium of 10 species (denoted below by letters  $A - J$ , and sorted in descending order of volatility,  $A$  being the most volatile component).

The equilibrium reactions are as follows:

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

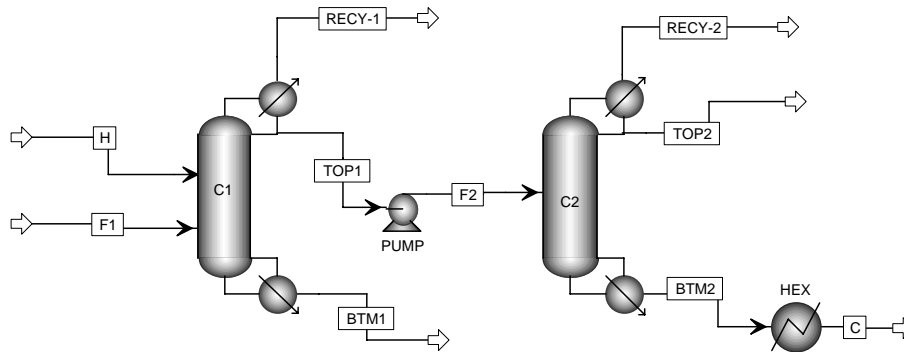


Figure 1. Aspen Plus flowsheet of the two-columns distillation sequence.

The main reaction is catalyzed by a homogeneous catalyst. The reactor outlet mixture (F1: *ABCDEHI*) is separated in a series of distillation columns. Most of the streams are recycled to reactor while component *H* is purified (min. 98.5%) and sold as the main product. However, due to the market demand changes, the by-product *C* became more expensive than the main product *H*. Therefore, the production focus has to change from the main product *H* to component *C*.

The problem is that the current plant design is not suitable for producing more by-product *C*, at the cost of main product *H*. Moreover, the option of adding another reactor and two distillation columns for this production switch, was discarded due to the unavailable floor area and the high investment costs involved. To solve this problem we investigated the obvious design alternative, namely a two-column design that uses a reactive distillation column (RDC), followed by a conventional distillation column (DC). The operating parameters, such as temperature and pressure, are similar in these two columns. Therefore we further integrated the design to a reactive dividing-wall column (RDWC).

### 3. Results and discussion

The flowsheet of the base case design (RDC+DC) is shown in Figure 1. This sequence has two columns, two reboilers and two condensers, and it requires a lot of piping and floor area – not available in the existing plant. The advantage of this setup is the flexibility, as the columns can operate at different pressures. Figure 2 shows the composition and temperature profiles in these columns. The top product of the first column is a mixture of most volatile components *A*, *B*, and *C*. The second column separates *A + B* in the top, and *C* as bottom product. The temperature profile in these columns show small differences, suggesting RDWC as logical choice. Note that the dimensionless temperature is calculated by dividing the temperature on a specific stage to the maximum temperature of all columns ( $T_{\text{stage}} / T_{\text{max}}$ ), namely the reboiler temperature of RDWC.

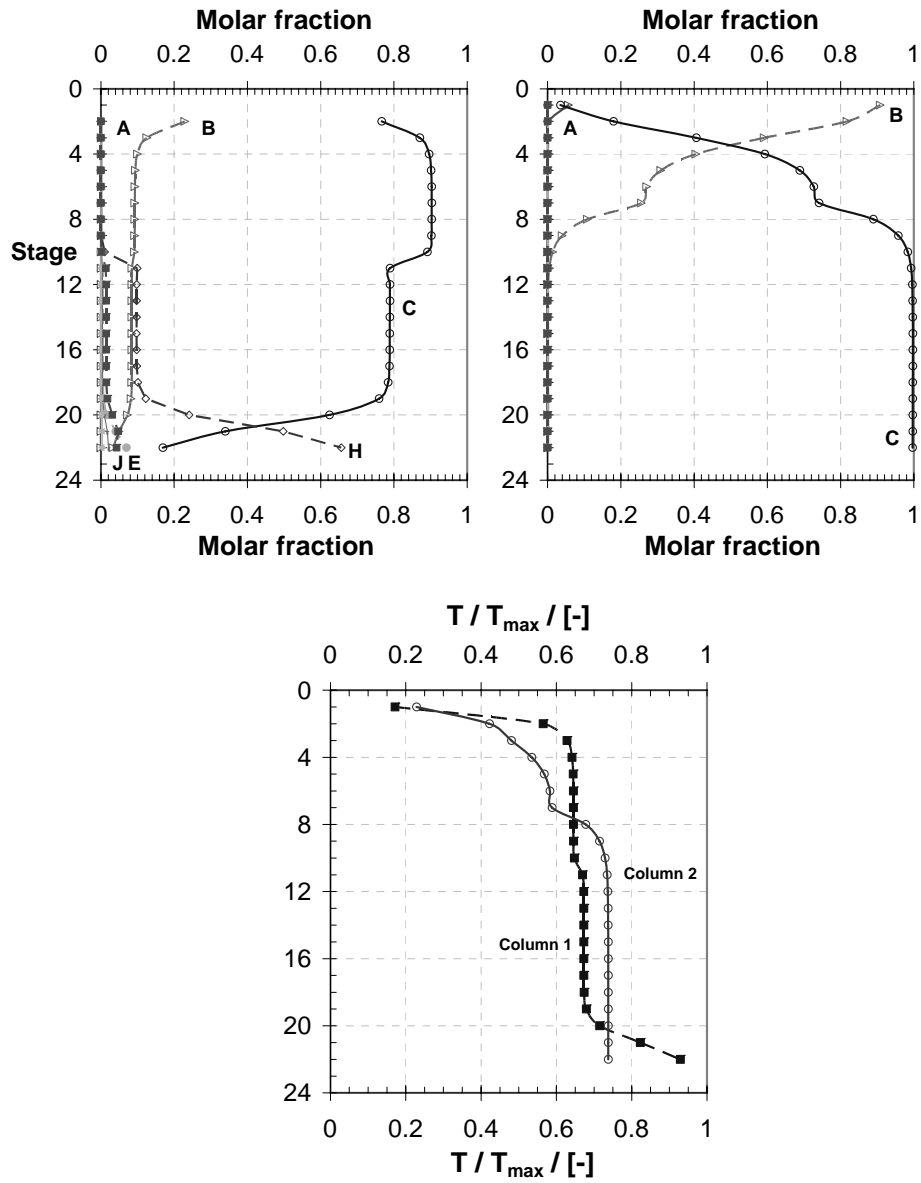


Figure 2. Composition and temperature profiles in the two columns (base case).

In addition to the base case, we considered the more integrated design that combines reaction and separation into one RDWC (Figure 3). Due to the absence of a DWC unit in AspenONE Aspen Plus, this was simulated using two rigorous RADFRAC distillation units – the thermodynamic equivalent of DWC.

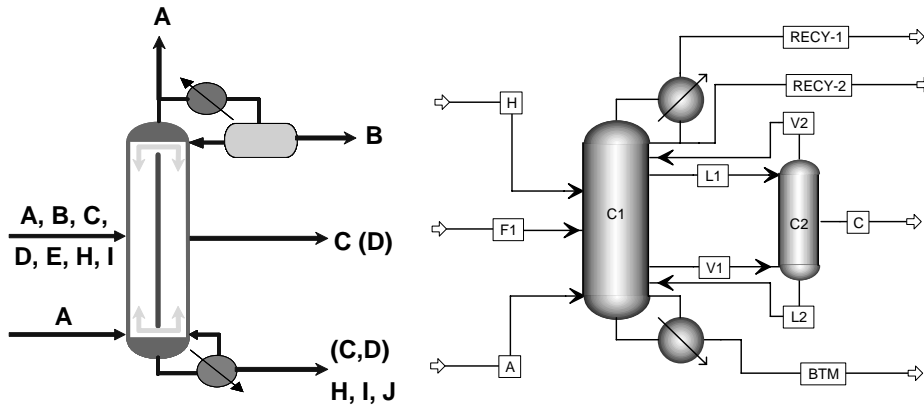
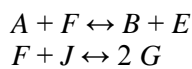


Figure 3. Reactive dividing-wall column alternative and Aspen Plus flowsheet.

The DWC setup consists of only one shell, one reboiler and one condenser and requires less piping and floor space compared to the base case. However, the column diameter is relatively larger compared to the diameter of the columns presented in the base case. For the RDWC case the total investment is 35% less compared to the base case, due to the need for only one condenser and reboiler. In addition, about 15% less energy is required since the mid-boiling product *C* is evaporated only once. The key factor that allows such an integration is the similar pressure and temperature conditions in the standalone columns.

Figure 4 shows the liquid composition and the temperature profiles in the RDWC. Chemical reactions take place only on the feed side of the column, where the light components are separated from the heavy ones. The formation of heavy components *F* and *G* (waste by-products) is avoided by adding an extra feed stream of light component *A* in the bottom of the column. Reactant *A* consumes the heavier component *F* and avoids the parallel conversion of *F* into by-product *G*, according to the following reactions:



The product side of the column performs only the separation of product *C* from *B*, no reactions taking place here. Main product *C* is collected as high purity side stream from the product-side of the column. Note that component *C* has a high purity on a large range of stages (Figure 4, left), thus the column is very robust and able to cope with disturbances in feed flow rate and composition.

The temperature differences between the feed- and product-side of the RDWC are reasonable small (the maximum difference being less than 25°C) and can be relatively easily achieved in practice. Note that the height of the RDWC remains the same but the diameter slightly larger compared to the base case.

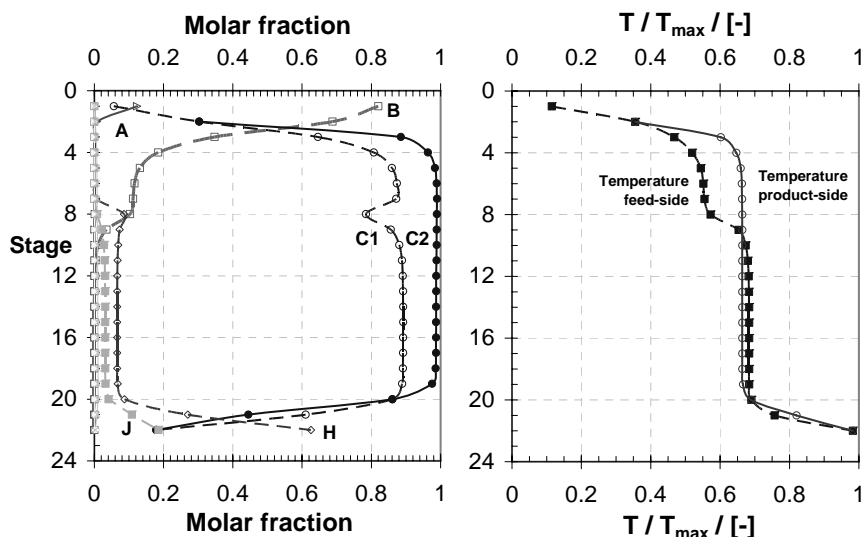


Figure 4. Composition and temperature profiles in RDWC (C1/C2 – feed/product side)

#### 4. Conclusions

This study shows that equilibrium limitations can be overcome and high purity components can be obtained by integrating reaction and separation into a reactive dividing-wall column. The key factor that allows this integration is the similar pressure and temperature conditions in the two standalone columns. The column copes well with disturbances in both feed flow rate and composition. Practically the RDWC unit integrates a reactive distillation column with a conventional distillation tower. Compared to the base case using two distillation columns, the RDWC design presented in this industrial case-study allows 35% savings in capital costs and 15% savings in energy costs, respectively.

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