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# A Novel Method for Determining the Optimal Operating Points of Reactive Distillation Processes

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Reactive distillation (RD) allows reaction and separation to take place simultaneously in the same unit, thus giving major benefits especially to equilibrium limited reactions. Although the application of RD in chemical industries is attractive, it is considerably challenging. Unlike classic distillation, the optimal configuration of RD from an economical perspective is hardly identified quickly. Usually, any specific reaction system may need extensive studies and rigorous simulations to develop a RD model.

This study aims to determine the optimal operating points of a RD application in a quick and reliable way. A novel method is employed for a clear visualization of the RD applicability area (i.e. a plot of reflux ratio vs number of stages). Using this method, an economic analysis can be performed resulting in essential insights into the optimal configurations. The production of amyl acetate by esterification of amyl alcohol and acetic acid is selected as case study, since this reaction sufficiently represents non-ideal behaviours in real systems. The outcome of the analysis reveals that the boundary line of its RD applicability graph consists of the optimal points of RD configurations which generate the lowest total annual cost in the RD operation. Furthermore, it is observed that the additional cost for the reactive section (relative to a separation section) is marginal, which means that the rules of thumb for the optimal configurations in classic distillation could also be applied.

## 1. Introduction

As most processes in chemical industries, reaction and separation typically require different equipment units. Since the mid of 20<sup>th</sup> century, the number of research studies in the improvement of reaction and separation technologies has been growing enormously (Reay et al., 2008). Reactive distillation (RD) is now one of the most promising process intensification units considering its major benefits in industry (Kiss, 2014): 1) a higher conversion and an improved selectivity due to the shifting of the chemical equilibrium (Li et al., 2017), and 2) high savings in capital costs and energy usage due to the process integration (Shah et al., 2012).

Apart from the benefits offered by the RD technology, its applicability to a wide range of chemical reaction systems is still challenging. First of all, extensive studies are generally required in order to decide whether a proposed RD configuration is acceptable, i.e. adequate amount of catalyst, sufficient residence time and/or liquid hold-up, appropriate reactive section size and placement (Kiss, 2017). Furthermore, detailed economic calculations are usually required to select the most optimal RD configuration from the economical perspective as so far that there is no relevant suggestion for a quick determination. Unlike classic distillation which features well known rules of thumb for determining the number of theoretical stages (NTS) as double the minimum required ( $NTS = 2 \cdot NTS_{min}$ ) and/or the reflux ratio as 1.1-1.3 times the minimum reflux ratio required ( $1.1 \cdot RR_{min} < \text{reflux ratio (RR)} < 1.3 \cdot RR_{min}$ ), similar rules for the RD technology are unknown yet.

This study presents a novel method for determining the optimal points of RD configurations, by providing the applicability area (i.e. the plot of RR vs NTS), to visualize the RD operations. This graph describes how far the RD performs in case of kinetically controlled reactions vs equilibrium limited reaction, thus allowing the users to estimate the improvement in the RD operations. The ultimate outcome of this study is to provide rules for pre-defining the optimal RD configurations before performing any detailed simulations/economic evaluations.

## 2. Approach and methodology

### 2.1 RD applicability region

Figure 1a shows an illustrative RD applicability area proposed by the novel method (Muthia et al., 2018). Our previous work describes the mathematical basis and the novel method for quickly mapping the applicability of RD based on pre-defined maps calculated for generic cases (Muthia et al., 2018). In this study, the RD applicability area is employed to support the users in evaluating the RD column configuration (e.g. number of rectifying, stripping and reactive stages, reflux ratio) and improving the RD operation. On the dotted boundary line and inside the applicable area (Figure 1a), multiple converged RD configurations (as shown in Figure 1b) are available, which meet the minimum requirement of the targeted product purity. Along the boundary line, the lowest RR values are reported for various NTS values. The  $NTS_{min}$  is the smallest NTS required and the  $RR_{min}$  is the lowest RR that is obtained at infinite NTS. A flat horizontal asymptote shows that  $RR_{min}$  is already achieved at the specified  $NTS > 60$  on the x-axis. Related to the availability of multiple RD configurations, as presented in Figure 1b, the points 1 and 2 in Figure 1a are located at the same  $NTS (=40)$ . At point 2, a higher RR is applied, but a lower number of reactive stages can be obtained.

In this study, the targeted product purity has to be equal to or larger than 98 mol% in order to fulfil the common product requirements in industry. Considering the RR value which is typically still acceptable for RD, the RD applicability area presented in this work is limited to the scales of 0-20 for RR and 0-100 for NTS.

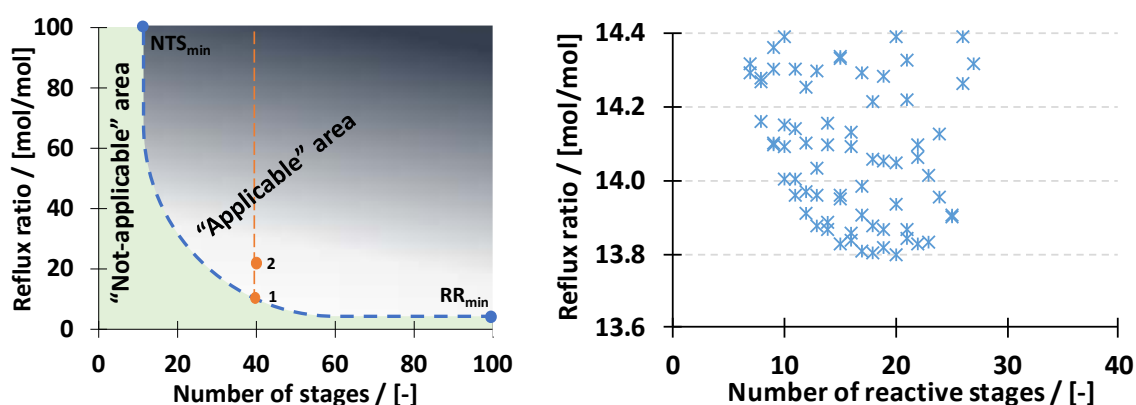


Figure 1: (a) Illustrative RD applicability area for a certain chemical system and (b) multiple RD configurations available inside the RD applicability area at  $NTS = 40$

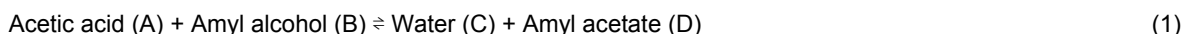
### 2.2 Optimal operating points in the RD applicability region

In classic distillation technology, RR and NTS are the most important variables that are directly linked to the energy requirement and the investment cost, thus those variables provide sufficient information about the optimal configuration. In RD processes, besides considering the lowest RR point, also the number of reactive stage (NRS) should be evaluated since less NRS may give an essential reduction of the costs. An extensive investigation of RD can be carried out using the applicability area as proposed by the novel method. In order to perform this task, another boundary is added to indicate the RD configurations with the lowest NRS. The optimum points of the RD configurations are logically either on the boundary line of the applicable area with the lowest RR or at points with the lowest NRS or at points in between the lowest RR and lowest NRS.

Economic analyses were performed using self-constructed Excel sheets with detailed calculations as discussed in Douglas (1988), Seider et al. (2008), Towler and Sinnott (2013). A sieve tray tower is assumed, with the cost of reactive trays 20% higher than the cost of separation trays (i.e., rectifying and stripping trays). The height of reactive trays is set 30% larger than the separation trays (with max. 30 vol% of catalyst) to avoid any possibility of flooding caused by change in hydrodynamics due to the addition of catalyst. The cost of the ion-exchange resin catalyst applied in this case study is 18.5 \$/kg, which is within the range of the cost for bulk IEX catalysts in industry. The catalyst life-time is assumed to be 3 years. The Marshall and Swift (M&S) index valued at 1468.6 (in 2012) was used to estimate the costs based on the formulas available in the book of Douglas (1988). Total annual cost (TAC) is specified as the key figure when comparing different RD configurations, and comprises two elements of costs: annualized investment costs (AIC) and total operating costs (TOC). The components of AIC include the costs of column shell and internals, condenser, reboiler and any additional equipment if applied. The depreciation period is assumed to be 3 years (depending on the economics of the product and raw material). TOC include the costs of cooling water, steam and catalyst.

### 3. Case study

The production of amyl acetate from an esterification reaction is selected as a representative case study. This reaction is a quaternary system ( $A + B \rightleftharpoons C + D$ ) with both reactants as mid-boiling compounds hence both products can be collected as top and bottom outlets with a high purity. The case study is shown in Eq (1):



NRTL-HOC was selected as adequate property model in order to characterize the non-ideal behaviours in this system (Chiang et al., 2002). There are five azeotropes found in the case study. The boiling points ( $T_b$ ) order is given in Table 1. Kinetics expressions from the use of Amberlyst 15 catalyst are taken from previous research by Tang et al. (2005). All the simulations are performed using the Aspen Plus (v8.6) process simulator. Sensitivity analysis and an optimization tool in the process simulator are applied in order to examine the presence of multiple RD configurations. The reactants are introduced as saturated liquids to the RD column operating at atmospheric pressure. The reactants are in a stoichiometric ratio hence the need for a recycle stream can be avoided when a high conversion is reached. For the best RD configuration, the lighter reactant is fed to the bottom part of the reactive section and the heavier reactant is fed to the top part of the reactive section (Figure 2a). Consequently, counter current flow occurs, especially along the reactive stages.

Table 1: Boiling points order and VLE data for the amyl acetate system

Type	$T_b$ (°C)	Compound	Mol fraction, VLE	Mol fraction, LLE	
				Liquid 1	Liquid 2
Ternary heterogeneous azeotrope	94.7	Amyl alcohol	0.04	0.01	0.33
		Water	0.83	0.99	0.19
		Amyl acetate	0.13	0.00	0.48
Binary heterogeneous azeotrope	94.9	Water	0.83	1.00	0.11
		Amyl acetate	0.17	0.00	0.89
Binary heterogeneous azeotrope	95.9	Amyl alcohol	0.15	0.02	0.62
		Water	0.85	0.98	0.38
Pure	100	Water	1.00	n/a	n/a
Pure	118	Acetic acid	1.00	n/a	n/a
Pure	138	Amyl alcohol	1.00	n/a	n/a
Ternary homogeneous azeotrope	140	Amyl alcohol	0.59		
		Acetic acid	0.22	n/a	n/a
		Amyl acetate	0.19		
Binary homogeneous azeotrope	140.3	Acetic acid	0.26	n/a	n/a
		Amyl alcohol	0.74		
Pure	147.7	Amyl acetate	1.00	n/a	n/a

### 4. Results and discussion

This study investigated first the possibility of operating a classic RD column equipped with a condenser and a reboiler for the case study. However, the maximum product purity can reach only 85 mol% even in the case of equilibrium limited reaction (when not considering kinetics limitations) hence there is no plot of a boundary line in the RD applicability graph (the classic RD setup is simply unable to provide on-spec products due to the azeotrope between water and amylalcohol). This result implies that operating a simple RD column cannot fulfil the minimum targeted product purity based on the defined scale of RR and NTS in the applicability graph.

The next attempt is using a RD column equipped with a decanter (Figure 2a) and considering the presence of a heterogeneous azeotrope mixture as the lowest boiling compound (see Table 1). The water phase is removed as distillate product while the organic phase is returned to the RD column as reflux. The catalyst volume over the volumetric liquid hold-up is 30%. The residence time per stage is 30 s which is expected to provide an effective contact between the internal liquid and the catalyst. The dotted line in Figure 2b shows the boundary line of this configuration with  $NTS_{min} = 15$  and  $RR_{min} = 2.32$ . Compared to a classic RD setup (where the purity specs cannot be obtained), the RD applicability area shown in Figure 2b is significantly improved (and made feasible) by attaching a decanter to the column. Further simulations are carried out in order to check the position of the boundary line in the case of equilibrium limited reaction (solid line in Figure 2b). Figure 2b reveals that the performance of the RD column in the case of kinetically controlled reaction is sufficiently satisfying since the minimum reflux ratio is close to the case of equilibrium limited reaction.

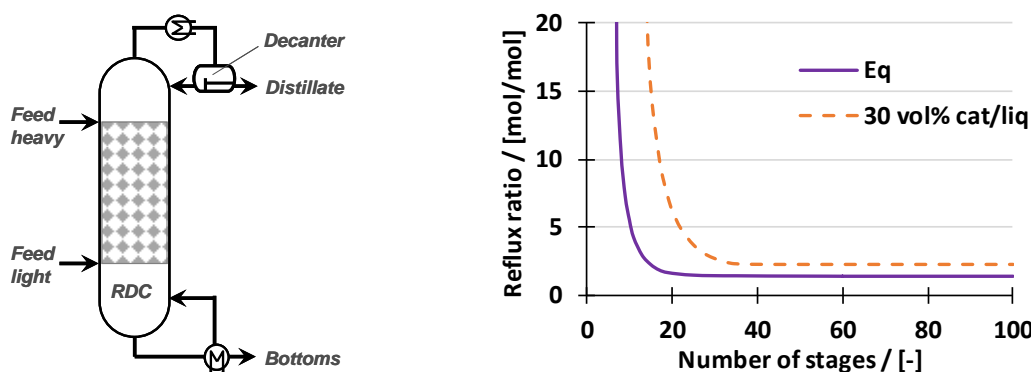


Figure 2: (a) Azeotropic RD configuration. (b) RD applicability graphs of the amyl acetate system in the cases of a RD column equipped with a decanter.

These results are then used for the economic analyses, as described hereafter. Applying the approach previously presented, the data with the lowest NRS are added to the RD applicability area (see Figure 3a). Moreover, the number of reactive stages in the configuration with the lowest RR and the lowest NRS are presented in Figure 3b. In the case of the lowest RR, the NRS increases significantly (see Figure 3b) until NTS = 45 where the RR value is very close to the  $RR_{\min}$  indicated by the flat horizontal asymptote in the applicability area (see Figure 3a). It implies that a larger reactive section improves the RD column performance since more reactants can be converted into products, resulting in a higher purity of the compounds leaving the reactive section, hence the lowest RR. When the lowest RR approaches the  $RR_{\min}$  it is obvious that any additional reactive stage will not improve anymore the RD column performance.

The lowest NRS hardly changes by the increase of NTS (see Figure 3b). On the other hand, its RR values get lower (see Figure 3a, green dots) due to the addition of more rectifying and stripping stages which enhances the separation performance but this effect levels off to a constant RR which is much higher than  $RR_{\min}$ .

To proceed with the economic analysis, four NTS points (NTS = 17, 30, 50 and 80) are selected and the corresponding RD configurations are examined along the vertical lines as presented in Figure 3. Based on the results of sensitivity analysis in Aspen Plus (v8.6), at least 2, 12, 122 and 438 solutions are available for NTS = 17, 30, 50, 80, respectively. Table 2 shows the economics of the RD configurations for NTS = 30. Note that at a fixed NTS the length of the reactive section for a RD configuration can be the same with other RD configurations, but its placement in the column is different (i.e., varied numbers of rectifying and stripping stages). Hence, for the same NRS at a fixed NTS, only the RD configuration with the smallest RR is analyzed. To provide useful insights, two additional RD configurations are also shown in Table 2. Configurations 4 and 6 have the same NRS, but the latter has a higher RR. Configuration 7 is located above the vertical line in Figure 3a and operates within the area given by the two points: the lowest RR and NRS in Figure 3b).

By the increase of NRS and the decrease of RR (configurations 1-5), the column diameter decreases due to the lower RR. To validate that it is not because of the effect given by NRS, configuration 4 is compared with the one with the same NRS, but with a higher RR (configuration 6) which clearly shows the effect of RR on the diameter of the RD column.

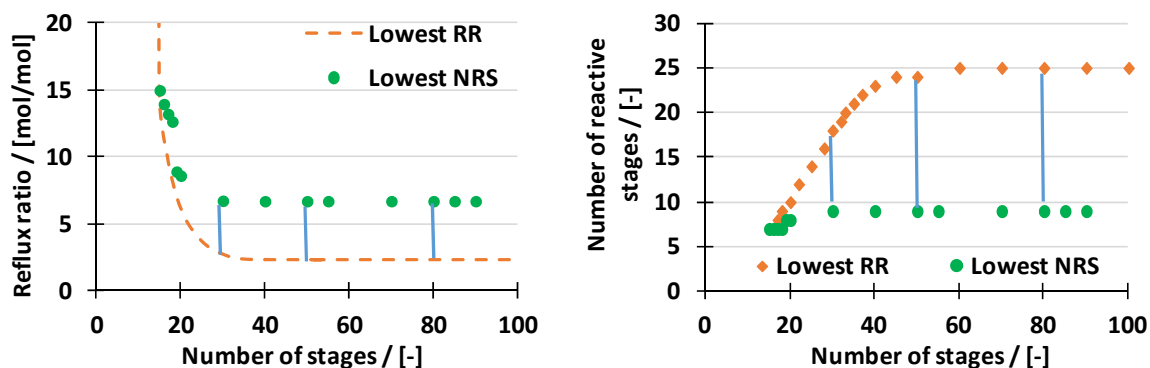


Figure 3: (a) RD applicability area of the amyl acetate system with additional points of the lowest NRS and (b) the NRS distribution for varied NTS points. Both figures are in the case of a RD equipped with a decanter.

Table 2: Economic evaluation of various RD column configurations with a total of 30 stages

RD Configuration	1 <sup>a</sup>	2	3	4	5 <sup>b</sup>	6 <sup>c</sup>	7 <sup>d</sup>
Number of stages (NTS=30)							
Rectifying	14	12	10	8	2	10	14
Reactive	<b>9</b>	10	11	12	18	12	13
Stripping	7	8	9	10	10	8	3
Reflux ratio (mol/mol)	6.8	5.3	4.4	3.8	<b>2.7</b>	4.3	12.1
Column							
Diameter (m)	1.5	1.3	1.2	1.1	1.0	1.2	1.9
Height (m)	31.0	31.3	31.5	31.8	33.3	31.8	32.1
Heat-transfer area							
Condenser (m <sup>2</sup> )	231	186	158	139	110	157	397
Reboiler (m <sup>2</sup> )	225	181	153	135	106	152	389
Decanter							
Diameter (m)	2.1	1.9	1.8	1.7	1.5	1.8	2.8
Height (m)	4.3	3.8	3.5	3.3	2.9	3.5	5.6
Total amount of catalyst (kg)	2018	1789	1661	1591	1781	1815	5410
Annualized investment cost (M\$/year)	2.24	1.95	1.77	1.64	<b>1.43</b>	1.76	3.20
Column shell and internal	0.82	0.73	0.67	0.64	0.58	0.68	1.12
Condenser and reboiler	1.20	1.04	0.94	0.86	0.74	0.93	1.71
Decanter	0.22	0.18	0.16	0.14	0.11	0.15	0.37
Total operating costs (M\$/year)	1.58	1.26	1.08	0.95	<b>0.75</b>	1.06	2.74
Cooling water	0.07	0.06	0.05	0.04	0.03	0.05	0.12
Steam	1.50	1.20	1.02	0.90	0.71	1.01	2.59
Catalyst	0.012	0.011	0.010	0.010	0.010	0.011	0.03
Total annual costs (M\$/year)	3.82	3.21	2.85	2.59	<b>2.18</b>	2.82	5.94

Note: <sup>a</sup>) lowest NRS, <sup>b</sup>) lowest RR, <sup>c</sup>) another RD configuration with NRS = 12, <sup>d</sup>) a RD configuration above the vertical line presented in Figure 3a at NTS=30. Bold letters show the lowest values of some parameters.

The column height increases as some extra space is added to the reactive trays (as discussed in the previous section). The results show that RR has a major effect on the size of both heat exchangers and decanter. Although the NRS increases gradually (see configuration 1-4, 6 and 7), the total amount of catalyst is reduced when RR is lower, due to the decrease of liquid hold-up per tray. On the contrary, the amount of catalyst for configuration 5 is higher than that for configuration 4, because there is a significant extension of reactive zone (i.e. six more reactive stages) which increases the total liquid hold-up in the reactive section.

The cost of the RD column shell and internals decreases with increasing the NRS, which is actually due to a decrease of RR. It shows that the additional cost needed due to a larger reactive section is only marginal. The cost substantially decreases due to a smaller diameter of the column which is the effect of a lower RR. As the size of the condenser, reboiler and decanter are smaller by the decrease of RR, the costs are also reduced. For each configuration, the costs of the heat exchangers are the major contribution (around 55%) to the AIC. The cost given by the column shell and internal is slightly lower at about 40%.

Due to the lower internal mass flows at lower RR, the requirements of cooling water in the condenser and steam in the reboiler are reduced. Among the three operating cost elements, the heating requirement takes the largest part of the TOC, being always higher than 90%. The cost of catalyst at about 1% is only marginal. In the case of a RD configuration that is located above the vertical line in Figure 3a and is operated within the area given by the two points: the lowest RR and NRS) presented in Figure 3b (configuration 7), the AIC and TOC increase dramatically. This result supports the approach presented in this study which disregards configuration located above the vertical line. Besides the multiple solutions at NTS = 30, detailed calculations are also performed for the other selected NTS points. All the results show that the RD configuration with the lowest RR generates the lowest TAC for each NTS value. Referring to the cost components of AIC and TOC, it is clear that the effect of RR on the costs is much more significant than the effect given by NRS. Therefore, the optimum operating points for the RD operation are located along the boundary line (at lowest RR) of its applicability area. Further investigation examined the most optimal RD configuration along the boundary line of the applicability area.

Figure 4 presents the costs profiles which reveals the lowest TAC valued at 2.06 M\$/year for NTS = 33, RR = 2.45. Compared to  $NTS_{min} = 15$  and  $RR_{min} = 2.32$  (see Figure 2b), it is found that the rules of thumbs applied in classic distillation ( $NTS = 2 \cdot NTS_{min}$  and/or  $RR = 1.1 \cdot RR_{min}$ ) are also valid in this case.

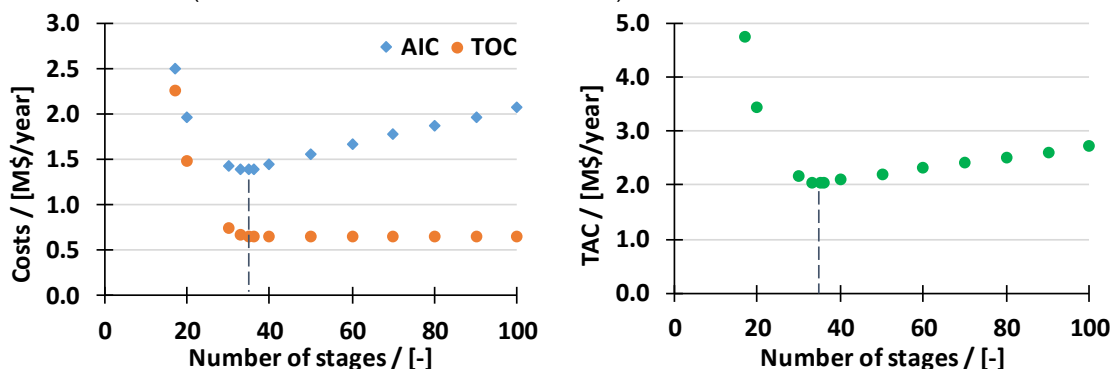


Figure 4: (a) AIC and TOC profiles and (b) TAC profile for RD configurations along the boundary line in its applicability area in the amyl acetate system

## 5. Conclusions

The novel method proposed here successfully visualizes the different RR-NTS combinations necessary for a specific RD operation, which gives valuable insights to the end-users of the method about the applicability of various RD configurations (see Figure 2b). Based on the detailed economic analyses carried out for the case study (amyl acetate synthesis by esterification), the optimal operating points of the RD column are located along the boundary line of the applicability area. Furthermore, based on the results of the case study, the rules of thumb to predict the economical optimal ( $NTS = 2 \cdot NTS_{min}$  and/or  $RR = 1.1 \cdot RR_{min}$ ) for classic distillation could be used in a first approach for RD too.

## Acknowledgments

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