

# Energy Minimum Design and Systematic Analysis of the Reactive Dividing Wall Column

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The reactive dividing wall column (RDWC) is a highly integrated apparatus, which combines a reactive distillation and a dividing wall column in one single shell. Thus, high savings in investment as well as operational costs can be achieved compared to conventional process alternatives. Due to the high grade of integration the process behavior of the RDWC is strongly nonlinear and extremely complex. Hence, it is not trivial to understand how the process performs in detail and to predict the advantageousness of the RDWC for a given task during conceptual design.

Still, for a safe and energy efficient design as well as a steady operation in the industrial praxis it is essential to know, how the process performances and for which tasks the RDWC is more advantageous than less integrated process alternatives. Therefore, the aim of this research is to generate a profound process understanding and identify process applications for the RDWC. The investigations carried out focus on the influence of non-ideal reaction system properties, such as azeotropic phase equilibria. To determine the best process integration level, the energy optimal designs of the RWDC and less integrated process alternatives are determined and compared. By applying this procedure suitable reaction system characteristics can be identified and so, process applications for the RDWC can be derived. Moreover, heuristics regarding the optimal level of process integration can be deduced. This leads to an easier determination of the optimal process integration level and an acceleration of the conceptual design phase.

## 1. Introduction

Process intensification has become an important concept to meet the challenges of an increasing global competition in the chemical industry. A promising possibility of process intensification is the integration of primarily separated process operations into one single shell (Lutze et al., 2010). Examples are the reactive distillation (RD) or the dividing wall column (DWC). A further integration step leads to the highly integrated reactive dividing wall column (RDWC), shown in Figure 1. The RDWC enables a reaction and a simultaneously multicomponent separation in one single shell. So, significant savings in investment as well as operating costs can be achieved with RDWC compared to process alternatives. So far, savings from 15 - 75 % of energy and more than 20 % of investment costs have been reported in literature (Weinfeld et al., 2018).

Even though RDWC is known since 1984 (Kaibel, 1984), it has still not been applied in industry. The high grade of integration leads to a high complexity and a strong nonlinear process behavior. Hence, design and operation of RDWC are extremely demanding. To date research regarding modelling, design, operation and control of RDWC has been published with an increasing tendency. For a detailed overview of the current research activities the reader is referred to Weinfeld et al. (2018).

Schröder et al. (2016) show that for energy optimal operation the component flows in the column and the resulting realized splits are important parameters. The split in the prefractionator of the RWDC can be characterized by the feedsplitt. Latter states the molar fraction of the feed stream that leaves the upper part of the prefractionator. The behavior in the prefractionator of the RDWC equals the one of a reactive distillation, so that the feedsplitt is equatable to the distillate/feed-ratio ( $D/F$ ) in the RD. The design for RDWC has been studied for various reaction systems using rigorous or shortcut models. In experiments with exemplary reaction systems equilibrium stage models (Delgado-Delgado et al., 2011; Egger and Fieg, 2017b; Ehlers et

al., 2017; Harbou et al., 2017) as well as non-equilibrium models (Müller, 2010) have been validated for RDWC. Additionally, first start-up and control strategies have been analyzed (Dai et al., 2015; Egger and Fieg, 2017a).

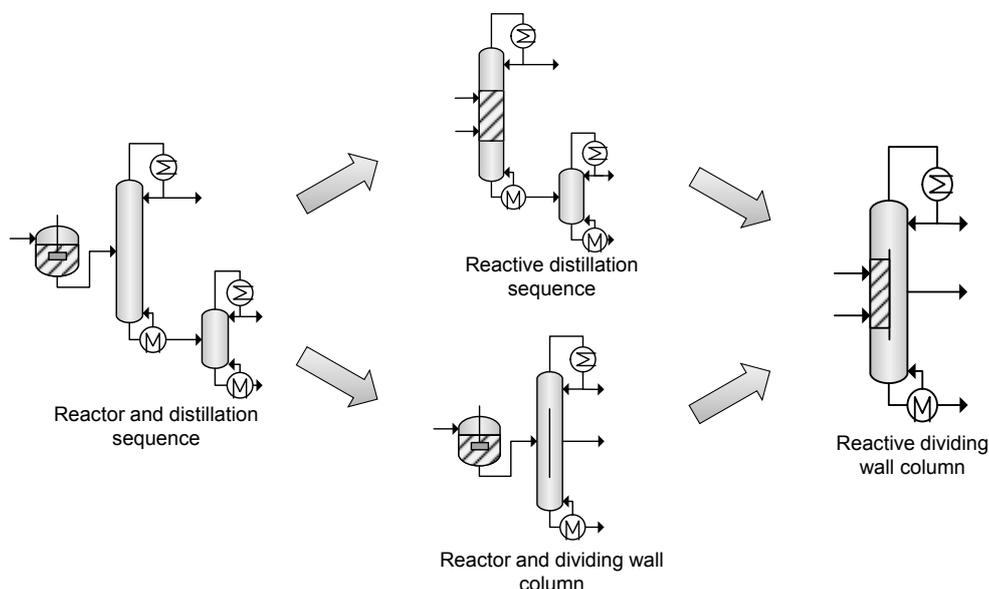


Figure 1: Levels of process integration: reactor and direct distillation column sequence, direct reactive distillation sequence, reactor and dividing wall column and reactive dividing wall column

Nevertheless, a detailed view on all the reaction systems published for RDWC shows a high diversity in their reaction system properties. Thus, the identification of suitable applications and the prediction of the advantageousness of the RDWC for a given task are quite challenging.

In general Müller (2010) states that reactive systems with three product fractions can be applied in RDWC. These fractions can be products of the reaction, non-reacting components or excessive reactants. Schröder and Fieg (2016) firstly analyzed the influence of ideal reaction system properties on the RDWC systematically. As a result, an ideal class of reaction systems has been identified, which offers optimal characteristics for RDWC. Additionally, two main mechanisms for energy savings compared to the process alternative of a reactive distillation sequence (RDS) have been determined: savings for the product separation and for the reaction.

Unfortunately, many reaction systems do not show ideal behavior. Therefore, the aim of this work is to analyze the effect of non-ideal reaction system properties on the energy minimum design and the energy saving potential of the RDWC systematically. As a result, suitable reaction systems characteristics can be identified and so process applications for the RDWC can be derived. Moreover, easy applicable heuristics regarding the optimal level of process integration can be deduced, so that the conceptual design phase can be accelerated.

## 2. Methodology

The analysis of the effect of non-ideal reaction system properties on the energy saving potential of the RDWC is carried out by systematic simulation studies. These simulation studies are applied to a quinary reactive system, shown in Figure 2a. The reactants A and B react to the products C and D. As is well known, additional secondary components with unknown kinetics, excess reactants or impurities often occur in industrial practice. These are represented by an inert component E, which, in addition to the reaction products C and D, is to be recovered as the third product stream in the RDWC. For a detailed description of this reaction system the reader is referred to Schröder et al. (2016), who identified the optimal order of boiling points of an ideal behavior of this reaction system for application in RDWC. Here, the products of the reaction are the heaviest and lightest boiling components, whereas the reactants act as intermediate boiling components. The middle boiling component of the reaction system is represented by the inert E (Figure 2a).

Based on these results the effect of non-ideal reaction system properties is investigated. As a first step, the influence of azeotropic phase equilibrium is analyzed. In practice, azeotropes can be divided into temperature maximum and temperature minimum azeotropes. Latter occur more often (Gmehling et al., 2015), so this work focuses on the influence of temperature minimum azeotropes. To utilize the advantage of the integration of

reaction and separation azeotropes of reactants and products are studied, as shown in Figure 2a. Here, the name of the study refers to the azeotrope added to the reaction system. For the simulation of these azeotropes vapor-liquid equilibrium data are mandatory. The required activity coefficients are calculated by the NRTL-method. An overview of the NRTL-parameters of the investigated azeotropes is given in Table 1. These parameters are chosen such that in all cases a homogeneous minimum temperature azeotrope is present in accordance with the boiling sequence shown in Figure 2a. In each study the phase equilibrium of two components of the ideal reaction system is modified only while the other components do not interact with each other. This approach allows a targeted analysis of the influence of azeotropes for the presented class of reaction systems on the process of RDWC.

Table 1: NRTL-parameters for the investigated azeotropes

	ij	CA	AE	EB	BD
NRTL-parameter					
$b_{ij}$		395.90	627.83	270.58	72.81
$b_{ji}$		234.55	-52.24	55.67	484.20

For each reaction system the minimum energy demand of the RDWC is compared to the energy demand of the process alternative, a reactive distillation sequence (RDS). In Figure 1 an exemplary direct RDS is shown. Both process models are implemented in Aspen Custom Modeler. To reduce calculation time, the RDWC is decomposed into a prefractionator and thermally coupled main columns. The energy demand of the prefractionator is equatable to the energy demand of a reactive distillation (Schröder et al., 2016), so that the total energy demand of the RDWC can be calculated by Equation 1 as the sum of the energy demand of a reactive distillation and the maximum of the additional vapor demand of the thermally coupled main columns (MC).

$$V_{min}^{RDWC} = V_{min}^{RD} + \max(V_{min}^{MC1}, V_{min}^{MC2}) \quad (1)$$

The RD is modeled by an equilibrium stage model assuming no heat losses and no pressure drop. The feed and product streams are boiling liquids and the reaction is heterogeneously catalyzed and occurs only in the liquid phase. The amount of each feed stream into the column is 50 kmol/h with a molar fraction of 10 mol% of inert and a molar fraction of 90 mol% of reactant. The additional columns are also modeled by an equilibrium stage model. For the main columns of RDWC a superheated/subcooled feed stream is assumed, whereas the feed stream of the distillation column in RDS is assumed to be a boiling liquid.

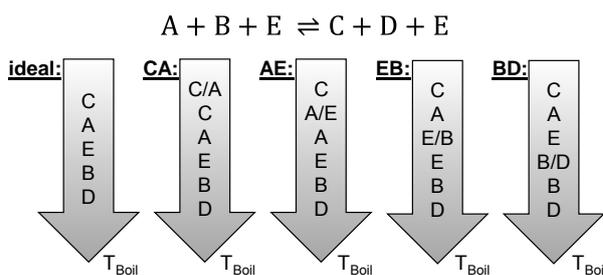


Figure 2a: Reaction and order of boiling points for all investigated reaction systems

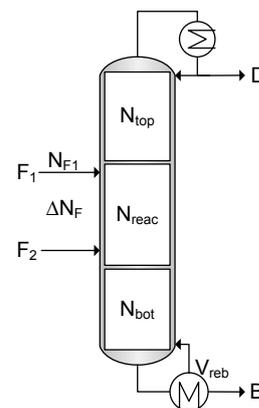


Figure 2b: Schematic design variables of reactive distillation column

For the determination of the energy minimum design the number of reactive and non-reactive stages as well as the upper feed position and the distance between the feed positions are changed systematically via an automatic procedure implemented in Matlab. As stated in the introduction, the D/F ratio is an important parameter for energy optimal operation. Thus, it is chosen as a design variable as well. For each combination of these design variables the minimum vapor demand ( $V_{Reb}$ ) for a molar conversion of 99.5 % of the reactant A is determined. A visualization of the design variables of the RD is given in Figure 2b. The discretization of these variables for the simulation studies is presented in Table 2.

Table 2: Design variables for systematic simulation studies

Design Variable	Lower Bound	Upper Bound	Step Size
D/F ratio	0.45	0.55	0.1
Upper feed position $N_{F1}$	1	$N_{\text{reac}}$	1
Distance of feed positions $\Delta N_F$	0	$N_{\text{reac}}$	1
Number of stages top segment $N_{\text{top}}$	10	50	10
Number of reactive stages $N_{\text{reac}}$	60	100	20
Number of stages bottom segment $N_{\text{bot}}$	10	50	10

Subsequently, the corresponding minimum vapor demands of the main column for RDWC and of the additional distillation column for RDS are calculated. As a result, the total minimum energy demand of the process alternatives RDWC and RDS can be compared objectively and the energy saving potential of the RDWC can be determined.

### 3. Results

The minimum vapor demand of the prefractionator to achieve a molar conversion of 99.5 % in dependency of the D/F ratio as a measure of the component flows in the column is shown in Figure 3 for all investigated reaction systems. It can be seen, that the vapor demand of the prefractionator is highly influenced by the D/F ratio. In the studies ideal, CA, AE and BD suitable designs over the whole range of the D/F ratio exist, whereas the study EB shows only designs for a small range of the D/F ratio. Additionally, it stands out that the study ideal and CA show a similar trend, whereas the trend of AE und BD differ clearly from the prior mentioned. In the following these results will be analyzed in detail.

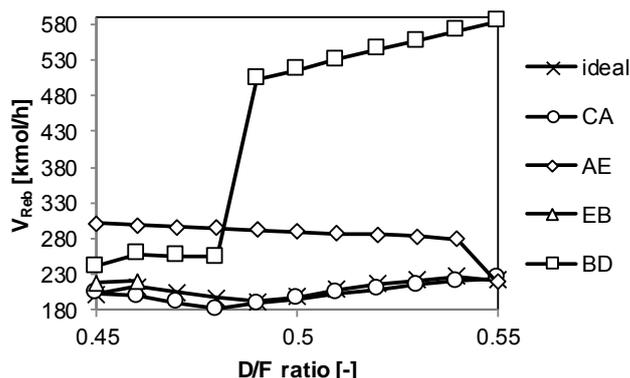


Figure 3: Minimum vapor demand of the prefractionator of RDWC for the investigated reaction systems

For an efficient reaction it is important that the products are continuously removed from the reactive zone. Additionally, the reactants need to stay in the reactive zone and do not get pushed out of it. Only then a nearly full conversion and consequently high purity product streams can be achieved. To ensure this high conversion a sharp split of the reactants A and B is required in the prefractionator. For the ideal reaction system this sharp split is realized for all D/F ratios investigated. At a D/F ratio of 0.45 the whole fraction of the middle boiling component E leaves the lower part of the prefractionator, whereas a ratio of 0.55 indicates that the whole fraction of E leaves the upper part of the prefractionator. Values between those bounds indicate a distribution of E to both ends of the prefractionator, which lead to a lower vapor demand for the reaction as described by Schröder and Fieg (2016). Additionally, a non-sharp split of the products CED is carried out in the prefractionator, which leads to a lower vapor demand than sharp product splits.

For the CA-azeotrope the described mechanisms persist, so that the results show a similar trend compared to the ideal reaction system. Due to the fact that the azeotrope is the lightest boiling component, C can be removed from the reactive zone easier resulting in a lower total vapor demand. However, component A has to be fully converted until the top of the reactive zone. Otherwise, the CA-azeotrope will impurify the distillate stream. This results in a smaller D/F ratio than for the ideal reaction system.

The reaction system with AE-azeotrope reaches the requested conversion for all D/F ratios. Though,  $V_{\text{Reb}}$  decreases continuously with an increasing D/F ratio. Additionally, compared to the ideal and CA case, a much higher  $V_{\text{Reb}}$  is required for D/F ratios from 0.45 to 0.54. Due to the AE-azeotrope component A needs to be

fully converted until the upper end of the reactive zone to avoid impurities in the distillate stream. Therefore, the feed position of the lower feed has to be in the lower part of the reactive zone. As a result, component A is also present in the lower non-reactive segment and has to be pushed back into the reactive zone. If a ratio of E has to leave the lower part of the prefractionator, a separation of D and E from A has to be carried out. Due to the non-ideal phase equilibrium this separation is much more difficult and thus, a higher  $V_{\text{Reb}}$  is required. For a D/F ratio of 0.55 the whole fraction of E leaves the upper part of the prefractionator, at which end A is fully converted. As a result, this sharp split of the heaviest boiling component D and the middle boiling component E in the prefractionator shows the minimum vapor demand. The resulting column configuration is a side-stripper configuration, since only a separation of the lightest boiling component C and the middle boiling component E has to be carried out in the main column.

The EB-azeotrope affects the order of boiling points in the region of the reactants and inert. To realize a sharp split of the reactants a split of component A and the EB-azeotrope has to be carried out in the prefractionator. Therefore, only designs with a low D/F ratio lead to the requested conversion. Other splits will lead to lower conversions and thus to lower product purities. This separation is more difficult compared to the separation of A and E due to a lower difference in the boiling points, so that  $V_{\text{Reb}}$  for the EB-azeotrope is higher than  $V_{\text{Reb}}$  for the ideal reaction system and the one with a CA-azeotrope. Since a D/F ratio of 0.45 and consequently a sharp split of C and E in the prefractionator leads to the lowest vapor demand, a side-rectifier configuration of the RDWC is preferable for this reaction system.

The BD-azeotrope hinders the removal of the reaction product D from the reactive zone. Due to the lower boiling point of the BD-azeotrope the product D is pushed back into the reactive zone, resulting in a lower conversion. To overcome this problem a higher  $V_{\text{Reb}}$  is required and the split in the prefractionator has to be chosen in a way that despite the azeotrope a continuous removal of D from the reactive zone is achieved. Therefore, only designs with a low D/F ratio ensure the requested conversion with a reasonable vapor demand. For higher D/F ratios the vapor demand increases drastically due to the difficult removal of D from the reactive zone. Thus, the energy minimum design of RDWC for the reaction system with BD-azeotrope is also a side-rectifier configuration as for the EB-azeotrope.

In summary, it can be concluded that the investigated azeotropic reaction systems highly affect the energy minimum design of the RDWC. For the CA-azeotrope symmetric configurations of the RDWC are preferable, whereas the AE-, EB- and BD-azeotrope lead to asymmetric configurations of the RDWC.

For all energy minimal configurations of the prefractionator the minimum vapor demand of the corresponding main column is calculated to obtain the total minimum vapor demand of the RDWC regarding Eq. 1. For the RDS only a direct or an indirect sequence are of practical relevance. For such splits the minimum vapor demand of the additional distillation column is calculated to determine the total vapor demand of the RDS. The results of the minimum vapor demand of the RDWC as the sum of the vapor demand in the prefractionator and the main column in comparison to the minimum vapor demand of the RDS (sum of vapor demand of the RD and the additional distillation column referred to as *sequence*) are shown in Figure 4.

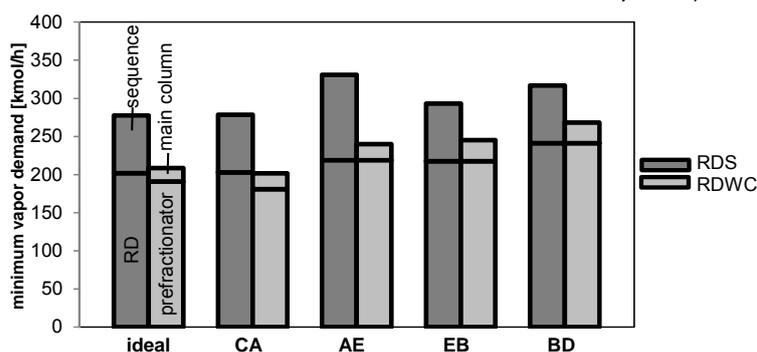


Figure 4: Minimum vapor demand of the RDWC compared to the minimum vapor demand of the RDS

As can be seen, the RDWC offers an energy saving potential compared to the RDS for all studied cases. Though, the total amount of the savings differs with the properties of the reaction system.

In the RDS the vapor demand of the distillation column is the same for all investigated cases except AE. Here, the energy minimum configuration is an indirect sequence, whereas for all other cases a direct sequence is preferable. Compared to the vapor demand of the main column in the RDWC the vapor demand of the sequence is much higher. So, for all cases the thermal coupling of the prefractionator and main column leads to a more efficient separation. Furthermore, the symmetric configurations of the RDWC (ideal and CA) show a reduced vapor demand in the prefractionator compared to the RD due to non-sharp splits in the prefractionator. For the azeotropes AE, EB and BD these additional savings do not apply. Due to the changed

order of boiling points, sharp splits in the prefractionator have to be carried out to achieve the requested conversion.

Overall, the reaction system with CA-azeotrope shows the highest energy saving potential of 27.6 %. Nearly the same amount of savings (27.5 %) can be achieved with the reaction system with AE-azeotrope due to high savings for the product separation. With the ideal reaction system savings of 24.9 % can be realized, whereas the azeotropic reaction systems EB and BD show a reduced energy saving potential of 16.4 % and respectively 15.4 %.

#### 4. Conclusions

In this work the effect of selected azeotropic reaction systems on the design and energy saving potential of the RDWC has been analyzed systematically. The results indicate suitable reaction systems characteristics and give a profound process understanding of RDWC. It was shown, that the reaction system with CA-azeotrope promotes the reaction and leads to high energy savings of up to 28 % compared to the process alternative of a RDS. For the reaction systems with AE-, EB- and BD-azeotrope a sharp split in the prefractionator is necessary to achieve a high conversion and minimum energy demand. Therefore, asymmetric configurations of RDWC are preferable. Nevertheless, still high energy savings of 15 – 28 % can be realized due to the thermal coupling of the prefractionator and main column.

Our future research will continue the analysis of non-ideal reaction system properties in the RDWC considering enthalpy of vaporization and reaction. With the results easy applicable heuristics regarding the optimal level of process integration will be deduced and process applications for the RDWC will be derived.

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