

# Journal of Engineering Research

## AN INTRODUCTION TO DIVIDING WALL COLUMNS DESIGN AND MODELLING (DWC)

---

*Alex Vazzoler*

Technology Center of Chemical and Textile  
Industry (Senai Cetiqt)

Rio de Janeiro, RJ

<https://orcid.org/0000-0001-8603-1307>

<http://lattes.cnpq.br/9540544293913068>

All content in this magazine is licensed under a Creative Commons Attribution License. Attribution-Non-Commercial-Non-Derivatives 4.0 International (CC BY-NC-ND 4.0).



**Abstract:** A Dividing Wall Column (DWC) is a distillation system that replaces two conventional columns separations by only one shell. Three, or more, component mixture are separated in individual components by a vertical wall in a distillation column section, improving components separation quality. Due to the increasing need and challenges for advanced distillation technologies (e.g. reactive distillation, thermal coupling, dividing-wall columns, heat pump assisted distillation, cyclic distillation and heat integrated distillation columns) which can meaningfully reduce the energy usage in modern chemical plants. Nevertheless, these distillation technologies should be analysed, as well conventional distillation operations, in the process context as a whole. Based on the overview provided in this book chapter, several opportunities and challenges for research directions are evidenced towards rethinking the energy use in distillation processes, for a more sustainable chemical industry. Dividing wall columns (DWCs) are a very promising technology allowing a significant energy requirement reduction. Moreover, the application of DWCs for azeotropic, heat pumps, extractive and reactive distillation are briefly pointed in this work. Otherwise, it's reviewed the design and modelling of dividing wall columns (DWCs). It's presented information about conceptual aspects, mathematical modeling and optimization of DWCs, together with successful case studies in pilot and industrial scale chemical plants. DWC four components separation is a challenge, but some results found in laboratory and pilot scale are encouraging.

**Keywords:** Dividing-wall column, distillation, petlyuk, thermal coupling.

## INTRODUCTION

Process intensification represents a revolutionary trend in the process engineering,

usually due to increasing awareness of the society of limited resources. Further, the last achievements in process modelling as well as growing computational resources and advanced numerical methods make process intensification feasible.

For multicomponent mixtures separation, conventionally a sequence of distillation columns is required. In the case of conventional three components separation, two columns are necessary. For instance, the direct and indirect sequence shown in Fig. 1a and Fig 1b, and an energetically favourable alternative configuration is shown in Fig. 1c. The third one, as known Petlyuk configuration, the liquid and vapour streams leaving the first column are fed to the second column (Petlyuk et al. 1965). An accurate split is carried out by the first distillation column between lighter (A) and heavier (C) components, whereas the middle boiling component (B) is distributed proportionally among the bottom and top streams. A additional high-purity components separation is performed in the second column. The energy savings by reason of avoiding inopportune streams mixing with the partition wall are about 30% (Schultz et al. 1965) compared to indirect or direct column sequences. Moreover, the capital costs are shortened because only one condenser and one reboiler are used in this arrangement (Yildirim et al. 2011).

Additional mass and energy integration and operational costs cutbacks can be achieved, through two columns combination into a single shell. This alternative configuration to the conventional two sequence columns is designated as a dividing wall column (DWC) and represented in Fig. 2 (Kaibel 1987).

The large number of design parameters represented a barrier, for many years, for DWCs simulation, design and construction. The first industrial application of DWCs was accomplished in 1985 by BASF SE (Parkinson

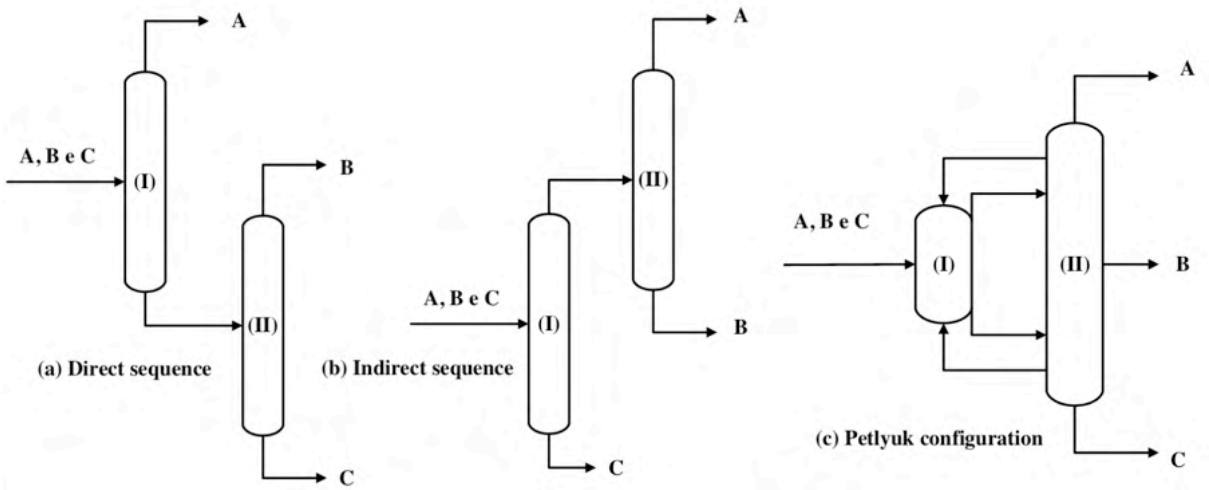


Figure 1. Representation of distillation column sequences.

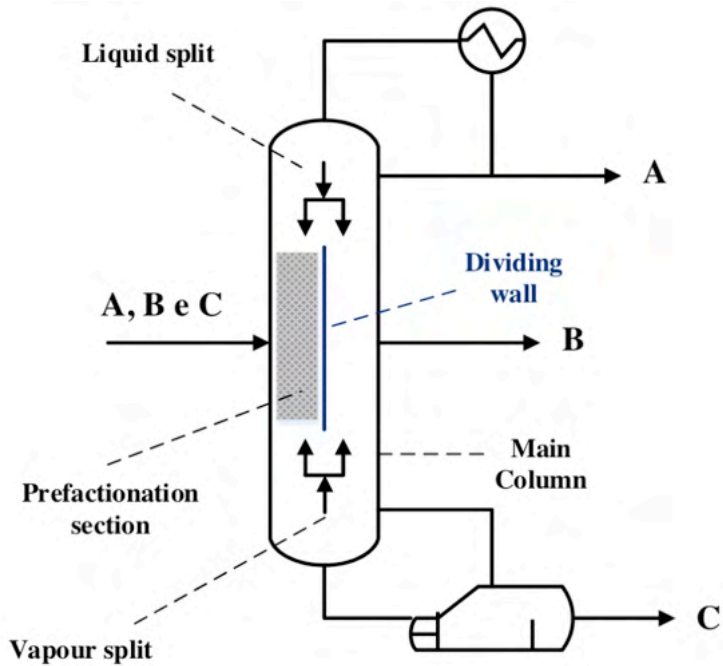


Figure 2. Dividing Wall column representation.

2007; Zang et al. 2020). Currently, thereabout 50 DWCs in operation at BASF. Around 10 other companies have been also installing and running dividing wall columns. Even if there has been some initial disinclination toward to this technology whose layout, construction, and control is more sophisticated than conventional. The DWCs substantial practical advantages are gradually becoming this technology more usual. Despite the current resilience, it is evident which DWCs going to be incorporated in several ternary and multicomponent separation systems, becoming a standard technology. Since then the number of application of DWCs has increased rapidly to more than 180 in 2021 (Harmsen 2010; Segovia-Hernández et al. 2021).

Dejanović et al. 2010, and posteriorly Battisti et al. 2020, gives a comprehensive overview of DWCs, covering both the theoretical description and the patent area.

Xie et al. 2018 carried out the ethanol esterification with acetic acid and ethanol to produce ethyl acetate using a scale laboratory reactive DWC. The model and simulation reliability was analyzed by liquid split ratio and reflux ratio variation. The results showed which reactive DWC configuration can be used both for butyl acetate and ethyl acetate co-production.

Segovia-Hernández et al. 2021 pointed some contributions made in simulation and experimental research, whose results lead to the first one experimental DWC implementation reported in Latin America. Their review lists Professor Jimenez's contributions involving DWCs studies, as well as it presents their national and international impacts, especially in DWCs development area. The next section will present some applications DWCs in chemical and related industries.

## APPLICATIONS IN CHEMICAL AND PROCESS INDUSTRIES

There are some convincing reasons for the gradual industrial increasing acceptance (Simon et al. 2019; López-Ramírez et al. 2020):

Dividing wall columns offer opportunities for substantial energy savings, the extent of which depends on application. Especially concentrations and temperature feed, relative volatilities and the desired products composition. For preliminary energy savings estimation a rule of thumb may be applied.

Verify conventional direct separation sequence energy consumption and compare to energy demands of equivalent DWC. The lowest DWC energy consumption should be considered as the savings when compared conventional separation sequence. Chemical companies report energy and capital savings of 30% on average. This is in line with academical predictions (Simon et al. 2019; Segovia-Hernández et al. 2021).

Two-column shells with total of two reboilers and two condensers can be substituted by only one-column shell with a reboiler and a condenser. The installation costs of a dividing wall are reasonable with an appropriate constructive execution, such as a nonwelded (nonfixed) wall. Even as, a lower construction volume is required (Simon et al. 2019).

Oversizing due to uncertainties in the feed composition are minimized, because DWC are intrinsically more flexible compared to conventional columns. The adjustment to new process conditions can be created by subtle modifications in gas and liquid streams distribution ratio at DWC's lower and upper ends. This improves all column sections use. Conventional column sequences do not perform this feature (Kiss and Olujić 2014). For instance, if the low-boiling concentration byproducts or its purity specifications increases, the overdimensioning has to be

made at the column for its separation. The separation among the medium (B) and the high volatility (C) components is performed in the second column, and there is no interaction with the most volatile component (A) removal in the first column. In counterpoint to a DWC whose all components (A, B and C) are adjusted according to the volatility differences and distribution ratios, and consequently, oversizing is minimized (Yildirim et al. 2011).

Thermal-sensitive components degradation is reduced through shorter residence time use in higher temperatures regions. Evading product passage through a second reboiler can increase product yield (Yildirim et al. 2011).

Dividing wall columns present some disadvantages, the more important are (Lorenza, et al. 2018; Kiss and Smith 2020):

- Higher columns with more theoretical stages;
  - Increasing in pressure drop due to the higher number of theoretical plates;
  - Only one working pressure is available.
- When separating components with high volatility differences, difficulties with the condenser and reboiler temperature values may occur. Two separate shells operating at different pressures, could provide better possibilities for energy integration.

In early applications, DWCs were used in final distillations, where the medium-boiling component was the most valuable product and had to be separated at high-purity specifications from the two others. For this goal, dividing wall columns exhibit their full potential. In some cases, dividing wall columns are used for extremely high purity chemicals production required for semiconductors processing (Diwekar and Agrawal 2021). Further applications involve solvents removal (Ma et al. 2021).

A more recent topic are the extractive

distillations, e.g., Bayer Technology Services' water-free ethanol aromatics separation distillation, and BASF's butadiene separation (Segovia-Hernández et al. 2021). Despite of DWCs operate under vacuum and above atmospheric pressure and pressurized distillations, working with a wide operating pressure range. Furthermore, the products range is broad. It includes hydrocarbons, alcohols, aldehydes, ketones, acetals, amines, and others. In other terms, there are no restrictions with respect to the chemicals sort. Staak and Grützner 2017 presented an industrial case study where it was made a combination of extractive distillation and dividing wall column allowing the separation of narrow-boiling or azeotropic components in one single column tube, using a suitable entrainer.

In the next topic, the main types of dividing wall columns and their respective functionalities will be presented.

## **DIVIDING WALL COLUMNS TYPES**

There are two most common plates dividing wall columns types. The simpler models represent a column which has the dividing wall assembled either at the lower (Figure 3b) or the upper (Figure 3c) end of the column (inferior and superior and partition). This structure represents the first dividing wall column that has been described already in 1935 by Monroe (Monroe 1935), but the first applications on production scale took place only in 2004 (Kaibel et al. 2004).

The most common plates DWC type is shown in Figure 3 (a). The dividing wall is settled in the column middle section, above and below the feed and the side draw. The first description of this configuration was published in 1946 (Patraşcu et al. 2018). The above configurations and others will be described in more detail below.

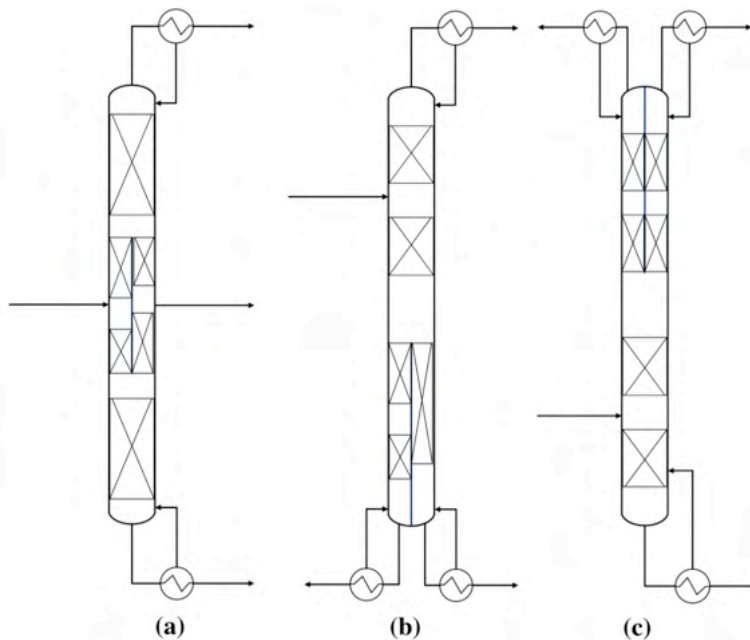


Figure 3. Basic configurations of plates dividing wall columns.

### DIVIDING WALL COLUMNS WITH SUPERIOR AND INFERIOR PARTITION

This DWC configuration is an example of the integration of a side rectifier or a stripper with the main column into one shell. It leads to investment savings, by eliminating purchase costs with a second column shell. In opposition to columns with a middle section dividing whose energy savings cannot be achieved (Long and Lee 2017). Energetically, this arrangement does not generate difficulties as the procedure corresponds to that utilized for the conventional, two-column configuration.

Temperature gradients at DWC both sides can be superior to columns with the dividing wall in the middle section. In cases with elevated temperature differences, 50 or more, the construction mechanical stress should be analysed. In severe situations, the welded dividing wall can be replaced by a joint construction. In situations with high-temperature difference in a region, may acuse to a wall dilation leading to a column inclination. Trays horizontal adjustment or

liquid distributors has to be rated (Long and Lee 2017). Undesired heat transfer across the dividing wall, is a direct consequence of high-temperature differences on both sides of the DWC. Therefore, thermal insulation must cover DWC critical regions. This is critical in packed columns with high-purity demands. In constrast, tray columns are less sensitive to these problems.

### MIDDLE SECTION PARTITION DIVIDING WALL COLUMN

Middle section partition dividing wall column approaches a thermodynamically optimal distillation system. For instance, during a three-component mixture separation, the thermodynamically ideal separation sequence is acquired. In the column feed section are only separated the lowest and highest boiling components. There are no restrictions for the medium boiling component separation. This component flows from the feed section to the outlet section over and above the middle partition. This phenomena avoids the mixing entropy formation on the feed plate as a

result of feed composition differences, and generates energy and capital savings. It can be analytically demonstrated that the formation of additional feed mixing entropy on the feed stage is completely eliminated if the following equation is preserved.

$$\frac{\dot{m}_{B,above}}{\dot{m}_{B,below}} = \frac{\sigma_A(\alpha_B - \alpha_C) + (1 - \sigma_C)(\alpha_A - \alpha_B)}{(1 - \sigma_A)(\alpha_B - \alpha_C) + \sigma_C(\alpha_A - \alpha_B)} \quad (1)$$

when there are abrupt splits on the middle wall,

$$\frac{\dot{m}_{B,above}}{\dot{m}_{B,below}} = \frac{\alpha_B - \alpha_C}{\alpha_A - \alpha_B} \quad (2)$$

where  $\sigma$  is the components relative volatility, as designated by corresponding indexes A,B and C, and  $\alpha$  is the DWC feed section lowest (A) and highest (C) boiling components separation yield. These equations provide a preliminary distribution ratio estimation of component B in the column thermodynamic rating.

The avoidance of the additional mixing generation on the feed stage is the fundamental thermodynamic explanation to lower DWC energy demand compared to more conventional distillation technologies (Long and Lee 2017).

## FOUR AND MORE COMPONENT MIXTURES SEPARATION

Dividing wall columns, with packing or stages, can execute separation of feed mixtures containing more than three components. For example, the four-component mixture separation which can be performed in a single dividing wall column (Figure 4a), proposed by Dejanović et al. 2011, replacing three separate column shells that would be necessary in a conventional column arrangement. Columns of this type have already found industrial application. Lorenza, et al. 2018 e Ränger et al. 2018 presented recently some commercial applications of DWC in chemical industry.

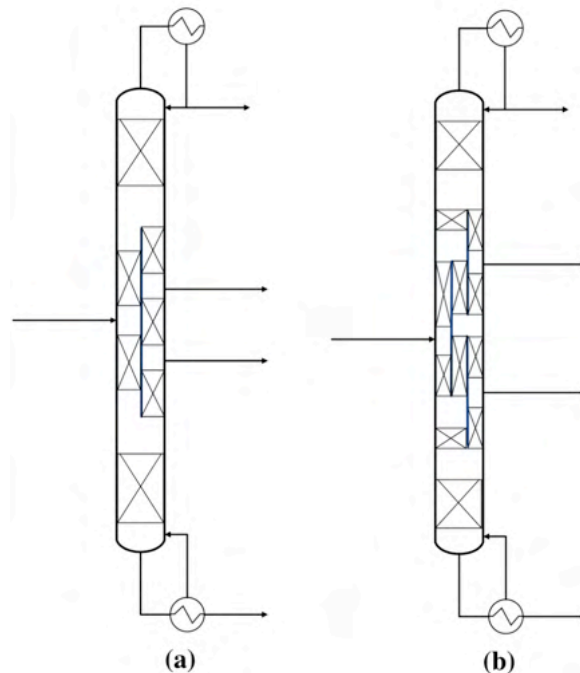


Figure 4. Dividing wall column with (a) and without (b) mixing entropy formation during a four component mixture separation (Dejanović et al. 2011).

In the case of a four-component mixture separation in a DWC with a single partition, a possible result is a deviation from the thermodynamically optimal separation sequence. The formation of additional mixing entropy may not be completely avoided, as a subtle split between the two intermediate boiling components. This point implies which the extent of energy savings in single partition DWC disappointing. To overcome this limitation, should be inserted three dividing walls in the column as illustrated by Figure 4 (b). This configuration reduces substantially the feed plate mixing entropy generation carrying to lower energy costs. This thermodynamical column configuration have not yet been applied at industry scale according to literature (Dejanović et al. 2011; Segovia-Hernández et al. 2021). In the meantime, a significant number of pilot plant scale tests have been carried out in the last decade with promising results (Diwekar and Agrawal 2021).

At first, larger number of dividing walls arrangements could be applied for multicomponent feed systems. Potential applications should be analysed carefully, because as the number of theoretical stages increases, the temperature difference between reboiler and condenser achieves infeasible high values in some applications (Lorenza, et al. 2018).

### THERMALLY COUPLED DISTILLATION COLUMNS (TCDC)

To deal with wide boiling mixtures, thermally coupled columns should be considered in substitution to dividing wall columns. They exhibit similar energy savings to DWC, as they also provide the thermodynamically optimal separation and minimize mixing entropy generation on the feed plate. There are four basic arrangements of thermally coupled distillation columns shown in Figure 5 (Klauzner et al. 2020).

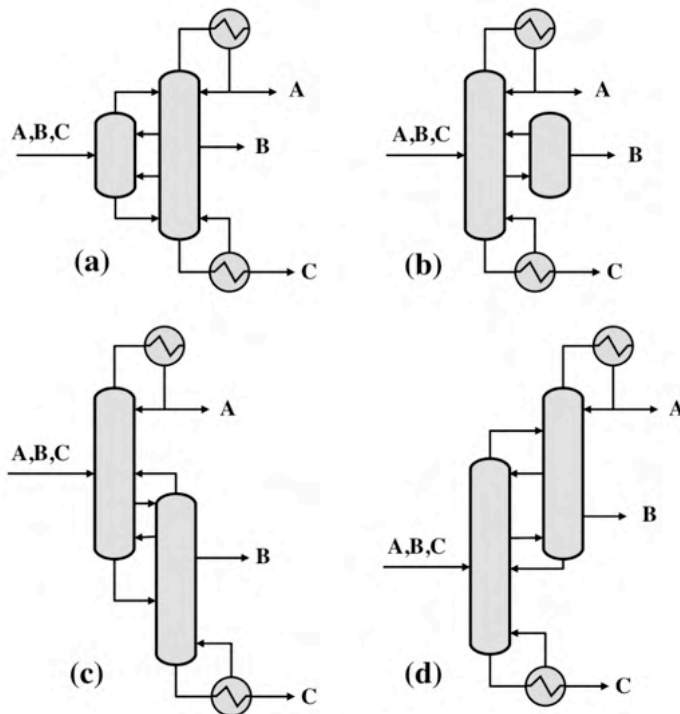


Figure 5. Typical arrangements of thermally coupled distillation columns (Sandoval-Vergara et al. 2008).



## **MODELLING, SIMULATION AND OPTIMIZATION OF DWCS**

### **MODELING IN DIVING WALL COLUMNS**

In previous works, nonreactive DWCS have been usually described like a columns single combination, linked together by vapor and liquid streams to replicate a DWC. The distillation column models are based on the equilibrium stage concept, which following postulates must be made: (i) all components mass-transfer resistances are equal (e.g., the height equivalent to a theoretical plate (HETP) value is used), (ii) no heat transfer occurs through the dividing wall between the prefractionator and the main column and (iii) Vapor distribution in the lower region the dividing wall is considered ideally (vapor distribution close to the dividing wall doesn't suffer pressure drop influence) (Mueller and Kenig 2007a).

Mueller and Kenig (Mueller and Eugeny Y. K. 2007) pointed the equilibrium stage concept application to complex systems presents some bottlenecks, even in conventional distillation (Taylor et al. 2003). Then, it is a better alternative applying the rate-based stage model approach, considering the mass and heat transfer rates and process hydrodynamics (Kenig and Gorak 1995; Kenig et al. 2004).

The DWC model structure presented in this work uses a column internal arrangement description very close to reality. The internals are composed of packing sections and distributors between them (Figure 6). In the distributor model, heat and mass transfer between liquid and vapor phases are not included. Nonetheless, the distributors are used to disperse the feed inside the column. Also, they have another function of splitting and mixing the streams below and above the dividing wall. For the modeling development, each packing section is discretized into infinitesimal intervals (stages).

In contrast to DWCS thermally coupled columns work at different pressures to reduce the column temperature spread, in the case of both columns hold their own reboilers and condensers as in Figure 5. The column with the lowest boiling fraction works with higher pressure, and the other with the highest boiling fraction run in a higher pressure (Triantafyllou and Smith 1992).

Carranza-Abaíd and González-García 2020 presented a dynamic simulation (analyzing hysteresis and bifurcations) of thermally coupled distillation columns (TCDC) in Matlab 2019b and confirmed by Aspen Plus v8.8. The analysis showed that internal flows degree induces multiple steady-state solutions generating isolated bifurcation branches. Further, it is demonstrated which the TCDC operational holes in their steady states are created by saddle-node bifurcations. This evidence indicates that a non-smooth optimization algorithm is more adequate for TCDC design.

Zhu et al. 2021 investigated two cases involving extractive dividing-wall columns (EDWC): acetone and methanol, and bioethanol dehydration. For a better EDWC controllability and operation understanding. The dynamic simulation results showed that the coupling effect and interaction behavior impacts deeply EDWC controllability. To overcome this adversity, it was proposed intermediate heating use to introduce one more parameter in EDWC control and operation.

Thermally coupled columns utilization implies in higher investments compared with DWCS, by reason of second column shell necessity. A detailed account on this topic can be found in the article on Thermally Coupled Columns can be found in Long & Lee's book (Long and Lee 2017).

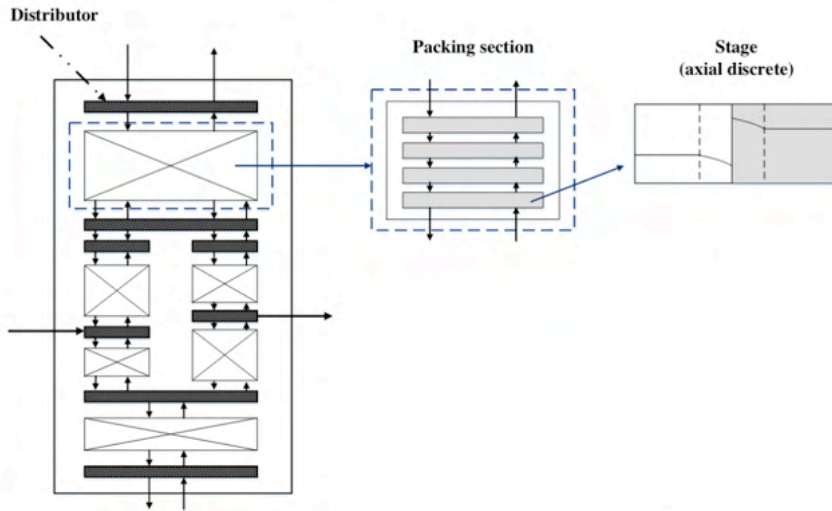


Figure 6. Column Structure, discretized section, and a column stage (left middle, and right panels, respectively), as described by the film model (Lewis and Whitman 1924).

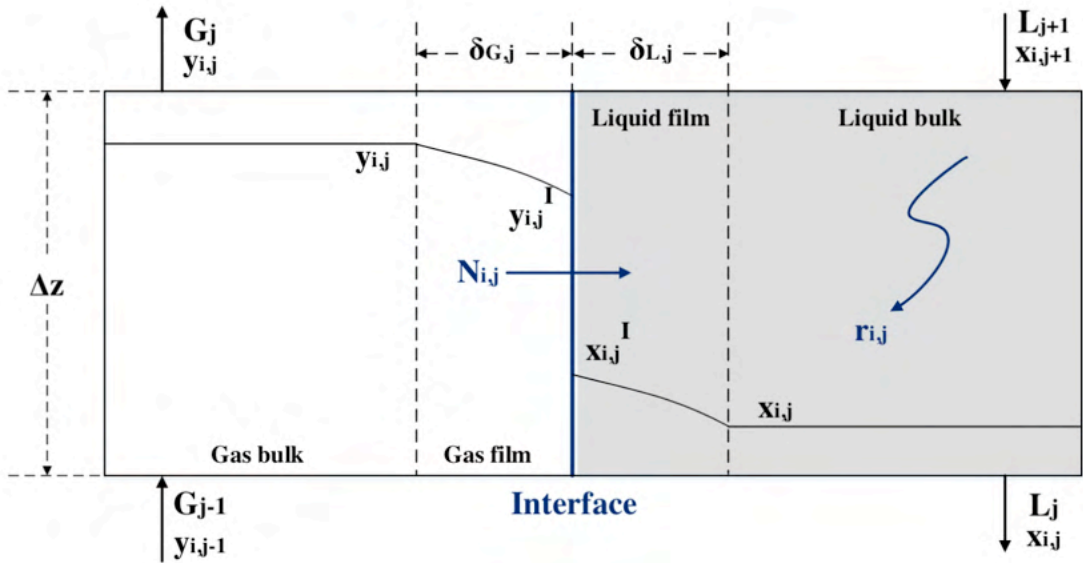


Figure 7. Film model for a nonreactive packing discrete (stage) (Lewis and Whitman 1924).

Lewis and Whitman (Lewis and Whitman 1924) proposed the film model, whose applications are well established in absorption and distillation (Mueller and Kenig 2007b), illustrated by Figures 6 and 7. By analogy, one can consider a DWC equipped with trays, since each tray is related to one rate-based stage.

In reactive dividing wall columns, in addition to the models used nonreactive column, liquid-phase reactions occur in the reactive zone. Furthermore, in the following section, we present a rate-based stage model which describes both nonreactive and reactive systems (Mueller and Kenig 2007b).

### Mass-transfer equations applied to DWC

A rigorous model for heterogeneously catalyzed reactive distillation processes has been developed by Gorak and Hoffmann 2001 and further elements were introduced to cover different reactive and nonreactive separation operations and different column configurations (Kloeker et al. 2003; Mueller and Eugeny Y. K. 2007).

The rate-based stage principle is illustrated in Figure 7. The liquid bulk phase catalyzed reactions with solid catalyst are modeled as pseudo-homogeneous system. For the steady-state operation, the component balances for the vapor and liquid phase at a stage  $j$  are written as

$$0 = G_{j-1}y_{i,j-1} - G_j y_{i,j} - N_{i,j} a_j A_j \Delta z \quad (3)$$

$$0 = L_{j+1} x_{i,j+1} - L_j x_{i,j} + (N_{i,j} a_j + r_{i,j} \Psi_{cat} P_{cat}) A_j \Delta z \quad (4)$$

According equations 3 and 4, it is assumed that mass transfer from the vapor phase to the liquid phase is positive. Widely, equation 4 describes both reactive and nonreactive cases. For the stages without reactions (out reaction zone), the reaction term  $r_{i,j}$  becomes zero. The molar fluxes  $N_{i,j}$  are related to the diffusional fluxes by

$$N_{i,j} = J_{i,j}^L + x_{i,j} \sum_{k=1}^n N_{k,j} = J_{i,j}^G + y_{i,j} \sum_{k=1}^n N_{k,j} \quad (\text{for } i = 1, \dots, n-1) \quad (5)$$

And the composition summation restriction must be followed:

$$\sum_{i=1}^n x_{i,j} = \sum_{i=1}^n y_{i,j} = 1 \quad (6)$$

Two different approaches are applied in this work for the mass-transfer rates: a rigorous description using the Maxwell-Stefan equations and the Fick's law with effective diffusivities (Mueller and Kenig 2007a).

Maxwell-Stefan approach is based on Krishna and Standard's approach (Krishna and Standart 1979) used to combine binary mass-transfer coefficients and multicomponent mass transfer rates. The diffusional fluxes can be determined from

$$\overline{J}_j^L = -c_{t,j}^{L,av} \overline{k_{L,j}^{av}} \overline{\Gamma}_j (\overline{x}_j - \overline{x}_j^I) \quad \text{Liquid flux} \quad (7)$$

$$\overline{J}_j^G = -c_{t,j}^{G,av} \overline{k_{G,j}^{av}} (\overline{y}_j^I - \overline{y}_j) \quad \text{Gas flux} \quad (8)$$

Whose mass transfer coefficients matrix is defined as

$$\overline{k}_j^{av} = [\overline{R}_j^{av}]^{-1} \quad (9)$$

with

$$R_{i,n,j}^{L,av} = \frac{x_{i,j}^{av}}{\kappa_{i,n,j}^L} + \sum_{k=1, k \neq i}^n \frac{x_{k,j}^{av}}{\kappa_{i,k,j}^L} \quad [i = 1, k = 1 \dots, n-1 (i \neq k)] \quad (10)$$

$$R_{i,k,j}^{L,av} = -x_{i,j}^{av} \left( \frac{1}{\kappa_{i,k,j}^L} - \frac{1}{\kappa_{i,n,j}^L} \right) \quad [i = 1, k = 1 \dots, n-1 (i \neq k)] \quad (11)$$

The binary mass-transfer coefficients ( $\kappa_{i,k}$ ) can be estimated from appropriate mass-transfer correlations, using the appropriate Maxwell-Stefan diffusion coefficients ( $D_{i,k}$ ) (Krishna and Standart 1979). Conform to the linearized theory (Stewart and Prober 1964; Toor 1964) the matrices are calculated using average mole fractions, defined as

$$x_{i,j}^{av} = \frac{x_{i,j} + x_{i,j}^l}{2} \quad (i = 1, \dots, n) \quad (14)$$

$$y_{i,j}^{av} = \frac{y_{i,j}^l + y_{i,j}}{2} \quad (i = 1, \dots, n) \quad (15)$$

Furthermore, the films physical properties (for example, average molar density,  $c_t^{av}$ ) are calculated using these average compositions. In the second approach, the diffusional fluxes are calculated with Fick's law:

$$\bar{J}_j^L = -c_{t,j}^{L,av} \overline{k_{L,j}^{eff}} (\bar{x}_j - \bar{x}_j^l) \quad \text{Liquid flux} \quad (16)$$

$$\bar{J}_j^G = -c_{t,j}^{G,av} \overline{k_{G,j}^{eff}} (\bar{y}_j^l - \bar{y}_j) \quad \text{Gas flux} \quad (17)$$

The required effective mass-transfer coefficients are generally calculated from empirical correlations by applying effective diffusivities  $D_i^{eff}$ ; the latter can be developed from different methods, a usual method was proposed by Wilke-Chang (Reid et al. 1987). Compared to the Maxwell-Stefan matrix approach, the Fick's law application provides a simpler equation system for mass transfer modeling. Hence improving both simulation and convergence speed. Phase equilibrium is accepted at the interface:

$$\bar{y}_j^l = \overline{K_{i,j}^{eq}} \bar{x}_j^l \quad (18)$$

where liquid-vapor equilibrium constants ( $K_{i,j}^{eq}$ ) are determined using particular thermodynamic models, an example is UNIQUAC for activity models and Antoine equation for the vapor pressure (Reid et al. 1987). The influence of process hydrodynamics is directly incorporated through mass-transfer coefficients correlations, liquid holdup, pressure drop and specific contact area. Bravo et al. 1985, 1986 presented some correlations and results in their works.

### Energy balances Equations in DWC

In the anterior section, the rate-based stage model mass balances are described. At this

topic, it will be addressed the heat transport phenomena, counting both heat conduction through the dividing wall and heat convection within the stage, which represents a column configuration singular characteristic. The heat transfer through the wall can affect separation efficiency (Lestak et al. 1994; Ehlers et al. 2015).

The dividing wall is involved by a liquid-vapor mixture whose near-wall phase state it is difficult to make an accurate estimation. Due to this inherent complexity, it is necessary to assume that the wall is covered by only one phase and consider two different situations. The first situation is when the dividing wall is surrounded by the vapor phase from both sides, and in the second both sides are surrounded with liquid.

For heat-transfer modelling, it is considered a complete DWC cross section, because prefractionator (at left-side) and main column stages (at right side) are connected by the heat-transfer flux between them (Figure 8).

The for the entire cross-section can be subdivided onto the balances for the vapor and liquid phases, which are formulated as bellow (Mutalib and Smith 1998; Hernández et al. 2009):

$$0 = G_{j-1}H_{G,j-1} - G_jH_{G,j} - q_j^l a_j A_{col} \Delta z \mp Q_{G,j}^w \quad (19)$$

$$0 = L_{j+1}H_{L,j-1} - L_jH_{L,j} - q_j^l a_j A_{col} \Delta z \mp Q_{L,j}^w \quad (20)$$

These equations describe both prefractionator and main column. For the prefractionator, the last term in equations 19 and 20 is negative, while for the main column, it is positive (just as presented in Figure 8). In analogy to mass transfer, heat transfer from the vapor to the liquid phase is presumed positive. The heat flux across the vapor-liquid interface is expressed by a convective component plus a conductive component:

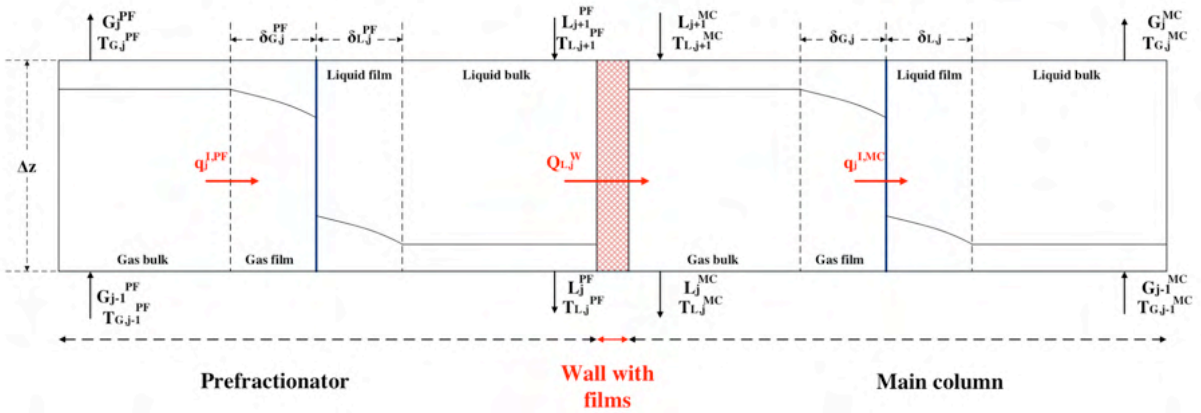


Figure 8. Heat transfer in a cross section of the dividing wall column for the case of the liquid-liquid heat transfer at the wall.

$$q_j^l = \frac{\lambda_{G,j}}{\delta_{G,j}^{av}} (T_{G,j} - T_j^l) + \sum_{i=1}^n N_{i,j} H_{G,i,j} = \frac{\lambda_{L,j}}{\delta_{L,j}^{av}} (T_j^l - T_{L,j}) + \sum_{i=1}^n N_{i,j} H_{L,i,j} \quad (21)$$

The average film thickness ( $\delta_{L,j}^{av}$ ) for both liquid and vapor film is decisive to calculate the interfacial conductive heat transfer and can be derived as the weighted effective film thickness:

$$\delta_{L,j}^{av} = \sum_{i=1}^n x_{i,j} \delta_{L,i,j} = \sum_{i=1}^n x_{i,j} \frac{D_{L,i,j}^{eff}}{k_{L,i,j}^{eff}} \quad (22)$$

$$\delta_{G,j}^{av} = \sum_{i=1}^n x_{i,j} \delta_{G,i,j} = \sum_{i=1}^n y_{i,j} \frac{D_{G,i,j}^{eff}}{k_{G,i,j}^{eff}} \quad (23)$$

The dividing wall heat flux rate ( $Q_j^W$ ) is depending on wall adjacent phases. Where as for vapor phase,

$$Q_{G,j}^W = k_j^W \Delta A^W (T_{G,j}^{PF} - T_{G,j}^{MC}) \quad (24)$$

and for liquid phase:

$$Q_{L,j}^W = k_j^W \Delta A^W (T_{L,j}^{PF} - T_{L,j}^{MC}) \quad (25)$$

For a plane wall with thickness ( $s^W$ ), the stage  $j$  overall heat-transfer coefficient ( $k_j^W$ ) can be estimated using the adjacent phases heat transfer coefficients ( $a_j^{W,PF}$  and  $a_j^{W,MC}$ ) and wall conduction coefficient ( $\lambda_j^W$ ):

$$\frac{1}{k_j^W} = \frac{1}{\alpha_j^{W,PF}} + \frac{s^W}{\lambda_j^W} + \frac{1}{\alpha_j^{W,MC}} \quad (26)$$

The value of  $\lambda^W$  is dependent on the wall material and can be found in the literature. The convective heat-transfer coefficient calculation ( $a^W$ ) are more complex because there are no correlations for distillation columns walls available in literature. Although, the near-wall heat resistances neglectation may result in unrealistically implausible large values of heat fluxes. As a first estimation, can be applied overall heat-transfer coefficients constant values (Rocha et al. 1993, 1996).

### Liquid and vapor splits modelling

Vapor and liquid interphases mass exchange flows (in prefractionator and main column) are modeled in two regions: below and above the dividing wall. Below the dividing wall ( $b^{DW}$ ), the liquid streams are combined and the vapor streams are split (see Figure 9). Otherwise, above the dividing wall ( $a^{DW}$ ), the prefractionator ascending vapor streams and main column are mixed, whereas the main column liquid stream is split in two streams, which flows along dividing wall both sides (Kiss 2013). Column both sides where is positioned partition wall, could have

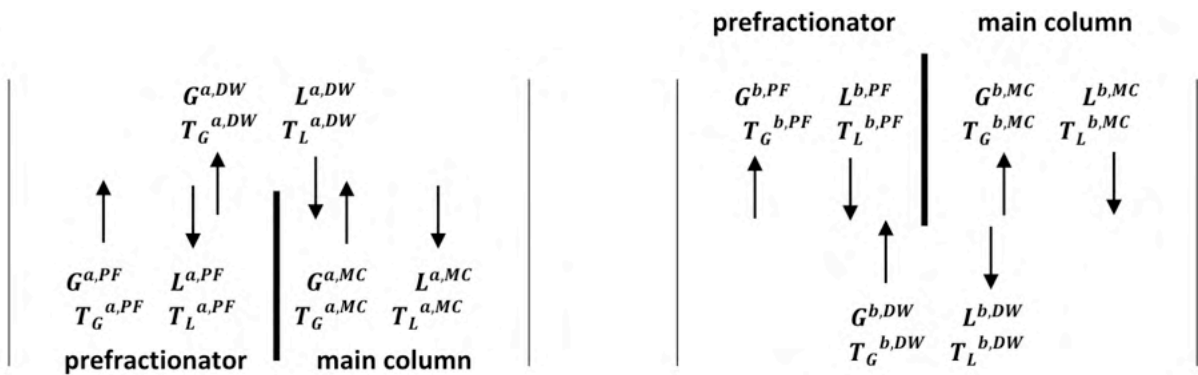


Figure 9. Liquid and vapor splits above (left) and below (right) the dividing wall.

different pressure drops which affects the hydrodynamics, and consequently, changes the composition profile due to preferential gas flow channels formation in wall side with lower pressure drop.

The combination of the two downstreaming liquid flows  $L_b^{MC}$  (main column side) and  $L_b^{PF}$  (prefractionator side) below the dividing wall to stream  $L_b^{DW}$  is expressed as:

$$L^{b,DW} x_i^{b,DW} = L^{b,MC} x_i^{b,MC} + L^{b,PF} x_i^{b,PF} \quad (\text{for } i = 1, \dots, n) \quad (27)$$

The vapor stream  $G^{a,DW}$  above the dividing wall ( $a^{DW}$ ) is calculated by

$$G^{a,DW} y_i^{a,MC} = G^{a,MC} y_i^{a,MC} + G^{a,PF} y_i^{a,PF} \quad (\text{for } i = 1, \dots, n) \quad (28)$$

while the composition summation conditions are valid (Kiss 2013):

$$\sum_{i=1}^n x_i^{b,DW} = \sum_{i=1}^n y_i^{a,DW} = 1 \quad (29)$$

Liquid and vapor mixtures temperatures are calculated applying enthalpy balances:

$$L^{b,DW} H_L^{b,DW} = L^{b,MC} H_L^{b,MC} + L^{b,PF} H_L^{b,PF} \quad (30)$$

$$G^{b,DW} H_G^{b,DW} = G^{a,MC} H_G^{a,MC} + L^{a,PF} H_L^{a,PF} \quad (31)$$

To describe the splitting, is defined the stream split ratio ( $\varphi$ ). Whose value for liquid phase is the ratio between liquid flow rate entering the prefractionator ( $L^{a,PF}$ ) and the total dividing wall stream flow rate ( $L^{a,DW}$ ):

$$\varphi_L = \frac{L^{a,PF}}{L^{a,DW}} \quad (32)$$

Additionally, for gas phase

$$\varphi_G = \frac{G^{b,PF}}{G^{b,DW}} \quad (33)$$

Despite the flow rates balances are required:

$$L^{a,DW} = L^{a,MC} + L^{a,PF} \quad (34)$$

$$G^{b,DW} = L^{b,MC} + L^{b,PF} \quad (35)$$

Concentrations and temperatures unchange in the split streams:

$$x_i^{a,DW} = x_i^{a,MC} = x_i^{a,PF} \quad (36)$$

$$y_i^{b,DW} = y_i^{b,MC} = y_i^{b,PF} \quad (37)$$

$$T_L^{a,DW} = T_L^{a,MC} = T_L^{a,PF} \quad (38)$$

$$T_G^{b,DW} = T_G^{b,MC} = T_G^{a,PF} \quad (39)$$

The liquid split ratio ( $\varphi_L$ ) works as a control parameter for the DWC adjustment. Although, the vapor distribution is nontrivial. By reason of the DWC vapor distribution must afford an equal pressure drop at column both sides (Rocha et al. 1993):

$$\Delta P^{MC} = \Delta P^{PF} \quad (40)$$

If satisfactory pressure drop correlations are not available or for initialization approaches, the vapor split can be set equal to the cross-sectional area ratio ( $\phi_{Area}$ ), defined as:

$$\phi_G \approx \phi_{Area} = \frac{A^{PF}}{A_t} \quad (41)$$

Many factors generate vapor resistances at both wall sides, especially different liquid and gas loads and different internals (if operational suitable) in the prefractionator or main column. For a more realistic model, the real vapor split ratio diverge from the cross-sectional area ratio, altering the column performance (Rocha et al. 1996).

Harvianto *et al.* tested an enhanced active vapor distributor (EAVD) in a laboratory-scale DWC. An expressive number of different experimental conditions were taken to evaluate EAVD control under pressure drop values range. The results revealed that EAVD compensated pressure drop variations and the requested vapor split ratio was reached during operation, improving flexibility and operability of DWCs.

## DESIGN AND OPTIMIZATION OF DWC

### Shortcut methods

Halvorsen and Skogestad 2003 elaborated the *V<sub>min</sub> diagram method* to determine the minimum energy consumption in Three-Product Petlyuk Arrangements. The method assumes constant molar flowrates, infinite number of stages and constant relative volatilities ( $\alpha$ ). Firstly, the  $V_{min}$  is calculated through the Underwood equation. The separation minimum energy requirement of a  $n$  components feed mixture into  $n$  pure products is estimated by:

$$V_{min}^{Petlyuk} = V_{min} \approx \max \sum_{i=1}^j \frac{\alpha_i z_i F}{\alpha_i - \theta_j} ; j \in (1, n-1) \quad (42)$$

Where,  $\theta_j$  are the  $n - 1$  Underwood roots found from,

$$1 - q = \sum_{i=1}^n \frac{\alpha_i z_i}{\alpha_i - \theta} \quad (43)$$

Underwood roots must embrace the following conditions:  $\alpha_1 > \theta_1 > \alpha_2 > \theta_2 > \dots > \alpha_{n-1} > \theta_{n-1} > \alpha_n$ . Where  $q$  is liquid fraction in the feed ( $F$ ) and  $z$  is feed composition.

In the next step, flowrate is taken around 10% and the minimum number of stages was calculated based on the Underwood equation. Calzon-McConville et al. 2006 developed a thermally coupled distillation sequences design procedure for energy efficiency optimization based on the conventional distillation sequences design. First, it is assumed components recovery of 98% for key components recoveries (light and heavy keys) and by applying the shortcut method (FUG equation), the approximate conventional distillation number stages schemes are obtained. Next, the stage arrangements for integrated configurations are calculated. By last, energy consumption is minimized using an optimization procedure. The thermal optimal design for thermally coupled distillation sequences is applied not only for ternary or quaternary mixtures separation as well as five or more component mixtures separation. Ryu and Maravelias (Ryu and Maravelias 2021) presented a generalized distillation network synthesis model whose application is suitable for dividing wall columns.

Sotudeh and Shahraki 2007, 2008 developed a DWC shortcut design method using only Underwood equation because Fenske equation for calculating stages minimum number is not adequate for dividing wall columns design.

By using Underwood equation for minimum stages number calculation, the prefractionator and side section stages number are calculated as the same. Compared to some rigorous methods in literature, there are a margin error around 10 to 15% (Zhou et al. 2019).

Ramírez-Corona et al. 2010 presented an optimization method for Petlyuk distillation system. The procedure used the FUG model to determine the DWC stages number, along with mass and energy balances, thermodynamic relationships, and cost equations. Total annual cost (TAC) was set as the objective function minimization. In this approach, the interconnection streams composition between the prefractionator and the main column are calculated by using the feed line and the operating line equations respectively.

$$y_{i,j+1} = \left(\frac{q}{q-1}\right)x_{i,j} - \frac{x_{i,D}}{q-1} \quad \text{Feed} \quad (44)$$

$$y_{i,j+1} = \left(\frac{R}{R+1}\right)x_{i,j} - \frac{x_{i,D}}{R+1} \quad \text{Rectification} \quad (45)$$

By above equations combination, is obtained:

$$x_i = \frac{z_i(R+1) + x_{i,D}(q-1)}{R+q} \quad (46)$$

and

$$y_i = \frac{Rz_i + q_i x_{i,D}}{R+q} \quad (47)$$

Chu et al. 2011 presented a shortcut method based on the efficient net flow model to determine the composition of the key components. Then it was applied the shortcut method of Fenske, Underwood, Gilliland and Kirkbride (FUGK) to estimate the stages number of each DWC section. Due to constant molar flow premise, Liquid split  $R_L$  and vapor split  $R_V$  are dependent variables. The values of  $R_L$  and  $R_V$  are defined to reach the same trays number in side section and the

prefractionator.

In a recent work, Di Pretoro et al. 2021 used ProSimPlus® process simulator to initialize the design algorithm coupled with rigorous process simulations, proposed an innovative design procedure based on feasible paths for an ABEW mixture separation case study. Beginning from shortcut methods results, the trays number can be increased or decreased from the selected DWC section using composition profiles analysis. This procedure is especially effective for non-ideal mixtures separations (e.g. ABEW one) to run through simulation convergence failures. This procedure provides a solution close to the optimal one in a reasonable time and without the MINLP problem solution need. Pazmiño-Mayorga et al. 2021 presented a conceptual design of a dual reactive dividing wall column for downstream processing of lactic acid.

Based on literature presented in this chapter, additional works are needed to develop an approximate method with a view to minimize the drawbacks observed in the previously mentioned works. Triantafyllou and Smith 1992 applied the FUGK model to easily determine DWC operational reflux ratio and stages number. Elseways, the Fenske equation application for the DWC stages minimum estimation is not proper. Since the liquid stream composition returning from the main column is not equal to the vapor composition entering in the main column through connection points.

Kim 2002 applied a stage-to-stage computation method in substitution to Fenske equation for the prefractionator. This method overdimensioned the stages number by doubling the minimum number of stages. Sotudeh and Shahraki 2007 used Underwood equation to compute the minimum stages number in the main column and they set prefractionator to be the same side section stages. Ramírez-Corona et al. 2010 as well



applied the FUGK method and estimated the interconnecting streams composition. Furthermore, all the previous methods have not considered the position and configuration of dividing wall in the column and a great part of them are restricted to ternary mixtures with a feed quality ( $q$ ) equal to 1. On the other hand, works like. Di Pretoro et al. 2021 e Pazmiño-Mayorga et al. 2021 obtained more accurate results using more rigorous simulation methods combined to shortcut methods.

### More rigorous design methods

#### a) Traditional DWC/Petlyuk

Several works have simulated diferent types of dividing wall columns (see Table 1). Dejanovic et al. 2011 simulated a aromatic process DWC using the Wang-Henke method involving a 15 component feed mixture, using data from INA Sisak Refinery. The DWC system required 43% less energy than the two column configuration.

The energy savings do not take into account the heating and cooling degrees required. Heat transfer across the dividing wall was

not included in the model, and the hydraulics were approximated to a standard column. The optimal vapor split from the design was not uniformly distributed across the wall, with more vapor flow to the prefractionator (PF) than the main column side (MC) (Kang et al. 2017).

Dejanović et al. 2010, Dejanovic et al. 2011 and Halvorsen et al. 2013, 2016 design approach corresponds to the wall being centrally located, but as allowed more vapor flow to the prefractionator. There were hydraulic changes not incorporated in the model. A DWC may have an overall lower reboiler duty, but could not be the best system design choice. In a conventional two column sequence separation, two reboiler temperature utilities levels can be applied, whereas a DWC has only one reboiler and one condenser. This approach is based on the assumptions adopted by most of DWC simulations (Uwitonze et al. 2021):

- Pressure drop and heat transport are neglected;
- Liquid and vapor split optimization not taking into account friction factors, wall

DWC type	Author	Modeling Methodology	Process separation
DWC/Petlyuk	Dejanović et al. 2010; Dejanovic et al. 2011; Halvorsen et al. 2013, 2016	four column, equilibrium	15 chemical platformate feed
DWC/Petlyuk with various wall placements	Ho et al. 2011	two column, DSTWU	- benzene, toluene and ethyl benzene; - n-butane, iso-pentane, and n-pentane; - n-C5, n-C6 and n-C7.
DWC/Petlyuk	Long et al. 2016	two column, equilibrium	benzene, toluene and oxylene
DWC/Petlyuk	Mueller and Kenig 2007a	rate based and equilibrium	butanol, ipropanol and methanol
DWC/Petlyuk	Pattison et al. 2016	Steady state	methanol, dimethyl ether and water
DWC/Petlyuk	Rangaiah et al. 2009	two column, rate based approach	six industrial applications
DWC/Petlyuk	Suphanit et al. 2007	two column, rate based approach	Benzene, toluene and p-xylene
DWC/Petlyuk	Wang 2013	two column	Industrial naphthalene

Table 1. DWC Simulation and Optimization open literature summary.

DWC type	Author	Modeling Methodology	Process separation
DWC/Petlyuk	Zhai et al. 2015	two column	Cumene production
DWC/Petlyuk	Parra-Santiago et al. 2015	2 column	Styrene, benzene and toluene.
DWC/Petlyuk	Biyanto et al. 2017	2 column	N-pentane, n-hexane & n-heptane
DWC/Petlyuk	Zang et al. 2020	Kaibel DWC column	benzene, toluene, o-xylene & trimethyl-benzene
DWC/Petlyuk with side stripper	Kazemi and Mehrabani-Zeinabad, A. Beheshti 2018	two column and vapor recompression (VRC)	Mixture containing C4 hydrocarbons
More than 3 product DWC	Halvorsen and Skogestad 2003; Dejanović et al. 2011; Halvorsen et al. 2013	4 column, equilibrium	15 chemical platformate feed
More than 3 product DWC	Okoli and Adams II 2015	2 column, equilibrium	methanol, ethanol, butanol, & pentanol from biomass stream
More than 3 product DWC	Shi et al. 2020	2 column with side rectifier and side stripper	Separation of acetone, methanol, butanone & tert-butyl alcohol
Retrofitting	Premkumar and Rangaiah 2009	2 column, equilibrium	6 industrial applications
Heat Pump with azeotrope	Li et al. 2016	3 columns	Azeotrope separation of t-butanol & water
Heat Pump - azeotrope	Li et al. 2021	3 columns	Azeotrope separation of benzene, isopropanol and water
Heat Pump - azeotrope	Patraşcu et al. 2018	3 columns	Azeotrope separation of t-butanol & water
Heat Pump - azeotrope	Ghalavand et al. 2021	3 columns	Azeotropic separation of ethanol & water
Heat Pump - extractive azeotrope	Klauzner et al. 2020	2 columns with side rectifier	Azeotropic separation of isobutanol-Isobutyl acetate Mixture Using Dimethylformamide
Heat Pump - reactive distillation	Chen et al. 2020	2 columns with side rectifier	Energy-saving for the isobutyl acetate synthesis
Controllability and operation of extractive DWC	Zhu et al. 2021	2 columns with thermal coupling	Acetone and methanol separation
Controllability and operation of DWC	Wu et al. 2020	2 columns and side rectifier configuration	Separation of the mixing diols

Table 1. DWC Simulation and Optimization open literature summary (continuation).

placement or column internals design;

- Change feed or sidedraw location are fixed;
- Feed temperature or feed phase are not optimized as variables;
- Total Annual Cost (TAC) minimization;
- Energy minimization is not taken account;

Before executing a DWC design, a simulation looking at design factors should be applied, instead of at a high level approach.

### **b) DWC with four products or more**

Dividing wall columns (DWC) could obtain energy and capital savings if this technology would be applied to obtaining four or even more products. As discussed previously in this chapter, the commitment to push the technology further is being explored. A conventional DWC achieves high purity tertiary products, but new designs are trying to add sidestreams to perform multiproducts separation (Waltermann et al. 2019). The Kaibel column is a proposed design, which includes one dividing wall and four product streams with two sidestreams (Kaibel et al. 1998). This design may not be able to reach high purity side streams products, but it achieves high purity of the overhead and bottoms products. Another modification of the Kaibel column is the 4<sup>th</sup> column addition (Christiansen et al. 1997). This column separates the feed side of the dividing wall into two sections to prevent reflux thermodynamic losses (mixing entropy generation) coming out of the sidestream products (Waltermann et al. 2019).

More works involving multiple wall dividing wall columns are in development (Lorenza, et al. 2018); however, industrial applications with this configuration until this year were not made yet (Di Pretoro et al. 2021). Optimizations, simulations and plant pilot tests have been implemented on above DWC configurations and the results are promising

(Preißinger et al. 2019). Nonetheless, no enough empirical works has been completed accosting these columns in academic and open industrial literature. Notwithstanding, further research for rating multiple walls hydraulic effects are required.

Shi et al. 2020 presented two new energy-saving extractive distillation configurations for single and double-dividing-wall columns, based on a conventional four-column extractive distillation process —CFC-ED, to efficiently separate a quaternary azeotropic mixture of acetone, methanol, butanone and tert-butyl alcohol with chlorobenzene as a solvent.

Sánchez-Ramírez et al. 2020 designed and tested four product (quaternary) DWCs according performance indexes: environmental impact, energy consumption, inherent safety and process dynamics and controllability. They observed many of the conventional thermal couplings columns could be substituted for liquid splits whose implementation enhances the performance indicators mentioned previously.

Cui et al. 2020 to improve the inferential control scheme effectiveness, proposed a modified structure with a internal composition controller able to handle  $\pm 20\%$  step changes. Furthermore, their work verifies the simpler liquid transfer stream control. Their result present a competitive substitute to the Petlyuk column configuration, for both academic and industrial purposes.

In the last topic, will be presented some further considerations and conclusions.

## **CONCLUSIONS**

As discussed before in this book chapter, a DWC is a singular distillation column arrangement that combines conventional equipment and a partition wall, which introduces some difficulties and uncertainties to design and operation. From better known

three components feeds, to lesser known four-product separations, makes everything more complex, and potential additional constraints must be evaluated minutely. These constraints will be different for each case: plate and packed columns, retrofit, reactive system and others.

If it's considered a new project, then a DWC will always be taller than any of the individual columns from the original sequence, creating a higher temperature difference between bottom and top products.

In severe separations, taller distillation columns may be required, which, in conjunction with smaller diameters (lower capacity), become an economical concern. By hydrodynamics side, this means larger pressure drops and higher temperature differences between top and bottom ends. This will be more pronounced in trayed compared to packed DWCs, and will depend on the feed mixture species volatility differences. Furthermore, close boiling mixtures are easier separated in a DWC than wide boiling mixtures.

If operation with a single-pressure is not profitable, there are some energy-saving options to be evaluated. In a four-product case, a first approach, is the three-product DWC connection with a conventional column in series. In three-product situations, the prefractionator and main column side could be splitted in two thermally coupled shells with different pressures. This arrangement will provide similar energy savings with lower capital investment.

There are some alternatives like pressure cascades, where a high-pressure condenser serving as a low-pressure column reboiler. In this case, the temperature gradient increase between the top and bottom becomes a problem if this requires utilities modification from a cheaper one to more expensive cooling or heating system.

Otherwise conventional distillation

columns, DWCs also present a lateral temperature gradient in partitioned sections, which if higher than 30 , may cause operational problems. Heat transfer across the partition wall may decrease distillation column performance, both trayed and packed arrangements. In columns with trays heat transfer across the partition wall can generate excessive vaporization in the regions near to the feed plate location. Then, we should provide sufficient insulation in the partition wall.

In structured packed columns, heat transfer across the partition wall can be minimized to by using wall wiper systems, which not only center the packing inside the column even as remove liquids falling down the wall. Using this system, no liquid on the cold side evaporates and no vapor condenses on the hotter side, because heat flow across the dividing wall is radically reduced.

For the partition wall construction a non-welded wall is a much better option and should be considered first. Due to potential for mechanical damages caused by welding thermal stresses and partition wall inevitable expansion (possibly deformation). Nonetheless, the gap existence between partition and column walls is a potential problem for the process side. During process and mechanical design, must be prevented vapor or liquid (or both) flow going to the partition wall wrong side, which could lead to a product contamination.

A challenge that can involve great complexity occurs when main products ultra-high purity separations are needed. Long packed beds extension may develop excessive pressure drop values. For instance, the vapor stream can penetrate through the gap among partition and column walls, if prefractionator height is shorter than main column side. A possible solution is an adequate sealing system instalation, obtained by combining nonwelded with welded parts. Twophase feed

needs proper provisions installation to avoid vapor impact on the partition wall.

A DWC specific design and operation challenge in current development level is the vapor split control, which becomes more complex in DWCs with a four-product configuration. Project designs are made for a specific operating condition, and the required vapor splits can be regulated according pressure drops for a given column section. For example, by choosing the most appropriate liquid collectors free area section. On the other

hand, the column should be be robust to allow proper responses to common oscillations in flowrate and composition feed, then, adequate systems for vapor flow resistance adjusting in parallel sections should be applied.

Based on the topics discussed previously, there are many opportunities and challenges for research directions, and we must rethinking the distillation processes energy use, in a more competitive and sustainable chemical industry context.

## NOMENCLATURE

$a$	Specific interfacial area	$m^2 m^{-3}$
$A$	Cross-sectional area	$m^2$
$\Delta A_w$	Dividing wall area for a discrete stage	$m^2$
$c$	Molar concentration	$mol m^{-3}$
$D^{eff}$	effective diffusivity	$m^2 s^{-1}$
$G$	Gas molar flow rate	$mol s^{-1}$
$H$	Specific enthalpy	$J mol^{-1}$
$\mathcal{J}$	vector of diffusional fluxes	$mol m^{-2} s^{-1}$
$K^{eq}$	vapor/liquid equilibrium constant	
$k^w$	Heat-transfer coefficient for the dividing wall	
$\bar{k}$	matrix of binary mass-transfer coefficients	$m s^{-1}$
$L$	Gas molar flow rate	$mol s^{-1}$
$N$	Interfacial molar flow rate	$mol m^{-2} s^{-1}$
$n$	Number of components	
$p$	Pressure	$N m^{-2}$
$Q$	Heat flow rate	$W$
$\bar{R}$	Inverse matrix of the mass-transfer coefficients	$s m^{-1}$
$R$	Gas constant	$J mol^{-1} K^{-1}$
$s^w$	Thickness of the dividing wall	$m$
$T$	Temperature	$K$
$x$	Liquid-phase mole fraction	
$V$	Volume flow	$m^3 h^{-1}$
$y$	Vapor-phase mole fraction	
$\Delta z$	Discrete (stage) height	$m$

## GREEK LETTERS

$a$	Wall film heat-transfer coefficient Relative volatilities	$W m^{-2} K^{-1}$
$\bar{\Gamma}$	Matrix of thermodynamic correction factors	
$\delta$	Film thickness	$m$
$\kappa$	Binary mass-transfer coefficients	$m s^{-1}$
$\lambda$	Heat-conduction coefficient	$W m^{-1} K^{-1}$
$\phi_{Area}$	Cross-sectional area ratio (PF/total column)	$m^2 m^{-2}$

## SUBSCRIPTS

$G$	Gas Phase
$i,k$	Component index
$j$	Stage index
$L$	Liquid phase
$m$	Reaction index
$t$	Total

## SUPERSCRIPTS

$av$	Average
$a,DW$	Total stream above the dividing wall
$a,PF$	Stream at the upper dividing wall ending in prefractionator
$a,MC$	Stream at the upper dividing wall ending in main column
$b,DW$	Total stream below the dividing wall
$b,PF$	Stream at the lower dividing wall ending in prefractionator
$b,MC$	Stream at the lower dividing wall ending in main column
$G$	Gas Phase
$I$	Interphase
$L$	Liquid Phase
$MC$	Main column
$PF$	prefractionator
$W$	Dividing wall

## REFERENCES

- Aurangzeb M, Jana AK (2019) Double-partitioned dividing wall column for a multicomponent azeotropic system. *Sep Purif Technol* 219:33–46. <https://doi.org/10.1016/j.seppur.2019.03.007>
- Battisti R, Machado RAF, Marangoni C (2020) A background review on falling film distillation in wetted-wall columns: From fundamentals towards intensified technologies. *Chem Eng Process - Process Intensif* 150:107873. <https://doi.org/10.1016/j.cep.2020.107873>
- Biyanto TR, Rahman JA, Sarwono, et al (2017) Techno Economic Optimization of Petlyuk Distillation Column Design Using Duelist Algorithm. *Procedia Eng* 170:520–527. <https://doi.org/10.1016/j.proeng.2017.03.083>
- Bravo JR, Rocha JA, Fair JR (1985) Mass transfer in gauze packings. *Hydrocarb. Process.* 64:91–95
- Bravo JR, Rocha JA, Fair JR (1986) Pressure drop in structured packings. *Hydrocarb Process* 65:45–49
- Calzon-McConville CJ, Rosales-Zamora MB, Segovia-Hernandez, J. G., et al (2006) Design and Optimization of Thermally Coupled Distillation Schemes for the Separation of Multicomponent Mixtures. *Ind Eng Chem Res* 45:724–732. <https://doi.org/10.1021/ie050961s>
- Carranza-Abadía A, González-García R (2020) A Petlyuk Distillation Column Dynamic Analysis: Hysteresis and Bifurcations. *Chem Eng Process - Process Intensif* 149:107843. <https://doi.org/10.1016/j.cep.2020.107843>
- Chen L, Ye Q, Feng S, et al (2020) Investigation about energy-saving for the isobutyl acetate synthesis in a reactive divided-wall column via vapor recompression heat pump. *Chem Eng Process - Process Intensif* 147:107783. <https://doi.org/10.1016/j.cep.2019.107783>
- Christiansen C, Skogestad S, Lien K (1997) Partitioned Petlyuk arrangements for quaternary separations
- Chu KT, Cadoret L, Yu CC, Ward JD (2011) A new shortcut design method and economic analysis of divided wall columns. *Ind Eng Chem Res* 50:9221–9235. <https://doi.org/10.1016/j.cep.2016.02.012ff>
- Cui C, Zhang Q, Zhang X, Sun J (2020) Eliminating the vapor split in dividing wall columns through controllable double liquid-only side-stream distillation configuration. *Sep Purif Technol* 242:116837. <https://doi.org/10.1016/j.seppur.2020.116837>
- Dejanović I, Matijasevic L, Halvorsen I, et al (2011) Designing four-product dividing wall columns for separation of a multicomponent aromatics mixture. *Chem Eng Res Des* 89:1155–1167. <https://doi.org/10.1021/ie1020206>
- Dejanovic I, Matijasevic L, Olujić Z (2011) An Effective Method for Establishing the Stage and Reflux Requirement of Three-Product Dividing Wall Columns. *Chem Biochem Eng* 25:147–157
- Dejanović I, Matijašević L, Olujić Ž (2010) Dividing wall column - A breakthrough towards sustainable distilling. *Chem Eng Process Process Intensif* 49:559–580. <https://doi.org/10.1016/j.cep.2010.04.001>
- Di Pretoro A, Ciranna F, Fedeli M, et al (2021) A feasible path-based approach for Dividing Wall Column design procedure. *Comput Chem Eng* 149:107309. <https://doi.org/10.1016/j.compchemeng.2021.107309>
- Diwekar U, Agrawal R (2021) Novel use of dividing wall columns for intensification multicomponent batch distillations. *Chem Eng Process - Process Intensif* 164:108400. <https://doi.org/10.1016/j.cep.2021.108400>
- Ehlers C, Schröder M, Fieg G (2015) Influence of heat transfer across the wall of dividing wall columns on energy demand. *AIChE J* 61:1648–1662. <https://doi.org/10.1002/aic.14747>
- Ghalavand Y, Nikkhah H, Nikkhah A (2021) Heat pump assisted divided wall column for ethanol azeotropic purification. *J Taiwan Inst Chem Eng* 123:206–218. <https://doi.org/10.1016/j.jtice.2021.05.00>
- Gorak A, Hoffmann A (2001) Catalytic distillation in structured packings: Methyl acetate synthesis. *AIChE J* 47:1067–1076. <https://doi.org/10.1002/aic.690470513>
- Halvorsen IJ, Dejanović I, Maråk KA, et al (2016) Dividing-Wall Column for Fractionation of Natural Gas Liquids in Floating Liquefied Natural Gas Plants. *Chem Eng Technol* 39:2348–2354. <https://doi.org/10.1002/ceat.201500698>

- Halvorsen IJ, Dejanović I, Skogstead S, Olujić Z (2013) Internal configurations for a multiproduct dividing wall column. *Chem Eng Res Des* 91:1954–1965. <https://doi.org/10.1016/j.cherd.2013.07.005>
- Halvorsen IJ, Skogstad S (2003) Minimum Energy Consumption in Multicomponent Distillation. 2. Three-Product Petlyuk Arrangements. *Ind Eng Chem Res* 42:605–615. <https://doi.org/10.1021/ie0108649>
- Harmsen J (2010) Process intensification in the petrochemicals industry: Drivers and hurdles for commercial implementation. *Chem Eng Process Process Intensif* 49:70–73. <https://doi.org/10.1016/j.cep.2009.11.009>
- Hernández S, Sandoval-Vergara, R. Barroso-Muñoz, F. O. Murrieta-Dueñas, R. Hernández-Escoto, H. Segovia-Hernández JG, Rico-Ramirez V (2009) Reactive dividing wall distillation columns: Simulation and implementation in a pilot plant. *Chem Eng Process Process Intensif* 48:250–258. <https://doi.org/10.1016/j.cep.2008.03.015>
- Ho YC, Ward JD, Yu CC (2011) Quantifying Potential Energy Savings of Divided Wall Columns Based on Degree of Remixing. *Ind Eng Chem Res* 50:1473–1487
- Kaibel G (1987) Distillation columns with vertical partitions. *Chem Eng Technol* 10:92–98. <https://doi.org/10.1002/ceat.270100112>
- Kaibel G, Stroezel M, Pfeffinger J (1998) Distillation column for separating a liquid into a plurality of pure fractions. USPTO #5,785,819
- Kaibel GC, Miller M, Stroezel R, et al (2004) Industrieller Einsatz von Trennwandkolonnen und thermisch gekoppelten Destillationskolonnen. *Chem Ing Techn* 76:258
- Kang KJ, Harvianto GR, Lee M (2017) Hydraulic Driven Active Vapor Distributor for Enhancing Operability of a Dividing Wall Column. *Ind Eng Chem Res* 56:6493–6498. <https://doi.org/10.1021/acs.iecr.7b01023>
- Kazemi A, Mehrabani-Zeinabad, A. Beheshti M (2018) Evaluation of various heat pump assisted direct, indirect, Petlyuk and side stripper sequences for three-product separations. *Chem Eng Sci* 181:19–35. <https://doi.org/10.1016/j.ces.2018.02.007>
- Kenig EY, Gorak AA (1995) Film model-based approach for simulation of multicomponent reactive separation. *Chem Eng Process* 34:97–103
- Kenig EY, Pyhalachti A, Jakobsson K, et al (2004) Advanced rate-based simulation tool for reactive distillation. *AIChE J* 50:332–342
- Kim YH (2002) Structural design and operation of a fully thermally coupled distillation column. *Chem Eng J* 85:289–301. [https://doi.org/10.1016/S1385-8947\(01\)00170-X](https://doi.org/10.1016/S1385-8947(01)00170-X)
- Kim YH (2015) Side-rectifier divided wall column for offshore LNG plant. *Sep Purif Technol* 139:25–35. <https://doi.org/10.1016/j.seppur.2014.11.002>
- Kiss AA, Olujić Ž (2014) A review on process intensification in internally heat-integrated distillation columns. *Chem Eng Process Process Intensif* 86:125–144. <https://doi.org/10.1016/j.cep.2014.10.017>
- Kiss AA, Smith R (2020) Rethinking energy use in distillation processes for a more sustainable chemical industry. *Energy* 117788. <https://doi.org/10.1016/j.energy.2020.117788>
- Kiss AM (2013) *Advanced Distillation Technologies Design, Control and Applications*
- Klauzner PS, Rudakov DG, Anokhina EA, Timoshenko A V. (2020) Use of Partially Thermally Coupled Distillation Systems and Heat Pumps for Reducing the Energy Consumption in the Extractive Distillation of an Isobutanol–Isobutyl Acetate Mixture Using Dimethylformamide. *Theor Found Chem Eng* 54:397–406. <https://doi.org/10.1134/s0040579520030070>
- Kloeker M, Kenig EY, Schmitt M, et al (2003) Influence of operating conditions and column configuration on the performance of reactive distillation columns with liquid-liquid separators. *Can J Chem Eng* 81:725–732. <https://doi.org/10.1002/cjce.5450810352>
- Krishna R, Standart GL (1979) Mass and energy transfer in multicomponent systems. *Chem. Eng. Commun. Chem Eng Commun* 3:201–275. <https://doi.org/10.1080/00986447908935865>



- Lestak F, Smith R, Dhole VR (1994) Heat transfer across the wall of dividing wall columns. *Trans Inst Chem Eng* 72A:639–644
- Lewis WK, Whitman WG (1924) Principles of gas absorption. *Ind Eng Chem* 16:1215–220. <https://doi.org/10.1021/ie50180a002>
- Li M, Cui Y, Shi X, et al (2021) Simulated annealing-based optimal design of energy efficient ternary extractive dividing wall distillation process for separating benzene-isopropanol-water mixtures. *Chinese J Chem Eng* 33:203–210. <https://doi.org/10.1016/j.cjche.2020.08.041>
- Li R, Ye Q, Suo X, et al (2016) Improving the Performance of Heat Pump-Assisted Azeotropic Dividing Wall Distillation. *Ind Eng Chem Res* 55:6454–6464. <https://doi.org/10.1021/acs.iecr.6b00937>
- Long H, Clark J, Benyounes H, et al (2016) Optimal Design and Economic Evaluation of Dividing-Wall Columns. *Chem Eng Technol* 39:1077–1086. <https://doi.org/10.1002/ceat.201500106>
- Long NVD, Lee M (2017) *Advances in distillation retrofit*. Springer
- López-Ramírez MD, Barroso-Muñoz FO, Cabrera-Ruiz J, et al (2020) Some Insights in Experimental Studies on the Start-up Operation of a Reactive Dividing Wall Column. *Chem Eng Process - Process Intensif* 159:108211. <https://doi.org/10.1016/j.cep.2020.108211>
- Lorenza, HM, Staak D, Grütznerb T, Repkec JU (2018) Divided Wall Columns: Usefulness and Challenges. *Chem Eng Trans* 69:229–234. <https://doi.org/10.3303/CET1869039>
- Ma Y, Zhang N, Li J, Cao C (2021) Optimal design of extractive dividing-wall column using an efficient equation-oriented approach. *Front Chem Sci Eng* 15:72–89. <https://doi.org/10.1007/s11705-020-1977-y>
- Monroe D (1935) Fractionation apparatus, US-Patent 2,134,882. 1–22
- Mueller I, Eugeny Y. K. (2007) Reactive Distillation in a Dividing Wall Column: Rate-Based Modeling and Simulation. *Ind Eng Chem Res* 46:3709–3719. <https://doi.org/10.1021/ie0610344>
- Mueller I, Kenig EY (2007a) Reactive Distillation in a Dividing Wall Column: Rate-Based Modeling and Simulation. *Ind Eng Chem Process Des Dev* 46:3709–3719. <https://doi.org/10.1021/ie0610344>
- Mueller I, Kenig EY (2007b) Reactive Distillation in a Dividing Wall Column: Rate-Based Modeling and Simulation. *Ind Eng Chem Res* 46:3709–3719. <https://doi.org/10.1021/ie0610344>
- Mutalib MIA, Smith R (1998) Operation and Control of Dividing Wall Distillation Columns. *Chem Eng Res Des* 76:308–318. <https://doi.org/10.1205/026387698524956>
- Okoli CO, Adams II TA (2015) Design of dividing wall columns for butanol recovery in a thermochemical biomass to butanol process. *Chem Eng Proc* 95:302–316. <https://doi.org/10.1016/j.cep.2015.07.002>
- Olujic Ž, Dejanovic I, Kaibel B, Jansen H (2012) Dimensioning multi-partition dividing-wall columns. *Chem Eng Technol* 35:1392–1404. <https://doi.org/10.1002/ceat.201100709>
- Parkinson G (2007) Dividing-wall columns find greater appeal. *Chem Eng Prog* 103:8–11
- Parra-Santiago JJ, Guerrero-Fajardo CA, Sodr e JR (2015) Distillation process optimization for styrene production from a styrene-benzene-toluene system in a Petlyuk column. *Chem Eng Process Process Intensif* 98:106–111. <https://doi.org/10.1016/j.cep.2015.10.017>
- Patle DS, Agrawal V, Sharma S, Rangaiah GP (2021) Plantwide control and process safety of formic acid process having a reactive dividing-wall column and three material recycles. *Comput Chem Eng* 147:107248. <https://doi.org/10.1016/j.compchemeng.2021.107248>
- Patraşcu I, Bildea CS, Kiss AA (2018) Heat pump assisted azeotropic DWC for enhanced biobutanol separation. In: 28th European Symposium on Computer Aided Process Engineering. pp 791–796

- Pattison RC, Gupta AM, Baldea M (2016) Equation-oriented optimization of process flowsheets with dividing-wall columns. *AIChE J* 62:704–716. <https://doi.org/10.1002/aic.15060>
- Pazmiño-Mayorga I, Jobson M, Kiss AA (2021) Conceptual design of a dual reactive dividing wall column for downstream processing of lactic acid. *Chem Eng Process - Process Intensif* 164:108402. <https://doi.org/10.1016/j.cep.2021.108402>
- Petlyuk FB, Platono VM, Slavinskii DM (1965) Thermodynamically optimal method for separating multicomponent mixtures. *Int Chem Eng* 5:555–561
- Preißinger U, Ränger LM, Grützner T (2019) Design Considerations of a Simplified Multiple Dividing Wall Column Pilot Plant. *ChemEngineering* 3:34. <https://doi.org/10.3390/chemengineering3020034>
- Premkumar R, Rangaiah GP (2009) Retrofitting conventional column systems to dividing-Wall Columns. *Chem Eng Res Des* 87:47–60. <https://doi.org/10.1016/j.cherd.2008.06.013>
- Ramírez-Corona N, Jiménez-Gutiérrez A, Castro-Agüero A, Rico-Ramírez V (2010) Optimum design of Petlyuk and divided-wall distillation systems using a shortcut model. *Chem Eng Res Des* 88:1405–1418. <https://doi.org/10.1016/j.cherd.2010.02.020>
- Rangaiah GP, Ooi EL, Premkumar R (2009) A Simplified Procedure for Quick Design of Dividing-Wall Columns for Ind. Applications. *Chem Prod Process Model* 4:1. <https://doi.org/10.2202/1934-2659.1265>
- Ränger LM, Preißinger U, Grützner T (2018) Multiple Dividing-Wall Columns - Current Status and Future Prospects. *Chemie Ing Tech* 91:420–428. <https://doi.org/10.1002/cite.201800080>
- Rawlings ES, Chen Q, Grossmann IE, Caballero JA (2019) Kaibel column: Modeling, optimization, and conceptual design of multi-product dividing wall columns. *Comput Chem Eng* 125:31–39. <https://doi.org/10.1016/j.compchemeng.2019.03.006>
- Reid RC, Prausnitz JM, Poling BE (1987) *The Properties of Gases and Liquids*, 4th Editio. McGraw-Hill, New York
- Rocha JA, Bravo JL, Fair JR (1993) Distillation columns containing structured packings: A comprehensive model for their performance. 1. Hydraulic models. *Ind Eng Chem Res* 32:641–651. <https://doi.org/10.1021/ie00016a010>
- Rocha JA, Bravo JL, Fair JR (1996) Distillation columns containing structured packings: A comprehensive model for their performance. 2. Mass-transfer model. *Ind Eng Chem Res* 35:1660–1667. <https://doi.org/10.1021/ie940406i>
- Ryu J, Maravelias CT (2021) A generalized distillation network synthesis model. *Chem Eng Sci* 244:116766. <https://doi.org/10.1016/j.ces.2021.116766>
- Sánchez-Ramírez E, Ramírez-Márquez C, Quiroz-Ramírez JJ, et al (2020) Design of dividing wall columns involving sustainable indexes for a class of quaternary mixtures. *Chem Eng Process - Process Intensif* 148:107833. <https://doi.org/10.1016/j.cep.2020.107833>
- Sandoval-Vergara R, Barroso-Muñoz FO, Hernández-Escoto H, et al (2008) Implementation of a reactive dividing wall distillation column in a pilot plant. *Comput Aided Chem Eng* 25:229–234. [https://doi.org/10.1016/S1570-7946\(08\)80043-0](https://doi.org/10.1016/S1570-7946(08)80043-0)
- Schultz MA, Stewart DG, Harris JM, et al (1965) Reduce costs with dividing-wall columns. *Chem Eng Prog* 98:555–561
- Segovia-Hernández JG, Hernández S, Sánchez-Ramírez E, Mendoza-Pedroza J (2021) A Short Review of Dividing Wall Distillation Column as an Application of Process Intensification: Geographical Development and the Pioneering Contribution of Prof. Arturo Jimenez in Latin America. *Chem Eng Process - Process Intensif* 160:108275. <https://doi.org/10.1016/j.cep.2020.108275>
- Shi X, Zhao X, Zhang Z, et al (2020) Energy-saving quaternary extractive distillation processes with single- or double-dividing-wall column for separation of acetone/methanol/butanone/tert-butyl alcohol. *Chem Eng Process - Process Intensif* 153:107999. <https://doi.org/10.1016/j.cep.2020.107999>
- Simon LL, Kiss AA, Cornevin J, Gani R (2019) Process engineering advances in pharmaceutical and chemical industries: digital process design, advanced rectification, and continuous filtration. *Curr Opin Chem Eng* 25:114–121. <https://doi.org/10.1016/j.coche.2019.02.005>

- Sotudeh N, Shahraki BH (2007) Extension of a method for the design of divided wall columns. *Chem Eng Technol* 31:83–86. <https://doi.org/10.1002/ceat.200700378>
- Sotudeh N, Shahraki BH (2008) Extension of a Method for the Design of Divided Wall Columns. *Chem Eng Technol* 31:83–86. <https://doi.org/10.1002/ceat.200700378>
- Staak D, Grützner T (2017) Process integration by application of an extractive dividing-wall column: An industrial case study. *Chem Eng Res Des* 123:120–129. <https://doi.org/10.1016/j.cherd.2017.04.003>
- Stewart WE, Prober R (1964) Matrix calculation of multicomponent mass transfer in isothermal systems. *Ind Eng Chem Fundam* 4:224–235. <https://doi.org/10.1021/i160011a010>
- Suphanit B, Bischert A, Narataruksa P (2007) Exergy loss analysis of heat transfer across the wall of the dividing-wall distillation column. *Energy* 32:2121–2134. <https://doi.org/doi.org/10.1016/j.energy.2007.04.006>
- Taylor R, Krishna R, Kooijman H (2003) Real-world modelling of distillation. *Chem Eng Prog* 7:28–39
- Toor HL (1964) Solution of the linearized equations of multicomponent mass transfer: II. Matrix methods. *AIChE J* 10:460–465. <https://doi.org/10.1002/aic.690100410>
- Triantafyllou C, Smith R (1992) The design and optimization of fully thermally coupled distillation columns. *Inst Chem Eng* 70:118–132
- Uwitonze H, Lee I, Suh S-B, Lee I (2021) CFD study of oscillatory motion effect on liquid flow distribution into structured packed divided wall column. *Chem Eng Process - Process Intensif* 165:108429. <https://doi.org/10.1016/j.cep.2021.108429>
- Waltermann T, Sibbing S, Skiborowski M (2019) Optimization-based design of dividing wall columns with extended and multiple dividing walls for three- and four-product separations. *Chem Eng Process - Process Intensif* 146:107688. <https://doi.org/10.1016/j.cep.2019.107688>
- Wang EQ (2013) Application of Dividing Wall Column in Ind. Naphthalene Distillation: A Simulation Study. *Appl Mech Mater* 602:423–426
- Wu Y, Zhang G, Xu J, et al (2020) Enhanced separation of mixing diols by distillation in dividing wall column. *Chem Eng Process - Process Intensif* 149:107859. <https://doi.org/10.1016/j.cep.2020.107859>
- Xie J, Li C, Peng F, et al (2018) Experimental and simulation of the reactive dividing wall column based on ethyl acetate synthesis. *Chinese J Chem Eng* 26:1468–1476. <https://doi.org/10.1016/j.cjche.2018.01.021>
- Yildirim Ö, Kiss AA, Kenig EY (2011) Dividing wall columns in chemical process industry: A review on current activities. *Sep Purif Technol* 80:403–417. <https://doi.org/10.1016/j.seppur.2011.05.009>
- Zang L, Huang K, Yuan Y, et al (2020) Vapor recompressed dividing-wall distillation columns: structure and performance. *Chinese J Chem Eng* 28:1891–1897. <https://doi.org/10.1016/j.cjche.2020.05.005>
- Zhai J, Liu Y, Li L, et al (2015) Applications of dividing wall column Technol. to industrial-scale cumene production. *Chem Eng Res Des* 102:138–149. <https://doi.org/10.1016/j.cherd.2015.06.020>
- Zhou J, Kooijman HA, Taylor R (2019) Parallel column model for Dividing Wall Column simulations. *Comput Chem Eng* 125:114–133. <https://doi.org/10.1016/j.compchemeng.2019.02.008>
- Zhu J, Jing C, Hao L, Wei H (2021) Insight into controllability and operation of extractive dividing-wall column. *Sep Purif Technol* 263:118362. <https://doi.org/10.1016/j.seppur.2021.118362>