Novel method for mapping the applicability of reactive distillation

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ABSTRACT

Reactive distillation (RD) is a great process intensification concept applicable to equilibrium limited reaction systems, but how can anyone decide quickly if RD is indeed worth applying? To answer this question, this study proposes a mapping method for checking the applicability of reactive distillation (RD). The initial development is for one of the most relevant subset of quaternary reversible reactions (A + B ⇄ C + D, with boiling points \( T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D} \), by using only basic chemical (equilibrium and kinetics) and physical (relative volatilities) parameters. Generic cases, assuming ideal thermodynamics and constant parameters, are used to obtain a set of RD applicability graphs that provide broad insights into the RD operation. In addition, the new mapping method provides reasonable estimates of the RD applicability to real (non-ideal) chemical systems based on the available pre-defined maps (which are actually applicability graphs of the generic ideal cases). This new approach leads to a straightforward estimation of the applicability of RD to real systems, prior to performing any rigorous process simulations and without any clear-cut decision making (as used in previous studies).

1. Introduction

Reaction and separation, the most important operations in the chemical industries, are usually carried out in different sections of a production plant, and require different types of process equipment. A reactor is an operating unit where the actual transition of feedstock into products takes place. In most cases, next to the desired main product, some by-products are also formed. Accordingly, a separation step is needed to obtain the desired product(s) at sufficient purity. Distillation is a separation technology that is most commonly applied, but it is also one of the major energy users in the chemical industry. Since the mid of 20th century, scientific literature and patents related to the improvement of reaction and separation equipment design focus on energy savings and economic efficiency [1]. Combining reaction and separation in a single unit is an excellent example of process intensification. Reactive distillation (RD) is one of such processes and it stands out as a successful story of a process intensification technology for enhanced manufacturing of chemicals [2,3]. RD combines a reactor and a distillation column into a single unit operation (see Fig. 1). In the RD column, the reactants are converted while simultaneously separation of the products occurs. The advantages and limitations of RD over conventional multi-unit processes for specific applications have been known for a long time and can be found in many articles and books [4–8]. RD configuration is especially beneficial for chemical equilibrium limited reactions, e.g. (trans-)esterification, etherification, hydrolysis, alkylation, as the equilibrium composition can be shifted towards product formation. The most encountered class of reactions are:

\[
A + B ⇄ C + D \text{ (quaternary systems)} \\
A + B ⇄ C \text{ (ternary systems)}
\]

RD has been industrially used for more than 25 years, for applications with capacities up to 3000 kton/year [9]. Current applications of RD are mostly for esterification reactions, with the production of methyl acetate as a prime example [10]. Other processes in which RD has been successfully applied are in the production of ethers: methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME) [8]. Many prospective chemical systems (which are neither extremely exothermic nor endothermic) for the RD application are also listed in the open literature [11–13].

The available reactive distillation design methods can be classified into three main groups, based on: 1) graphical/topological considerations, 2) optimization techniques, 3) heuristic/evolutionary approaches [14], which are presented in literature [7,15–24]. There are various outputs of those design methods consisting of RD structure (operating conditions and RD configurations), feasibility assessment, and/or RD...
controllability. In addition, there are also methods to check the feasibility of RD for various systems, but they rely mostly on clear-cut decision making procedures (e.g. if the equilibrium constant or the reaction rate is lower than a specific value then RD can be dismissed) while the reality shows that grey areas also exist and they should not be easily discarded (especially for systems with high value products).

Most of the current design methods in literature are well-established and can be used to design a RD column. However, rigorous calculations and/or detailed simulations are usually required to apply the methods for each chemical system and repeated calculation efforts are needed when other chemical systems are investigated, therefore they are considerably complex and time consuming. Following the progressive growth of the number of developed RD design methods, a critical consideration is to enable a quick assessment of the RD applicability, prior to performing any rigorous simulations of the RD process, thus providing sufficiently accurate information about the applicability of RD and being an important aid for a go / no-go decision at an early stage of the process design.

2. Approach and methodology

At the initial stage of the development of the RD mapping method, the focus has been limited only to certain levels (but this will be extended further in future studies):

- The assessed quaternary systems are reactions with mid-boiling reactants (A + B ⇌ C + D, with T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}) as this subset of the quaternary systems is the most commonly encountered.
- The RD configuration (see Fig. 1) is a single column with three different sections (i.e. rectifying, reactive and stripping sections), a condenser at the overhead part and a reboiler at the bottom part. For the sake of simplicity, the feed inlets are fixed on the top and the bottom parts of reactive section (as common industrial operation). Varying the feed inlets inside the reactive section may or may not (slightly) improve the achievable conversion.
- Case studies presented in this study are real reaction systems that are less hindered due to significant non-ideality. Further developments of the mapping method need to cover more complicated reaction systems (e.g., complex azeotropes, liquid split).

To perform any RD operation, some inputs have to be specified and fixed. Fig. 2 presents key parameters of the RD operation in this study. The fixed inputs in this study are highlighted by the bold letters. The feed streams of pure A and B are fed in a stoichiometric ratio (as saturated liquid) to the RD column operating at an atmospheric pressure. For the sake of simplicity, the light reactant is fed at the bottom part of the reactive zone and the heavy reactant is fed at the top of the reactive zone in order to obtain a counter current flow along the reactive zone. With those specified feed locations, the RD configuration used in this study is shown in Fig. 1. There are two important design criteria:

![Fig. 1. Schematic representation of a reactive distillation column.](image-url)
constraints specified, which are a bottom product purity and a 0.5 mol/mol bottom-to-feed (B/F) ratio. The specified value of the B/F ratio is in accordance with the stoichiometric ratio of these quaternary reaction systems. Except for the part of investigating the effect of product purity, a ≥ 99 mol% of bottom product purity was always set. By setting the B/F ratio and product purity, the minimum overall conversion is 99 mol%.

The RD mapping method uses a set of applicability graphs of RD, i.e. the plots of RR vs NTS, which are generated from generic cases. A generic case is defined by specifying ideal vapor-liquid behavior and constant parameters, i.e. α, K_eq and chemical kinetics. The combination of those basic parameters gives unique applicability graphs to a certain case (see the Supporting information, Table S1). A procedure to generate an applicability graph of a generic case is presented in Fig. 3. All simulations were performed using the process simulator Aspen Plus v8.6, by applying a sensitivity analysis and an optimization tool. The sensitivity analysis was utilized to vary the configurations of RD (i.e. numbers of rectifying, reactive and stripping stages) for each NTS. At the same time, for each configuration the optimization tool was used to provide a solution with a minimized RR. Combining the sensitivity analysis and the optimization tools to minimize RR for any RD configuration distinguishes the method proposed in this work from other design methods that aim to estimate the RR_{min} for an infinite NTS using short-cut methods, such as the works of Doherty et al. [26-29].

Fig. 4 shows an illustrative applicability graph of RD for a certain chemical system. The dotted line is a boundary line which divides the plot regions into ‘applicable’ and ‘not-applicable’ areas. Inside the applicable area and exactly on the boundary line, the operation of RD is conceivable since the product purity specification is equal or better than the minimum criterion. For each NTS, there are multiple solutions of RD configurations which are available with different RR values (see the Supporting information, Fig. S1 and Table S2). Along the boundary line, the lowest RR possible is plotted for each NTS. Above the boundary line, the RR is higher for each NTS with either higher product purity or varied distributions of number of rectifying, reactive and stripping stages.

Fig. 2. Key parameters of the RD operation.

Fig. 3. Procedure to generate an applicability graph of a generic case.
stripping sections. The vertical asymptote of the boundary line shows the NTS\textsubscript{min} which has different RD configurations by the increase of RR. Correspondingly, the horizontal asymptote of the boundary line indicates the RR\textsubscript{min} which has different column configurations by the increase of NTS (see the Supporting information, Fig. S2 and Table S3). Outside (left from or below) the boundary line, the design criteria cannot be achieved therefore the RD operation is not applicable.

Point 1 and 2 highlight two different spots on the boundary line and inside the applicable area, respectively, where both have the same NTS. At point 2, the RR is higher than the value at point 1. Operating a RD setup with a higher RR may not be interesting in terms of energy requirement, but it is also essential to consider the RD configurations (i.e. number of rectifying, reactive and stripping stages) and product criteria in its application. At some spots inside the applicable area (such as point 2, in comparison to point 1), RD configurations with either a higher product purity specification (which will be discussed in the next section) or less number of reactive stages (but more separating stages since NTS is constant), could be obtained. Obtaining a higher purity product may be preferred and having a shorter reactive section with a slightly higher RR may reduce the costs up to a certain level. Although point 1 provides the lowest RR, selecting point 2 or another spot with a better configuration or a higher purity product inside the applicable area can still be considered.

In practice, it is favorable to have an RD design with smaller NTS and lower RR. Although the RD configurations inside the applicable area are conceivable, the operation of RD is not attractive above a certain practical limit of NTS and RR. In Fig. 4, the color of applicable area from the bottom-left to the top-right corner shifts from lighter to darker shading. The lighter color illustrates the preferred region in the RD feasibility check, as lower capital investments and energy costs can be obtained.

For the sake of presenting clear images limited to realistic values, this study shows only the applicability graphs with the maximum scale of 100. The NTS\textsubscript{min} is defined as the NTS for RR = 100, the RR\textsubscript{min} is the lowest RR on the boundary line in the case of NTS = 100. In the RD design, engineers must consider the proportionality aspect, i.e. ratio of height to diameter of the column. Selecting the NTS\textsubscript{min} on the top-left of the applicable area leads to the requirement of a high RR which results in a short column with a large diameter. On the other hand, choosing the column configuration with the RR\textsubscript{min} on the bottom-right of the applicable area gives a slim and tall column.

Equilibrium limited reactions are investigated first, followed then by kinetically controlled reactions (where achieving the equilibrium is practically limited by the slow kinetics). The equilibrium system gives the best performance for the RD column, as it is only limited by the...
chemical equilibrium, so this is the best case scenario.

For slow(er) reactions, the RD operation is greatly affected by the extent and effectiveness of the contact between the internal liquid flow and the catalyst. To represent important parameters that give influence on the applicability of RD in the case of kinetically controlled reactions, the Damköhler (Da) number was specified. The Da number is a powerful parameter as it characterizes the effect of chemical kinetics and the RD design inputs, i.e. liquid residence time/hold-ups, catalyst loading. A small Da refers to slow kinetics, a low catalyst loading, a short liquid residence time due to low liquid hold-ups or high liquid flow rate in the reactive parts of an RD column. Utilization of the Da number in the kinetically controlled reactions for RD technology has been common practice in many previous research studies[30-33].

In this study, the formula of a modified Da number per stage is expressed in Eq. (1).

\[
Da = \frac{k_f \cdot \beta \cdot \tau}{\varepsilon} 
\]  

The Da number (dimensionless unit) indicates the ratio of a characteristic liquid residence time to a characteristic reaction time [33]. The liquid residence time per stage (\(\tau\)) is defined as the liquid hold-up per stage on volume basis relative to incoming volumetric flow rate per stage. The characteristic reaction time is taken from the reaction rate constant. The modified Da number has the concentration effect inside the \(k_r\) while \(\beta\) stands for the catalyst loading per stage which is expressed in the volumetric ratio between the catalyst amount and the total hold-up per stage. In this study instead of defining the liquid holds-up along the column, the \(\tau\) was specified as a design input to determine the Da number. Setting \(\tau\) is practical and easy for the RD operation, as usually there is a maximum allowed \(\tau\) of up to 4–5 min [6,34,35]. To the best of our knowledge, based on industrial experience, \(\tau\) is typically up to 120 s per stage.

In any real systems, the Da number along the column changes for each reactive stage as the rate constant is dependent on temperature. In the generic case, the Da number defined is constant for each stage, i.e. with more reactive stages and a higher RR (a larger diameter), more catalyst is loaded.

3. Insights into the RD operation

The influences of various input parameters on the applicability of RD are investigated in case of equilibrium limited and kinetically controlled reactions. In the subsection of equilibrium limited reactions, the influence of product purity, chemical equilibrium constant, relative volatility set is presented. To provide a comprehensive investigation, the \(K_{eq}\) was varied from 0.01 to 10 (covering the practical range of reactions in terms of the RD application). In the subsection of kinetically controlled reactions, the applicability of RD (with a low and a high \(K_{eq}\) values) is explained linked to the equilibrium limited reactions. The Da number is varied from 0.01 to 1. A relative volatility combination of \(\alpha_{AB} = 1.5, \alpha_{AC} = 2, \alpha_{CD} = 2 \left( K_A : K_B : K_C : K_D = 3 : 2 : 6 : 1 \right) \) was selected as a realistic base case (see for example Fig. 5).

The size of RD applicability areas is an essential indicator when the applicability of RD is evaluated for different cases with various input parameters. The \(NTS_{min}\) and the \(RR_{min}\) are essential parameters as they are limiting the boundaries of the applicability areas.

To provide the insights into RD operation, the RD column configuration at \(NTS = 2 NT_{S_{min}}\) is presented next to the applicability graph. For each NTS, various RD configurations with RR values up to 3% higher than the lowest RR-value were considered since there are multiple solutions available with only marginal change of RR (see an example in the Supporting information, Fig. S1 and Table S2). Setting this rule seems realistic as very slight change of RR (i.e. the difference is two decimal places) is often negligible in practice. Due to the existence of multiple RD configurations, many trends of RD configurations can be observed. Therefore, the users of the method can quickly draw different essential insights into the RD operation, which become a major advantage offered by the mapping method. In the current work, only some essential insights are presented based on hand-picked results from the RD configurations obtained, following the mentioned RR rule (\(NTS = 2 NT_{S_{min}}\)), so that trends of the RD configurations can be identified.

The variety of insights due to the availability of multiple RD configurations will be shown in the discussion of the influence of product purity (see subsequent section). Two possible trends of RD configurations are presented in that section based on results selected with the objective to keep either the number of separative or reactive stages (more or less) constant. For the rest of sections, a possible trend of RD configurations will be provided by primarily considering the RD configuration with the lowest RR, but still checking the other possible RD configurations with the RR values up to 3% higher than the lowest value.

Note that it is possible to use other points to provide the insights into the RD operation, e.g. the RD configuration at \(RR = 1.2 \cdot RR_{min}\) or at any other points. Referring to \(NTS = 2 NT_{S_{min}}\) this is only based on the previous knowledge for the estimation of the optimum configuration of conventional distillation columns. A rule of the thumb for the optimum configuration for reactive distillation systems needs to be developed in the near future. For a given RD configuration, the stage number includes condenser (defined as total condenser) and reboiler of the column. The underlined number shown above each bar (see for example Fig. 5, b) is the RR for each configuration.

3.1. Equilibrium limited reactions

3.1.1. Influence of product purity

Fig. 5 (a) displays the applicability graph of the base case (\(K_{eq} = 0.01\)) for different bottom product purities. Obviously, for higher product purity the applicability area becomes smaller. In line with the explanation about the applicability graph in the previous section, higher product purities can be obtained inside the applicable area of a 90 mol% of the bottom product purity.

A higher product purity results in a smaller size of the applicability area of RD. Comparing two end-points of the boundary line of the applicability area, the effect of higher product purity is more dominant on the growth of the \(NTS_{min}\) than the increase of \(RR_{min}\). This phenomenon is explained by two possible trends in the RD configurations. Firstly, Fig. 5 (b) shows the selected RD configurations with (more or less) constant number of separative stages. With that objective, the growth of NTS is mainly caused by the requirement of extra reactive stages for a better conversion/separation, as expected. This result shows that the reactive stages contribute to the separation task. For the highest product purity of 99.9 mol%, the addition of reactive stages alone is not sufficient and the number of separative stages needs to be increased.

Secondly, Fig. 5 (c) presents the RD configurations with (more or less) constant number of reactive stages. As the consequence of that objective, the addition of extra rectifying and stripping stages becomes a key solution to obtain higher product purity. Adding more reactive section could help to obtain a higher conversion, but without adequate product separation the conversion is limited at its equilibrium value (see Fig. S3 in the Supporting information). Since the targeted conversion in this study is much higher than its equilibrium conversion (corresponding to the specified product purity, see Fig. 5 a), adding stripping and rectifying stages can be more favorable than having more reactive stages.

In general, a higher RR might also help to endorse the reaction performance. However, a higher RR can lead to the accumulation of products along the column which in the end facilitates the backward reaction and gives difficulty to obtain very high product purity. Performing this analysis with other \(K_{eq}\) values and/or for kinetically controlled reactions gave identical insights into the RD operation.
Fig. 6. The applicability areas of RD and their configurations at NTS = 2
NTSmin in case of equilibrium limited reactions for (a and b) αAB = 1.5, αCA = 2, αBD = 2, (c and d) αAB = 1.5, αCA = 1.2, αBD = 2, (e and f) αAB = 1.5, αCA = 2, αBD = 1.2, (g and h) varied αAB, αCA = 2, αBD = 2 considering Keq = 10.
3.1.2. Influence of the chemical equilibrium constant

Fig. 6 (a) shows the impact of the Keq on the applicability areas of RD for the base case. For Keq = 0.01, the NTSmin (RR \(\approx\) 100) is 22 and the RRmin is 11, while for the most favorable case of Keq = 10, the NTSmin \(\approx\) 100 and the RRmin both are much lower, 12 and 2 respectively. Accordingly, the RD applicability area becomes larger for a higher Keq.

For the different Keq values, the RD column configurations for the base case are shown graphically in Fig. 6 (b). The Keq mainly influences the number of reactive stages and the RR where a lower Keq leads to more reactive stages and a higher RR. However, it is not followed by the growth of rectifying and stripping sections. On the contrary, slightly less rectifying and stripping stages for a lower Keq are needed due to the different product purity coming out of the reactive section. To show those different purities on the top and the bottom parts of the reactive zone, Fig. S4 in the Supporting information shows the liquid composition profiles in the cases of Keq values 0.1 and 1. In the case of Keq = 0.1, \(x_C = 0.38\) at the top section of the reactive zone, whereas \(x_D = 0.44\) at the bottom part the reactive stages. In the case of Keq = 1, those \(x_C\) and \(x_D\) are lower at 0.24 and 0.33, respectively. The profiles clearly show that the purities of products coming out of the reactive zone in the case of Keq = 1 are less than those with Keq = 0.1. The difference on the purity level between these both cases shows the role of reactive stages in performing separation task. Since less reactive stages are available at Keq = 1 compared to the case of Keq = 0.1, the simultaneous separation in the reactive stages is limited therefore requiring more rectifying and stripping stages.

3.1.3. Influence of the relative volatility

To investigate the influence of relative volatility on the RD performance, \(\alpha_{CA}\), \(\alpha_{BD}\) and \(\alpha_{AB}\) were varied separately. When the relative volatility for product C and reactant A is lower (\(\alpha_{CA} = 1.2, \quad K_A:K_C = 1:1.2\)), compared to the base case the applicability area becomes smaller for each Keq (compare Fig. 6 a and c). For Keq = 0.01, the NTSmin (RR \(\approx\) 100) and the RRmin are 47 and 25, respectively. This is a significant increase compared to the base case, with NTSmin and RRmin 22 and 11, respectively. A similar trend can be found for other values of the equilibrium constant.

Fig. 6 (d) shows that compared to the base case in Fig. 6 (b), more stages are required for the rectifying zone since \(\alpha_{CA}\) is lower. In addition, a larger rectifying section is also needed because the separation between product C and reactant B (\(\alpha_{CB} = \alpha_{CA} \cdot \alpha_{AB} = 1.8\)) is more difficult. In the base case, \(\alpha_{CB} = 3\). The smaller applicability area for the case of lower \(\alpha_{CA}\) compared to the base case, in fact, is not only caused by the larger rectifying section required. Due to more difficult separation in this case, it is preferred to have more reactive stages in order to prevent reactants from reaching the rectifying section. For instance, for Keq = 0.01 the number of reactive stages is 28 in the base case, whereas it is 64 for the case of lower \(\alpha_{CA}\). The increase of Keq in Fig. 6 (d) results in the decrease of the number of reactive stages and the RR due to higher conversion levels per stage.

The opposite effect is expected to happen when \(\alpha_{CA}\) is increased. For instance, for \(\alpha_{AB} = 1.5, \quad \alpha_{CA} = 4, \quad \alpha_{BD} = 2, \quad K_A:K_B:K_C:K_D = 3:2:12:1\), the relative volatilities for product C and other components are higher which are \(\alpha_{CB} = 6\) and \(\alpha_{CD} = 12\). In that situation, the separation of product C from the reaction mixture becomes easier. Therefore, the applicability area grows correspondingly and the values of NTSmin and RRmin decrease.

In analogy to the \(\alpha_{CA}\) reduction, the applicability area for the system with the lower \(\alpha_{BD}\) (\(\alpha_{AB} = 1.5, \quad \alpha_{CA} = 2, \quad \alpha_{BD} = 1.2, \quad Keq = 0.01\)) shows a decrease in the applicability area for the case of lower \(\alpha_{BD}\) (\(\alpha_{AB} = 1.5, \quad \alpha_{CA} = 2, \quad \alpha_{BD} = 1.2, \quad Keq = 10\)). The applicability areas of RD and their configurations at NTS = 2NTSmin in case of kinetically controlled reactions for \(\alpha_{AB} = 1.5, \quad \alpha_{CA} = 2, \quad \alpha_{BD} = 2, \quad Keq = 0.01\) and \(\alpha_{BD} = 1.2, \quad Keq = 10\).
The applicability of RD was investigated in the case of kinetically controlled reactions, with both low and high $K_{eq}$ values. Fig. 7 (a) and (c) present the applicability graphs of RD to the base case considering $K_{eq}$ values of 0.1 and 10, respectively. For both cases, the applicability areas of RD were performed with varied $K_{eq}$ and Da numbers. As result, a rule of thumb connecting the kinetically controlled reactions with their equilibrium limited reactions can be derived. Fig. 5S in the Supporting information presents the ratio of number of reactive stages in case of a kinetically controlled reaction over number of reactive stages at equilibrium ($Da = \infty$) as function of the ratio Da number over $K_{eq}$, which shows that for $Da/K_{eq} \geq 5$ the RD configurations of kinetically controlled reactions are identical to their equilibrium conditions. If Da/ $K_{eq} \geq 2$, it is within 10%. This Da/$K_{eq}$ rule of thumb allows the column designers to determine the required design parameters (i.e. catalyst loading and liquid residence time/liquid hold-up) to influence the performance of RD for any intended reaction.

Further study was done in order to check the correlation between column configuration to the catalyst-use. The catalyst amounts along the boundary lines of the applicability areas in the case of $K_{eq} = 0.1$ were calculated, assuming 20 vol% of the catalyst loading per stage (see Fig. 8). As RR values along the boundary lines go to infinity at $NTS_{min}$, the column diameter becomes infinite resulting in an infinite catalyst hold-up. The catalyst-use drops following the significant decrease of RR from the vertical asymptote of the boundary line because of less internal flow and a smaller column diameter, which leads to the minimum catalyst requirement at a certain point of NTS. The catalyst loading is then increased with more NTS (the RR remains lower) in which it is affected by more reactive stages needed. This investigation shows the importance of a balance between the RR and the required number of reactive stages in order to operate at the minimum catalyst hold-up for the targeted conversion. In the previous section, it has been discussed that the selection of the column configuration with either $NTS_{min}$ or $RR_{min}$ results in a disproportionate shape of the column. Choosing the column configuration close to the $NTS_{min}$ gives a short column with a large diameter. On the other hand, the column configuration with RR close to $RR_{min}$ results in a slim and tall shape. Related to the annual catalyst expenses, it is suggested to avoid the selection of the RD column configuration at extremes (either close to $NTS_{min}$ or $RR_{min}$) for better cost efficiency. A further detailed study is needed to find the optimum RD column configuration considering economics related to the capital investment, the energy requirement and the catalyst-use.

The insights into RD operation have been provided for both the equilibrium limited and kinetically controlled reactions. Having generic cases to perform this study, the insights into RD operation are listed in Table 1 which shows the main effects (on number of reactive and separating stages, reflux ratio) of the modifying specific types of basic parameters.

4. Development and validation of the RD mapping method

Next to the presented insights into RD operation, this study provides the early development of a new RD mapping method. For the end-users,
this approach works in a similar way to a global positioning system (GPS) in which the position of a subject is overlapped on some pre-defined maps (obtained in advance using generic systems). The new mapping method allows defining the applicability areas of real systems (i.e. non-ideal vapor–liquid behavior and temperature-dependent basic parameters, i.e. $\alpha$, $K_{eq}$, chemical kinetics) by only referring to the pre-defined applicability graphs of the generic cases. To match the applicability graphs of real and generic cases, a representing set of $\alpha$ values of the real systems has to be specified. For that reason, the components’ ratios of the real systems have been varied giving various combinations of the $\alpha$ set. Note that many trial simulations were carried out in order to validate the applicability graphs. After checking and validating the applicability graphs of real and generic cases, a representing set of $\alpha$ values of the real systems, $\alpha_{AB}$, $\alpha_{CA}$, $\alpha_{BD}$, at 50/50, 99/1 and 1/99 mol% based mixtures, respectively. The 50/50 mol% of reactants shows an equimolar ratio of feed streams that flow through the reactive section. The 99/1 mol% of product C and reactant A gives an estimation of mixture’s composition on the top part of the rectifying section. The 1/99 mol% of reactant B and product D indicates the mixture’s composition of the bottom part of the stripping section. Furthermore, it is observed that the average boiling point of reactants can be used to calculate the base $K_{eq}$ and $k_t$ values as an estimate for the real systems. A schematic procedure used in this study to develop the method can be found in the Supporting information (Fig. S6). Some examples of the results from extensive simulations which have been carried out during the process of the method establishment are shown in Figs. S7 and S8 in the Supporting information.

4.1. Case 1: transesterification of methyl benzoate with benzyl alcohol

Dimethyl terephthalate ester (DMT) is widely produced by the Witten-Hercules method [37]. In this process, large amounts of methyl benzoate containing waste are produced which are normally combusted. Methyl benzoate in a high purity can be used as a raw

<table>
<thead>
<tr>
<th>Type</th>
<th>Modification</th>
<th>Basic parameters</th>
<th>Effects*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{eq}$ (and $D_a$)</td>
<td>↓ Refer to Figure 6 (a-b) and Figure 7 (a-d)</td>
<td>Number of reactive stages</td>
<td>More, to boost the total conversion</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>↓ $\alpha_{CA}$ Refer to Figure 6 (c-d)</td>
<td>Number of separating stages</td>
<td>Less, because separation also takes place along the reactive section</td>
</tr>
<tr>
<td>$\downarrow \alpha_{BD}$ Refer to Figure 6 (e-f)</td>
<td>More, to increase the reactants conversion to deal with difficult separation in rectifying section</td>
<td>Reflux ratio</td>
<td>Higher</td>
</tr>
<tr>
<td>$\downarrow \alpha_{AB}$ Refer to Figure 6 (g-h)</td>
<td>The following effects are given by fixed $\alpha_{CA}$ and $\alpha_{BD}$ with varied $\alpha_{AB}$. Varying $\alpha_{AB}$ changes the $\alpha_{CB}$ and $\alpha_{AD}$ values which causes secondary and mixed effects (listed below).</td>
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</table>

*Reverse effects are obtained by increasing the value of each parameter.

Table 1
Summary of insights into RD operation presented in the current study.

<table>
<thead>
<tr>
<th>Basic parameters</th>
<th>Number of reactive stages</th>
<th>Number of separating stages</th>
<th>Reflux ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{eq}$ (and $D_a$)</td>
<td>↓ Refer to Figure 6 (a-b) and Figure 7 (a-d)</td>
<td>More, to boost the total conversion</td>
<td>Less, because separation also takes place along the reactive section</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>↓ $\alpha_{CA}$ Refer to Figure 6 (c-d)</td>
<td>More rectifying stages because $\alpha_{CA}$ and $\alpha_{CB}$ are smaller</td>
<td>Higher</td>
</tr>
<tr>
<td>$\downarrow \alpha_{BD}$ Refer to Figure 6 (e-f)</td>
<td>More stripping section because $\alpha_{BD}$ and $\alpha_{AD}$ are smaller</td>
<td></td>
<td>Higher</td>
</tr>
<tr>
<td>$\downarrow \alpha_{AB}$ Refer to Figure 6 (g-h)</td>
<td>The following effects are given by fixed $\alpha_{CA}$ and $\alpha_{BD}$ with varied $\alpha_{AB}$. Varying $\alpha_{AB}$ changes the $\alpha_{CB}$ and $\alpha_{AD}$ values which causes secondary and mixed effects (listed below).</td>
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<td></td>
<td></td>
<td>Less, because reactants’ ratio in liquid phase is closer to stoichiometric which results in a better conversion</td>
<td>More, because $\alpha_{CB}$ and $\alpha_{AD}$ are smaller which means more difficult separation</td>
</tr>
</tbody>
</table>
ingredient for the production of other chemicals such as benzyl benzoate. For the production of benzyl benzoate, methyl benzoate has to react with benzyl alcohol. This reaction is shown in Eq. (2).

\[
\text{A Methyl benzoate + B Benzyl alcohol \rightleftharpoons C Methanol + D Benzyl benzoate}
\]

\[
\begin{align*}
T_b &= 199.5 \degree C & 205.45 \degree C & 64.7 \degree C & 323.24 \degree C
\end{align*}
\]

The appropriate property model selected for this system is UNIQUAC-HOC. The Hayden-O-Connell correlation was used to take into account the non-ideal behavior of methanol and methyl benzoate in the vapor phase. There is no azeotrope present in this reaction system and the heat of reaction \(\Delta H_r\) is \(-13.79 \text{ kJ mol}^{-1}\).

The availability of chemical data in the literature is limited. The paper of Tang and Li [37] provides the equilibrium conversion for an equimolar feed. In their study, the process utilized tetrabutyl titanate catalyst to produce methanol and benzyl benzoate from the reactants. The equilibrium conversion is 78.1%, which corresponds with a \(K_{eq}\) value of 12.7 at 142 \degree C. There is a marginal effect of the temperature on the \(K_{eq}\) constant. By assuming a batch reactor, the \(k_t\) was determined from the conversion vs time plot which is provided in the paper of Tang and Li [37]. This results in \(D_a = 0.067\) for \(\tau = 30\ s\) and \(D_a = 0.133\) for \(\tau = 60\ s\), with a catalyst loading of 2 vol% per stage. In practice, the catalyst can be loaded up 50 vol% per stage. The use of 2 vol% of the catalyst per stage in this study is aimed to distinguish the results of kinetically controlled reaction from the equilibrium limited reaction.

**4.1.1. Equilibrium-based calculation**

A comparison is made between the case study \(K_{eq} = 12.7\) and the generic cases with \(K_{eq}\) values of 10 and 15. Calculating \(\alpha_{AB}, \alpha_{CA}\) and \(\alpha_{BD}\) at 50/50, 99/1 and 1/99 mol% based mixtures from the real system, respectively, \(\alpha_{AB} = 1.16, \alpha_{CA} = 256\) and \(\alpha_{BD} = 6.5\). Since the \(K_{eq}\) and \(\alpha\) are very favorable, the RD column with an equilibrium reaction is expected to be applicable. Fig. 9 (a) shows that the boundary line of the applicability area for the real system lies in between two generic cases, but closer to the generic case with \(K_{eq} = 10\) which is mainly caused by temperature influence, especially on \(\alpha\), in the real system. The temperature effect on the \(K_{eq}\) is marginal, therefore neglected. Fig. 9 (b) presents the actual RD configurations of the real and the generic cases which were obtained from performing simulations. The graph shows that the NTS and RR of the real case are nicely in the range of the NTS and RR of the two generic cases. Without considering
the simulation result of the real system, the linear interpolation was applied to estimate NTS and RR of the real system as shown in Fig. 10. According to that interpolation, the NTS and RR of the real system are 9 and 0.3, respectively. Comparison between the actual simulation result (NTS = 8 and RR = 0.4) and the estimate based on two generic cases via interpolation show deviation of +13% and −25%, respectively, for the NTS and RR. The complete set of results including deviations for all case studies is summarized in Table 2. The results show a good estimation of the applicability areas and a satisfying accuracy. The generic cases therefore can be used to predict the applicability of RD to this real system in the case of equilibrium-limited reaction. Since the separation is easy and the equilibrium conversion is very high, the application of a conventional system being a reactor followed by distillation might be considered.

4.1.2. Kinetics-based calculation

In this part, the RD applicability area for the real system with kinetically controlled reaction is compared to the generic case \( K_{eq} = 12.7 \) with \( \alpha_{AB} = 1.16, \alpha_{CA} = 256 \) and \( \alpha_{BD} = 6.5 \). Fig. 9(c) shows that the boundary lines of the applicability areas for the case study with different Da numbers (Da values are 0.067 and 0.133) lie between those belonging to the generic cases \((0.02 < Da < 0.2)\). Fig. 9(d) highlights the RD configurations for the case study based on simulation results, which are inside the range of the RR and the NTS of the generic cases. Again, interpolation was applied to estimate the RD configurations of the real case without relying on any simulations of the case study. As presented in Table 2, the NTS and RR for the case of Da number of 0.067 are 13 and 13.8, respectively. For the case of Da number of 0.133, the NTS and RR are 11 and 8.8, respectively. Comparing with the actual simulation results, the estimation of the RD configurations based on the generic cases gives satisfying outputs with deviations of less than +30%.

<table>
<thead>
<tr>
<th>Case</th>
<th>( K_{eq} ) (and Da)</th>
<th>NTS</th>
<th>Deviation</th>
<th>RR</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trans-esterification of methyl benzoate</td>
<td>( K_{eq} = 12.7 )</td>
<td>8</td>
<td>+13%</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>( K_{eq} = 12.7, Da = 0.067 )</td>
<td>12</td>
<td>13</td>
<td>+8%</td>
<td>12.3</td>
<td>13.8</td>
</tr>
<tr>
<td>( K_{eq} = 12.7, Da = 0.133 )</td>
<td>12</td>
<td>11</td>
<td>−8%</td>
<td>6.8</td>
<td>8.8</td>
</tr>
<tr>
<td>( K_{eq} = 0.96 )</td>
<td>20</td>
<td>21</td>
<td>+5%</td>
<td>2.7</td>
<td>2.5</td>
</tr>
<tr>
<td>( K_{eq} = 0.96, Da = 0.16 )</td>
<td>22</td>
<td>22</td>
<td>0%</td>
<td>10.8</td>
<td>8.2</td>
</tr>
<tr>
<td>( K_{eq} = 0.96, Da = 0.62 )</td>
<td>20</td>
<td>21</td>
<td>+5%</td>
<td>5.2</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Table 2

Comparison of actual results and estimates based on the new RD mapping method for the number of theoretical stages (NTS) and reflux ratio (RR) of two case studies.

Fig. 11 shows the applicability areas of RD and their configurations at NTS = 2NTSmin for the hydrolysis of methyl lactate \( (K_{eq} = 0.096 \text{ at } 122.4 \text{ °C}) \) compared to the generic ideal case \( (\alpha_{AB} = 5.5, \alpha_{CA} = 2.5, \alpha_{BD} = 6.5) \) for (a) an equilibrium limited reaction and (c and d) kinetically controlled reactions.
4.2. Case 2: hydrolysis of methyl lactate

Lactic acid is a chemical that can be used to produce biodegradable plastics. However, it is difficult to purify lactic acid from a fermentation mixture. Therefore, lactic acid is esterified with methanol to produce methyl lactate. The methyl lactate is then separated and hydrolyzed back to methanol and lactate acid:

\[
\text{A Water} + \text{B Methyl lactate} \rightarrow \text{C Methanol} + \text{D Lactic acid}
\]  

\[T_b \text{, } 100 \degree C \quad 144.8 \degree C \quad 64.7 \degree C \quad 216.85 \degree C\]
\[\Delta H_f = +33.6 \text{kJ mol}^{-1}\]

To run the simulations, the selected property model was UNIFAC-HOC since it is the most accurate model to describe the current system \([38,39]\). One azeotrope was found in this system: methyl lactate and water form an azeotrope at 97 mol% water in methyl lactate at 99.8 °C. This azeotrope should not have any negative effects on the feasibility and performance of the RD column since it is between reactants and at a high concentration of water. The azeotrope composition will therefore never be reached since the reactants are converted to the products and are fed separately to the column in a stoichiometric ratio.

The chemical data of Sanz et al. \([39]\) is used in this case study. The hydrolysis of methyl lactate is catalyzed by Amberlyst 15, an acidic cation-exchange resin. The quasi-homogeneous non-ideal (QH-NI) model is the best kinetic equation to describe the hydrolysis reaction of water and methyl lactate \([39,40]\). The kinetic data is shown in Table S4 in the Supporting information and depends on the catalyst concentration. The correlation between temperature and the chemical equilibrium constant is expressed by the Eq. (4). Using the given kinetic data, the forward reaction rate constant can be calculated with Eq. (5).

\[\ln(K_{eq}) = 2.6 - \frac{1954.2}{T}\]

\[k_f = k_f^0 \exp\left(-\frac{E_{a,f}}{RT}\right)\]

At the average boiling point of reactants, \(K_{eq} = 0.096\). To calculate the Da number, the \(k_r\) was then calculated at the average boiling point of reactants with Eq. (5). The Da numbers are 0.16 (7.1 vol% catalyst loading and \(\tau = 30\) s) and 0.62 (14.6 vol% catalyst loading and \(\tau = 60\) s).

4.2.1. Equilibrium-based calculation

The \(\alpha_{CA} = 5.5\), \(\alpha_{CA} = 2.5\) and \(\alpha_{CN} = 6.5\) at 50/50, 99/1 and 1/99 mol% based mixtures, respectively. \(\phi_{B,C} = 0.05\) and \(K_{eq} = 0.2\). Additionally the results of the case study \((K_{eq} = 0.096)\) simulations are added. In the graph, it can be observed that the boundary line of the applicability area for the case study mainly lies in between the lines belonging to the generic case for \(K_{eq}\) values of 0.05 and 0.2. Fig. 11 (b) gives the RD configurations based on the simulation results for the real and the generic cases. Without considering the simulation output of the real system and using the interpolation approach, the NTS and RR of the real case were estimated based on the two selected generic cases (see Table 2). Comparing the simulation of the case study and the interpolation result, the deviation of \(\pm 5\%\) is highly acceptable. Therefore, a satisfying estimation of the applicability area and the RD configuration of the case study can be obtained from the generic cases.

4.2.2. Kinetics-based calculation

In this part, the RD applicability area for the real reaction system is compared to the generic case \((K_{eq} = 0.096)\) with the kinetics-based calculation. The relative volatilities for the generic case are identical to the values in the equilibrium-based calculation section. In Fig. 11 (c), the applicability areas for the generic system and the case study are plotted. It can be observed that each boundary line of the applicability areas for the case study lies in between the two belonging to the generic cases. Fig. 11 (d) presents the RD configurations of all cases obtained from the simulations, which indicates that the RD configurations of the real system can be nicely predicted from the generic cases. Using the interpolation approach and without relying on the simulation results of the real system, the RD configurations for the real system were estimated with a deviation of \(-25\%\) to \(+5\%\).

5. Conclusions

Reactive distillation is indeed a proven process intensification method effectively applicable to equilibrium limited reaction systems. Yet, a key question is how can industrial users decide quickly if RD is indeed feasible and worth applying? This study has effectively developed a novel (graphical) approach to evaluate the applicability of RD to quaternary reaction systems, based on generic cases requiring only a few basic parameters, i.e. \(\alpha_{K_{eq}}\) and chemical kinetics. Having those basic parameters, the RD applicability graphs were generated as plots of the reflux ratio vs the number of theoretical stages, which provide information about the applicable configurations of the RD operation. The product purity can be set as a primary performance indicator which influences the size of the RD applicability areas.

Due to the existence of multiple RD configurations (with slight differences in the reflux ratio values) for the same boundary conditions, a broad range of insights and trends regarding RD configurations can be gathered. This feature is a key benefit offered by the new RD mapping method which allows the end user to obtain quickly a better understanding about the RD operation, prior to any detailed rigorous simulations. Some essential insights into the RD operation are conveniently summarized in Table 1.

The development of a new RD mapping method in this study provides satisfying outcomes. It seems promising to use the method for assessing the applicability of RD to real systems, by analyzing the predefined graphs of the generic cases. Furthermore, the method gives quick and good prediction of the RD configurations of real systems with the deviation of less than \(\pm 30\%\). The mapping method is able to eliminate the necessity of performing any rigorous simulations in the exploratory phase when considering a certain reaction for RD – although a detailed simulation is suggested in the detailed design phase. The valuable insight provided by the method can be used in the decision making process to go/no-go for RD. The initial development was carried out focusing on the most encountered subset of the quaternary systems \((T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D})\), but the method can be expanded further to other systems.

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Appendix A. Supplementary data

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References