A Novel Mapping Method for Assessing the Applicability of Reactive Distillation to Quaternary Reaction Systems

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Abbreviations and Nomenclature

Abbreviations

MESH   mass, equilibrium, summation and heat

NTS   number of theoretical stages

NTS_{min} minimum number of theoretical stages

PI   process intensification

RD   reactive distillation

RR   reflux ratio

RR_{min} minimum reflux ratio

Nomenclature

a_i activity of compound i, [-]

Da   Damköhler number, [-]

D_A diffusion coefficient, [$m^2\ s^{-1}$]

C_{Bs} reactant concentration in the liquid bulk, [$mole\ m^{-3}$]

$E_{a,f}$ activation energy for the forward reaction, [$kJ\ mole^{-1}$]

$E_{i,j}$ energy transfer rate on stage j, [$J\ s^{-1}$]

E_j^V interphase energy transfer rate of vapour phase on stage j, [$J\ s^{-1}$]

E_j^L interphase energy transfer rate of liquid phase on stage j, [$J\ s^{-1}$]

$f_{i,j}$ component feed stream, [$mole\ s^{-1}$]

F_j liquid feed stream on stage j, [$mole\ s^{-1}$]

Ha   Hatta number, [-]

H_j molar enthalpy, [$J\ mole^{-1}$]

K_{eq} chemical equilibrium constant, [-]

k_f forward reaction rate constant, [$mole\ g_{cat}^{-1}\ min^{-1}$]

k_f° pre-exponential factor for the forward reaction rate, [$mole\ g_{cat}^{-1}\ min^{-1}$]

k_L liquid-side mass transfer coefficient, [$m\ s^{-1}$]

k_2 forward reaction rate constant, [$mole\ m^{-3}\ s^{-1}$]

K_i vapour-liquid equilibrium constant of compounds i, [-]

L_j	liquid flow rate on stage j, [mole s^{-1}]
M_r	average molar mass of components, [g$_{mixture}$ mole^{-1}]
$N_{i,j}$	mass transfer rate on stage j, [mole s^{-1}]
P	total pressure, [atm] or [bar] or [Pa]
P_i°	vapour pressure of compound i, [atm] or [bar] or [Pa]
Q_j	heat duty on stage j, [J s^{-1}]
R	gas constant, [kJ K^{-1} mole^{-1}]
r_j^L	ratio of side-stream flow to liquid stream, [-]
r_j^V	ratio of side-stream flow to vapour stream, [-]
R_m	rate of reaction m, [mole m^{-3} s^{-1}]
S_j^L	liquid side stream, [mole s-1]
S_j^V	vapour side stream, [mole s-1]
t	time, [s]
T	temperature, [°C] or [K]
T_b	boiling point of compounds, [°C] or [K]
U_j	hold-up on stage j, [mole]
v_i	stoichiometric coefficient of compound i, [-]
V_j	vapour flow rate on stage j, [mole s^{-1}]
x_i	liquid mole fraction of compound i, [-]
y_i	vapour mole fraction of compound i, [-]

Greek letters

y_i	vapour mole fraction of compound i, [-]
$\alpha_{i,j}$	relative volatility between compounds i and j, [-]
β	catalyst loading, [g$_{cat}$ g$_{mixture}^{-1}$]
γ_i	liquid-phase activity coefficient of compound i, [-]
ΔG^θ	standard free energy, [kJ mol^{-1}]
ΔH_r	heat of reaction, [kJ mole^{-1}]
ε	reaction volume, [-]
ρ_{cat}	density of catalyst [g$_{cat}$/ m$^3_{cat}$]
ρ_{mix}	density of mixture [g$_{mix}$/ m$^3_{mix}$]
δ	thickness of the liquid-side diffusion film, [m]
τ	liquid residence time per stage, [s] or [min]

Abstract

A Novel Mapping Method for Assessing the Applicability of Reactive Distillation to Quaternary Reaction Systems

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The University of Manchester, 2020

Reactive distillation is a process intensification technology that promises significant improvements in the chemical industry by allowing the integration of reaction and separation to takes place simultaneously in a single apparatus. This integration, unfortunately, causes a complex interplay between mass transfer, chemical reaction and hydrodynamics within the column. As a consequence, the commercialisation of reactive distillation applications is hindered by challenges and difficulties in understanding, screening and designing the process. Many previous studies have developed different approaches for assessing the operability of reactive distillation during the conceptual design. Those methods provide a good basis for initialising the column design; however, their capability to generate reactive distillation design parameters, such as reflux ratio and the number of theoretical stages, tends to be limited to a single set of solutions. Furthermore, the assessment of the operability of reactive distillation has been reported to be lengthy and complicated mainly because of multi-nonlinear equations involved.

Driven by the current limitations, this research proposes a new conceptual method that can simplify the assessment of the applicability of reactive distillation at the conceptual design by reducing computational effort. This novel approach, which is called a mapping method, is developed for quaternary reaction systems that are frequently encountered in industrial reactive distillation applications. This method visualises the applicability of reactive distillation in a plot of reflux ratio vs the number of theoretical stages that is called an "applicability graph". The applicability of reactive distillation is assessed by employing hypothetical "generic" cases with two or three process characteristics, namely relative volatilities, chemical equilibrium constant and, in case of kinetically controlled reactions, the Damköhler number.

To begin with, the method is introduced and developed for (near-) ideal reaction systems with both reactants as mid-boiling compounds, $T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$. With this order of boiling points, an ease of products separation is anticipated as product C is predominantly present at the top and product D is largely present at the bottom part of reactive distillation columns. Next, the development of the mapping method is extended for (near-) ideal systems with other boiling point orders of compounds. And finally, the mapping method is developed for non-ideal reaction systems containing homogeneous and/or heterogeneous azeotropes. The development of the mapping method gives rise to the synthesis of a new framework that offers an aid for process engineers to make a go-/no-go decision about the application of reactive distillation before performing any rigorous simulations of RD processes.

The proposed method is validated by either performing rigorous simulations for case studies or comparing the results of this work with those reported in previous studies using different approaches. The validation using case studies aims to demonstrate the advantages proposed by the mapping method, along with its limitation. This assessment is carried out by comparing the predicted applicability graph from pre-generated applicability graphs of generic cases and the actual applicability graph generated from rigorous simulations for case studies. The validation referring to previous studies aim to seek a possible agreement between the results generated in this work by employing generic cases and those obtained by previous studies by performing detailed computations for real reaction systems.

This thesis demonstrates the potential usefulness of the mapping method to assess the applicability of reactive distillation for both near-ideal quaternary reaction systems that are not hindered by the formation of azeotropes and non-ideal quaternary reaction systems involving the existence of homogeneous and/or heterogeneous azeotropes. The proposed method is identified to be unsuitable for strongly non-ideal reaction systems; this limitation is analogous with that of shortcut methods for conventional distillation. This research shows the capability of the mapping method to envisage the applicability of reactive distillation based on pre-generated generic applicability graphs, prior to performing any rigorous computations for real reaction systems. Therefore, end-users of the mapping method, i.e. process engineers in the chemical industry, can expect to save time and reduce computational effort when evaluating the performance of reactive distillation at the conceptual design level.

Declaration

No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

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Chapter 1

General Introduction

- Introduction to Reactive Distillation
- Research Motivation
- Research Objectives
- Structure of PhD Thesis

Chemical engineering is a key discipline contributing to the design of processes with an effective transformation of raw materials into any kinds of desired products. To describe such transformation in processes with or without the inclusion of chemical reactions, chemical engineering relies on the concept of unit operations that are widely used to perform the physical steps of preparing reactants, separating and purifying products, recycling unconverted reactants and controlling the energy transfer through chemical reactors (McCabe et al., 1993). Unit operations deal with the processes involving (a) fluid flow, such as fluid transportation and agitation, (b) heat transfer, such as heat exchange and evaporation, and (c) mass transfer, such as distillation and extraction.

Among existing unit operations in the chemical processes, distillation is possibly the most popular separation and purification technique and it has been used for over two hundred years (Kockmann, 2014; 2017). Distillation is a thermal unit operation that can separate multi-components based on the difference in their volatilities. This unit operation has been applied in many industrial sectors, such as the crude oil fractionation, distilled beverages production, water desalination and air separation. Despite its versatility at the commercial scale, distillation column remains an energy intensive process (Delgado-Delgado et al., 2012). On account of extensive studies performed by the scientific community, different types of distillation technology have been developed including heat pump assisted distillation, dividing-wall column, internal heat-integrated distillation column, membrane distillation, reactive distillation and so on.

Previous studies showed that reactive distillation is a great process intensification method as it allows the combination of two key functions in the chemical processing, i.e. reaction and separation, to take place in a single apparatus (Agreda et al., 1990; Chiu et al., 2006; Kiss et al., 2006; Smith Jr., 1980). The application of reactive distillation processes promises key advantages, such as cost reduction, energy saving and CO_2 emissions reduction, as compared to conventional processes with a sequence of reaction and separation in different units (Shah, et al., 2012). Reactive distillation has gained growing interests from researchers and industrial players as proven by the progressive increase of the number of patents and scientific publications about reactive distillation processes since 1970 (Keller, 2014).

The application of reactive distillation, however, is hindered by challenging tasks in synthesising reactive distillation processes as a result of a complex interplay between chemical reaction, mass transfer and hydrodynamics within the column (Harmsen, 2007; Taylor and Krishna, 2000). Although different design approaches have been developed to some extent by many studies, the assessment of the performance of reactive distillation using those methods remains difficult and time consuming (Li et al., 2016; Segovia-Hernández et al., 2015). Driven by this problem, this PhD thesis aims to generate and develop a new conceptual tool, called a mapping method, to assess the applicability of reactive distillation. Herein, the word of applicability is defined as the state where a reactive distillation process is technically operable for desired product purity. Using the mapping method, this work proposes and demonstrates relatively simpler procedures to assess the applicability of reactive distillation to industrially relevant chemical reactions by using pre-calculated performance information for hypothetical and idealised generic cases and correlating process characteristics, i.e. some physical and chemical parameters, with the performance of reactive distillation.

This work focuses on the development of the mapping method for quaternary reaction systems ($A + B \rightleftharpoons C + D$) as these systems are frequently encountered in the operation of reactive distillation (Hiwale et al., 2004; Luyben and Yu, 2008; Sharma and Mahajani, 2002). Before discussing the development of the proposed method in the next chapters, this thesis presents a general introduction in this chapter that is divided into four sections. An introduction to reactive distillation is presented in Section 1.1. Research motivation and objectives are discussed in Sections 1.2 and 1.3, respectively. Finally, the structure of the present PhD thesis is given in Section 1.4.

1.1. Introduction to Reactive Distillation

Process intensification (PI) is a subject in chemical engineering that focuses on improvements in the chemical industry, and it can be interpreted in different ways. Cross and Ramshaw (1986) defined process intensification as the strategy of reducing the size of chemical plant needed to achieve a given objective function. Stankiewicz and Moulijn (2000) presented the meaning of process intensification as the development of novel apparatuses and techniques that, compared to those regularly used today, offer drastic

improvement in manufacturing and processes, substantially decreasing equipment volume, energy consumption, or waste generation, and ultimately bringing cheaper, safer and sustainable technologies. Franke (2007) described process intensification as a holistic approach starting with an analysis of economic constraints followed by the selection or development of a production processes, and it aims at drastic improvements of the performances of a process by rethinking the process as a whole. The improvements in the chemical industries, obtained by the implementation of PI, are driven through the integrations of unit operations, functions, phenomena and the improved phenomena/functions in an existing conventional process (Lutze et al., 2010).

Stankiewicz et al. (2019) classified the elements of process intensification into "equipment" and "methods" as listed in Table 1.1. Note that both classes have strong correlations between each other and there might be some overlap in their applications; novel equipment might employ new PI methods, and *vice versa.*

Table 1.1. Process intensification classifications according to Stankiewicz et al. (2019)

PI elements	Sub-elements	Examples
PI equipment	Reactors	Spinning disk reactor, microreactor, monolith reactor, static mixer reactor
	Equipment for non-reactive operations	Static mixer, compact heat exchanger, centrifugal adsorber, rotating packed bed
PI methods	Multifunctional reactors	Reactive distillation, reactive extraction, membrane reactor, reverse-flow reactor
	Hybrid separations	Membrane distillation, membrane absorption, adsorptive distillation
	Alternative energy sources	Ultrasound, microwave, plasma technology, solar energy
	Other methods	Supercritical fluids for the synthesis of natural products, dynamic reactor operation

Among PI methods, the application of a multifunctional reactor brings improvements in the chemical industry by integrating reaction and other task, i.e. separation, heat exchange, or phase transition, into a single unit. Reactive distillation (RD) is a multifunctional reactor technology that enables reaction and separation to take place simultaneously in a distillation column. Reactive distillation processes can be classified into auto-catalysed, homogeneous catalysed and heterogeneous catalysed processes. The vapour-liquid contact space in a conventional distillation column usually comprises rectifying and stripping zones, see Fig. 1.1 (a), whereas that in a reactive distillation column for a heterogeneously catalysed process consists of rectifying, reactive and stripping zone, see Fig 1.1 (b).

(a)   (b)
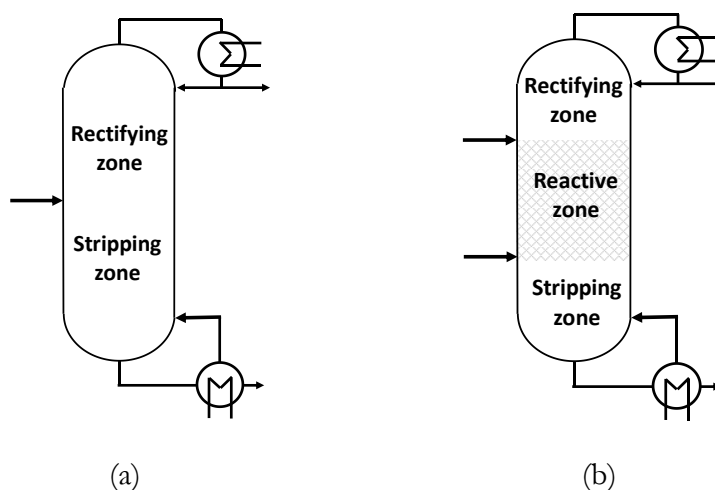
Fig. 1.1. (a) A classic distillation column, (b) a reactive distillation column for a heterogeneously catalysed process

Reactive distillation has existed for almost one century; the first patent was granted in 1921 for the manufacture of esters (Backhaus, 1921). In the following years, several scientific publications reported the use of reactive distillation mostly for auto-catalysed reactions (Berman et al., 1948; Keyes, 1932; Schniepp et al., 1945). The industrial interest in the application of reactive distillation has been renewed since the late 1970s, when the company Chemical Research & Licensing patented the first heterogeneously catalysed process for the synthesis of methyl *tert*-butyl ether (Smith Jr, 1980). Few years later, the Eastman Kodak company invented one of the most well-known reactive distillation processes for the production of methyl acetate (Agreda et al., 1990; Siirola, 1996).

The development of reactive distillation has been studied progressively across the world. The number of relevant research has significantly increased over the past 50 years. Malone and Doherty (2000) reported that 562 scientific publications about reactive distillation were identified in 30 years prior to 2000. Surprisingly, within the next 11 years, at least 1,979 scientific papers were published (Keller, 2014). Since then, it seems that the average publications number per year was kept constant. For instance, Wierschem and Górak (2018) reported that there are more than 1,000 research-based publications produced from 2013 to 2018 aimed to extend the performance of reactive distillation.

Reactive distillation is beneficial for equilibrium-limited reactions, such as (trans-) esterification, hydrolysis, etherification, alkylation, hydrogenation, isomerisation, which are usually performed in conventional processes with an excess of a reactant. Table 1.2 lists some examples of types of reactive distillation processes. These processes have been either implemented at a commercial level or tested at a laboratory scale with a promising pathway for process scale-up.

The use of reactive distillation in the chemical industries promises extensive benefits, as listed below (Kiss, 2018; Taylor and Krishna, 2000).

+ Increased conversion by pulling the reaction pathway to the product side, as well as improved selectivity by avoiding side reactions, because of the continuous removal of products from the column
+ Lower costs due to integrated reaction and separation functions in a reactive distillation column
+ Energy saving by the use of the exothermic heat of reaction for liquid vaporisation
+ Reduced footprint of chemical plants due to less equipment required
+ Improved health, safety and environment because of less CO_2 emissions and avoided hot spots and runaway reactions
+ Circumvented azeotropes by having them reacted away or preventing their presence due to simultaneous reaction and separation
+ Simplified separation of close-boiling components when using a reactive entrainer reacting with one of components to form an intermediate product that is easily separated and reacted to re-form the original component in a second reactive distillation column

+ Avoided chemicals degradation because of shorter residence time expected for the operation of a reactive distillation column in comparison that for a conventional reactor

+ Reduced catalyst requirement to gain identical conversion as that in conventional processes

Table 1.2. Examples of industrially relevant reaction systems using reactive distillation, either implemented at a commercial level or tested at a laboratory scale (Hiwale et al., 2004; Luyben and Yu, 2008; Sharma and Mahajani, 2002)

Class of systems	Examples
Binary systems (A $\rightleftharpoons$ B)	• 2-phenyl ethanol $\rightleftharpoons$ p-ethyl phenol • *trans*-2-butene $\rightleftharpoons$ 1-butene • α-isophorone $\rightleftharpoons$ β-isophorone
Ternary systems (A + B $\rightleftharpoons$ C or A $\rightleftharpoons$ B + C)	• *Iso*-butene + methanol $\rightleftharpoons$ methyl *tert*-butyl ether • *Iso*-amylene +methanol $\rightleftharpoons$ *tert*-amyl methyl ether • Ethylene oxide + water $\rightleftharpoons$ ethylene glycol • Propene + benzene $\rightleftharpoons$ cumene • 2-ethyl-1-butene + methanol $\rightleftharpoons$ 3-methoxy-3-methylpentane • Benzene + hydrogen $\rightleftharpoons$ cyclohexane • Butanediol $\rightleftharpoons$ tetrahydrofuran + water • *Tert*-butanol $\rightleftharpoons$ isobutylene + water
Quaternary systems (A + B $\rightleftharpoons$ C + D)	• Acetic acid + methanol $\rightleftharpoons$ methyl acetate + water • Acetic acid + amyl alcohol $\rightleftharpoons$ amyl acetate + water • Acrylic acid + *n*-butanol $\rightleftharpoons$ *n*-butyl acrylate + water • Methyl lactate + water $\rightleftharpoons$ lactic acid + methanol • Methyl acetate + *n*-butanol $\rightleftharpoons$ butyl acetate + methanol • Acetaldehyde + ethylene glycol $\rightleftharpoons$ 2-methyl-1,3-dioxolane + water • *Tert*-amyl alcohol + ethanol $\rightleftharpoons$ *tert*-amyl ethyl ether + water

In contrast to the significant advantages highlighted above, reactive distillation has some drawbacks to such an extent that it is unlikely to be used in some cases. The drawbacks of reactive distillation are listed below (Harmsen, 2010; Keller, 2014; Taylor and Krishna, 2000; Wierschem and Górak, 2018).

- Reduced flexibility: smaller operating windows (restricted selection of pressure and temperature) and fewer degrees of freedom because of the integrated reaction and separation processes
- Incompatible volatility order between reactants and products
- Difficulties in scaling up the process because of liquid distribution problems for large flows in a large column
- Risk of failure when operating reactive distillation columns due to simultaneous phenomena of separation and reaction in the column
- The presence of reactive azeotropes that causes difficult or even infeasible separation
- The presence of multiple steady states in which diverse conversions and different column profiles might result from a reactive distillation column running at specific conditions

1.2. Research Motivation

Although reactive distillation promises significant benefits over conventional processes, its application is not always technically applicable and economically attractive. The availability of reliable conceptual tools is crucial for screening and designing reactive distillation processes. One of those conceptual tools are residue curve maps that can represent an approximation of equilibrium behaviour and allow one to analyse the feasibility of separation where azeotropic mixtures exist (Fien and Liu, 1994; Malone and Doherty, 2000). By using residue curve maps to predict liquid compositions in continuous reactive distillation processes, Barbosa and Doherty (1988a; 1988b) developed a set of transformed compositions variables to quantify the minimum reflux ratios for RD columns. However, that approach enables only a single reflux ratio from an assessment,

which means that repetitive efforts should be performed when one wants to consider multiple configurations.

Other approaches to design reactive distillation processes are based on optimisation techniques, such as mixed-integer non-linear programming problem and mixed-integer dynamic optimisation (Bansal et al., 2000; Ciric and Gu, 1994). These approaches may use single or multi-objective functions that are maximised or minimised under specific constraints, and they often relate the design of reactive distillation to economic analysis. In spite of the vast development of optimisation-based techniques, one finds difficulty in quickly modelling and initialising the design of reactive distillation columns due to the existence of non-linear and multivariable equations (Almeida-Rivera et al., 2004; Segovia-Hernández et al., 2015). Note that integrated reaction and separation functions in a RD column result in complex interactions of mass transfer, chemical reaction and hydrodynamics (Agar, 1999; Keller, 2014). Because of this complexity, the assessment of the performance of reactive distillation processes is more difficult than that of conventional processes (Chen et al., 2000; Harmsen, 2007; Li et al., 2016).

Next to those challenges in initialising a reactive distillation design, one should keep in mind that operating reactive distillation with an optimal performance can only be done when appropriate design parameters, such as feed stage location, catalyst selection, the amount of catalyst, reflux ratio, hardware materials, liquid hold-up and residence time, are well considered. For instance, liquid hold-up and liquid residence time strongly affect the conversion and selectivity of reaction occurring in a reactive distillation (Towler and Frey, 2000). The promising benefits of reactive distillation could be nullified by improper selection of RD design parameters (Taylor and Krishna, 2000), and hence, appropriate approaches to determine these parameters are required.

Recently, Skiborowski (2018) highlighted that besides residue curve maps developed in 1990s, general methods for the synthesis of reactive distillation columns are still scarce. For initialising the design of conventional distillation columns, shortcut methods, such as the Fenske-Gilliland-Underwood methods, are well known and generally applied. Such shortcut methods that can be used to reduce computational effort seem to be unavailable for screening the designs of reactive distillation; therefore, rigorous computations are usually needed for a reactive distillation assessment.

Discussion with industrial experts during a poster session in the 11th international conference on Distillation and Absorption (September 16-19, 2018 in Florence) clearly highlighted the needs of simple approaches to assess the applicability of reactive distillation at the conceptual level as the use of many existing design methods relies on an in-depth knowledge about reactive distillation processes. Simple approaches should enable aids for process engineers to quickly make a go-/no-go decision regarding the operation of reactive distillation prior to performing extensive computations.

Driven by these problems and needs, research questions of this PhD thesis are developed: How can one perform the assessment of the applicability of reactive distillation with less computational effort? What kind of conceptual tools that can outperform the capability of existing methods in assessing the applicability of reactive distillation?

This PhD thesis proposes a new method for the assessment of the applicability of reactive distillation. To develop such method, it is necessary to create a "wish list" that the demanded method should have. The method should be able to:

- be applicable for many industrially relevant reaction systems,
- suggest multiple solutions of column configurations from an assessment; therefore, reducing computational effort,
- provide heuristics and insights into the design and performance of reactive distillation,
- be suitable for near-ideal reaction systems with the absence of any azeotropes and non-ideal reaction systems containing heterogeneous and/or homogeneous azeotropes, and
- aid process engineers to gain (semi)quantitative information for making a go-/no-go decision regarding the applicability of reactive distillation prior to performing rigorous simulations and detailed assessments.

1.3. Research Objectives

This PhD study aims to generate and develop a conceptual tool, called a mapping method, which is used with less computational effort for assessing the applicability of reactive

distillation. This work focuses on the application of reactive distillation processes for quaternary reaction systems, $A + B \rightleftharpoons C + D$. The objectives of this work are:

1. to investigate the effects of key process characteristics, which are considered in the mapping method, on the performance of reactive distillation,
2. to assess the applicability of reactive distillation by using pre-calculated performance information for hypothetical and ideal generic cases,
3. to validate the proposed mapping method by performing rigorous simulations for case studies representing real reaction systems and comparing the findings of this work with those of previous studies employing different conceptual approaches,
4. to generate heuristics for the initialisation of reactive distillation designs, and
5. to synthesise a systematic framework based on the use of the mapping method for assessing the applicability of reactive distillation.

1.4. Structure of PhD Thesis

This PhD thesis uses a journal-based format that is structured according to the theses policy regulated by the University of Manchester. The journal-based format allows the incorporation of published and submitted scientific papers in different chapters, as listed in Table 1.3, which arise from this research. These chapters address specific research objectives highlighted in Section 1.3 (see Fig. 1.2). Note that some overlaps and repetitions, especially in theoretical backgrounds and the introduction of the proposed conceptual tool, are necessary in different chapters to allow each of them to be readable as a standalone chapter.

Table 1.3. Details of publications presented in Chapters 3, 4 and 5.

Chapter	Publication	Publication details
3	Publication 1	Muthia, R., Reijneveld, A. G. T., van der Ham, A. G. J., ten Kate, A. J. B., Bargeman, G., Kersten, S. R. A. and Kiss, A. A. (2018). 'Novel method for mapping the applicability of reactive distillation', *Chemical Engineering and Processing: Process Intensification,* 128, pp. 263–275.

Chapter	Publication	Publication details
3	Publication 2	Muthia, R., Jobson, M. and Kiss, A. A. (2019). 'Innovative mapping method for screening reactive distillation designs', *Computer Aided Chemical Engineering*, 46, pp. 739–744.
4	Publication 3	Muthia, R., van der Ham, A. G. J., Jobson, M. and Kiss, A. A. (2019). 'Effect of boiling point rankings and feed locations on the applicability of reactive distillation to quaternary systems', *Chemical Engineering Research and Design*, 145, pp. 184–193.
5	Publication 4	Muthia, R., Jobson, M. and Kiss, A. A. (2020). 'A systematic framework for assessing the applicability of reactive distillation for quaternary mixtures using a mapping method', *Computers & Chemical Engineering*, 136, 106804.
	Publication 5	Muthia, R., Jobson, M. and Kiss, A. A. (2020). 'Determining the design parameters of reactive distillation processes by a quick mapping method', accepted for publication in *Computer Aided Chemical Engineering*.

The contents of next chapters in the present PhD thesis are explained as follows. Chapter 2 presents a critical evaluation of literature on the assessment of reactive distillation at the conceptual level. This chapter discusses the importance of process synthesis for developing reactive distillation processes, available methods to screen and design reactive distillation columns, mathematical models and process simulation for reactive distillation, and finally types and internals of reactive distillation columns.

Chapter 3 introduces the proposed mapping method in this PhD thesis. The development of the method in this chapter is limited to near-ideal quaternary systems, which are not hindered by the formation of azeotropes, for a subset of reaction systems with both reactants as mid-boiling compounds—$T_{b,C} < T_{b,B} < T_{b,A} < T_{b,D}$. The method is developed for: (1) investigating effects of process characteristics in the mapping method on the RD performance, and (2) predicting the applicability of reactive distillation to near-ideal

quaternary systems. The validation step using two case studies shows that the prediction of the RD applicability generated by the mapping method is in a good agreement with the results obtained from rigorous simulations of those case studies.

Objective 1
To investigate the effects of key process characteristics, which are considered in the mapping method, on the performance of reactive distillation.

Objective 2
To assess the applicability of reactive distillation by using pre-calculated performance information for hypothetical and ideal generic cases.

Objective 3
To validate the proposed mapping method by performing rigorous simulations for case studies and comparing the findings of this work with those of previous studies employing different conceptual approaches.

Objective 4
To generate heuristics for the initialisation of reactive distillation designs.

Objective 5
To synthesise a systematic framework based on the use of the mapping method for assessing the applicability of reactive distillation.

Chapter 3

Chapter 4

Chapter 5

Fig. 1.2. Addressed research objectives in Chapters 3, 4 and 5

Chapter 4 extends the development of the mapping method for near-ideal quaternary reaction systems with various orders of boiling points of compounds. In this chapter, the method is used for: (1) evaluating a preliminary economic ranking of process alternatives in quaternary reaction systems, and (2) generating heuristics for the feed stage locations of RD processes. The validation step in this chapter shows that insights and heuristics

generated by the mapping method using generic cases are in line with those obtained by previous studies that employed rigorous simulations for the real reaction systems.

Chapter 5 presents an advanced development of the mapping method for non-ideal quaternary reaction systems containing azeotropes that cause unique separation challenges. The method is utilised for: (1) generating heuristics for initialising the design of RD columns, and (2) predicting the applicability of reactive distillation to quaternary reaction systems classified into different groups of boiling point orders of compounds. The validation step in this chapter shows that the mapping method is suitable for non-ideal systems containing only one azeotrope between any binary mixtures affecting relative volatilities of compounds that characterise the performance of separation in the assessed systems. Ultimately, this chapter presents a systematic framework that aids process engineers to make a go-/no-go decision regarding the application of reactive distillation.

Finally, Chapter 6 summarises key findings of this work and critically evaluates the conceptual tool developed in this PhD thesis. Furthermore, this chapter makes recommendations for the directions of future work that may improve and complement the present work.

Chapter 2

Literature Review

- Process Synthesis for Process Intensification
- Methods for Designing Reactive Distillation Processes
- Mathematical Models of Reactive Distillation Columns
- Process Simulation for Reactive Distillation
- Types of Reactive Distillation Configurations
- Internals of Reactive Distillation

This chapter presents a critical evaluation of literature on the assessment of performance of reactive distillation (RD) at the conceptual level. Firstly, the importance of process synthesis in the assessment of reactive distillation is explained. Next, available methods to screen and design reactive distillation processes are explored according to three classifications: graphical, optimisation-based and heuristic approaches. Then, mathematical models and process simulation for reactive distillation, which enable quantitative evaluations of reactive distillation columns, are discussed. The internals and types of configurations of reactive distillation are presented to provide readers of this thesis with broader knowledge of reactive distillation designs. Finally, in the concluding remarks of this chapter, knowledge gaps are linked to the aim of this work and the discussed subjects in this chapter are connected to procedures to develop a new method in this study.

2.1. Process Synthesis for Process Intensification

Chemical process design is a creative engineering activity that allows constructing ideas and interpreting them into processes and equipment, with a main goal of manufacturing new materials or improving existing materials. In the development a chemical process route, one assesses process alternatives and determines the most beneficial option through a synthesis activity. Process synthesis activities reduce commercialisation risks due to untested technology for a novel process, and overcome certain challenges at the conceptual design level. In process synthesis activities, a design team is rarely supplied with adequate information, such as physical and chemical properties, operating conditions and catalyst options. Heuristics approaches, i.e. rules of thumbs and design guidelines, are usually applied to expedite the generation of alternative flowsheets (Seider et al., 2010).

Process synthesis is usually systematised by hierarchical steps that need to be followed by engineers. Some of well-known systematic approaches to synthesise chemical engineering processes were put forward by Douglas (1988) and summarised by Smith (2016). Douglas (1988) proposed the following hierarchy of process decisions to solve design problems:

1. batch vs continuous,

2. input-output structure of the flowsheet, e.g. the requirement of purification of feed impurities and the determination of the number of product streams,

3. recycle structure of the flowsheet, e.g. the use of an excess of a reactant and the determination of the number of recycle streams,

4. general structure of the separation system, i.e. vapour and/or liquid recovery systems, and

5. heat exchanger network.

The hierarchy of chemical process design can be represented by the layers of a so-called onion diagram (see Fig. 2.1), in which plant designers start with designing reactors, then introduce separation and recycle systems, consider heat recoveries, assess heating and cooling systems and, finally, take into account environmental aspects (Linnhoff et al., 1982; Smith, 2016).
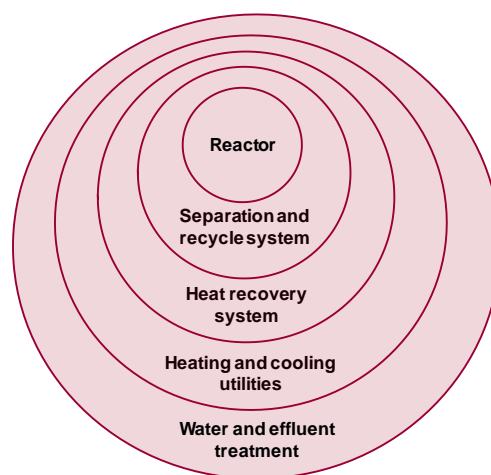
Fig. 2.1. Onion diagram for designing chemical processes (Linnhoff et al., 1982; Smith, 2016).

Process synthesis is crucial in the development of process intensification (PI) as it contains hierarchical steps that enable systematic approaches for determining and designing the most suitable PI units. For instance, Schembecker and Tlatlik (2003) proposed a process synthesis procedure that allows designers to evaluate the performance of reactive separation units when the available information is only qualitative chemical and physical behaviours. The evaluation starts by identifying "knock-out criteria" for phases of the entire system that hinder the process feasibility, e.g. reactive extraction is not applicable

when reaction takes place in vapour phase, then, distinguishing key benefits of the PI unit application, and assessing the overlaps of operating windows between reaction, separation and equipment, e.g. in terms of operating pressure and temperature.

For the development of reactive distillation technology, process synthesis particularly gives qualitative reference points to quickly screen reactive distillation processes. For instance, Shah et al. (2012) proposed a systematic framework for the feasibility and technical evaluation of reactive distillation processes that is used by checking some constraints, such as type of main reactions, stoichiometry of reaction, kinetics and equilibrium, vapour-liquid equilibrium data and enthalpy of reaction.

2.2. Methods for Designing Reactive Distillation Processes

This section aims to explore available methods for screening and designing reactive distillation processes that are reported in literature. Almeida-Rivera et al. (2004) distinguished methods for designing and evaluating the applicability and feasibility of reactive distillation based on three categories: graphical, optimisation- and heuristic-based methods. Note that the word of "feasibility" has been used by previous studies to describe one of the following two conditions: (1) reactive distillation is technically operable, but not proven to be economically attractive, or (2) reactive distillation is technically operable and economically attractive. For a consistency reason, in this thesis, the first condition is described by the word of "applicability", while the second condition is specifically represented by the word of "feasibility".

Graphical methods identify molar and mass compositions along the column using residue curves map and distillation lines. Optimisation techniques are commonly featured with mathematical relationships among the objectives or performance criteria to be optimised, the type of decision variables and the presence of several constraints in reactive distillation processes (Segovia-Hernández et al., 2015). Tables 2.1 and 2.2 summarise graphical and optimisation-based methods for evaluating and designing reactive distillation processes, which comprise description of the methods as well as their strengths and weaknesses.

Table 2.1. Graphical methods for designing reactive distillation processes

Design methods	Description	Strengths and weaknesses	References
Residue curves mapping	Residue curves map is a tool for performing the applicability analysis of both nonreactive and reactive distillation based on transformed molar compositions. Its structure relies on thermodynamics that strongly affect the shape of composition profiles and accordingly the attainable products from the operation of a (reactive) distillation column. For a kinetically controlled reaction occurring in a RD column, the applicability assessment can be performed with residue curves by using the Damköhler number. The residue curve ends at a pure component or a nonreactive azeotrope for the case with the Damköhler number equals to zero. The residue curve ends at a pure component, a chemical equilibrium point, or a reactive azeotrope for the case with a high Damköhler number.	+ Approximates the actual equilibrium behaviour where non-ideal and azeotropic mixtures are involved + Requires only basic parameters, e.g. feed compositions, phase equilibrium models and reaction stoichiometry - Limited to four components because of its intrinsic graphical nature - Requires very accurate thermodynamic data to characterise RD processes	(Almeida-Rivera et al., 2004; Barbosa and Doherty, 1988c; Espinosa et al., 1996; Fien and Liu, 1994; Qi et al., 2002; Ung and Doherty, 1995)
Statics analysis	This method is based on thermodynamic-topological analysis of distillation diagrams, assuming infinitely large vapour and	+ Requires little information (feed compositions, phase equilibrium models,	(Almeida-Rivera et al., 2004; Giessler

Design methods	Description	Strengths and weaknesses	References
Static analysis (*continued*)	liquid flow rates in the column and adequate capacity of the reactive section in the column for a given conversion rate. The statics analysis assumes a reactive distillation column as a succession of reactor and distillation units, where the feed is transformed to a pseudo-initial mixture—with certain compositions and a certain degree of reaction—and separated in a distillation unit. The number of theoretical stages is estimated from the distillation line, and the reactive stages are quantified based on the intersection of the distillation line and the boundary between the forward and backward reactions, which is called chemical equilibrium manifold.	chemical equilibrium and reaction stoichiometry) + Enables qualitative estimation of RD structure, such as maximum conversion, location and length of reactive section + Allows analysing possible products compositions and the column configuration for varied feed compositions - Assumes infinite efficiency for separation - May bring difficulties in matching the operating lines with the estimated products composition	et al., 1998; Giessler et al., 1999)
Attainable region technique	This method identifies applicable reactor networks based on graphical properties of plug flow and continuous stirred tank reactors. The attainable region means the segment of concentration space that can be obtained from a given feed composition by combination of reaction and mixing.	+ Considers mixing effect + Incorporates the theory derived for reactors + Can be extended to multiphase systems - Complicated graphical analysis	(Almeida-Rivera et al., 2004; Gadewar et al., 2003;

Design methods	Description	Strengths and weaknesses	References
Attainable region technique (*continued*)	The method assumes c1 and c2 as two attainable product compositions and identifies vector c1c2 as the part of a region. On the boundary of an attainable region, the reaction vector points inward. No reaction vector can intersect the region.		Nisoli et al., 1997)
Fixed-point algorithm	This method screen applicable column designs based on the use of residue curve map techniques. Fixed points that belong to pure components and azeotropic compositions are assessed. Their locations change when reflux ratio, external reboil ratio, and/or the Damköhler number are modified. In contrast to stable and unstable nodes, the location of fixed points relies on process parameters.	+ Flexible in providing designs of reactive distillation at different design parameters + The material and energy balances can be decoupled, so that one may assess the column profiles based on mass balance and equilibrium expressions - The application is limited by its graphical nature	(Almeida-Rivera et al., 2004; Buzad and Doherty, 1994)
Thermodynamics-based approach	This method identifies the applicability of reactive distillation based on the existence of reactive distillation lines and potential reactive azeotropes. Possible separation regions are determined by the calculation of the column mass balance.	+ Can be applied to both fast and slow equilibrium reactions + Feasible products can be calculated within a reactive distillation column	(Almeida-Rivera et al., 2004;

Design methods	Description	Strengths and weaknesses	References
Thermodynamics-based approach (*continued*)		- There might be difficulties in identifying reactive azeotropes - Applicability analysis needs detailed knowledge about phase equilibrium, reaction kinetics and residence time within the column	Frey and Stichlmair, 1999)
Reactive cascades	This method assumes rectifying, reactive and stripping sections as a series of cascade of flashes either in co-current or counter-current flow. A reactive distillation configuration is obtained for a given normalised Damköhler number, based upon the satisfaction of the product specification. The fixed-point algorithm assumes fixed residence time for every flash stage and an identical fraction of feed to be vaporised in each stage.	+ Its application is not restricted to a certain number of components in the assessed reaction + Easily implemented - Does not account for the effects of structural aspects, such as location of multiple feed stages, reflux and reboil ratios - Disregards energy balances	(Almeida-Rivera et al., 2004; Gadewar et al., 2003)
Conventional graphical techniques	These techniques, which are based on the McCabe-Thiele and Ponchon-Savarit methods, enable the distribution of reactive zones within a reactive distillation column for a certain extent	+ Capable of visualising tray-by-tray calculations - Specific for isomerisation reactions	(Almeida-Rivera et al., 2004;

Design methods	Description	Strengths and weaknesses	References
Conventional graphical techniques (*continued*)	of reaction by adjusting the catalyst hold-up. Some assumptions are applied: (a) a single reaction for a binary system, (b) constant molar overflow, and (c) attained vapour-liquid equilibrium.	- Limited by their graphical nature	Lee et al., 2000a; 2000b; 2000c)
Phenomena-based approach	This approach characterises mixing, separation and reaction in a reactive distillation as the phenomena vectors in the composition space. The summation of these vectors, which indicates the presence of a kinetic fixed point, is undesired as it describes flat concentration profiles. Therefore, some actions to move away from that point, such as changing design parameters and operating conditions, are employed.	+ The estimation of the phenomena vectors requires only physical and chemical data + Allows the assessment of equipment design and operating conditions that accounts for composition changes - Its suitability requires further study	(Almeida-Rivera et al., 2004; Hauan and Lien, 1996)
Scalar/vectorial difference points technique	This technique combines approaches in the phenomena-based and reactive cascade methods, with the following assumptions/conditions: known top and bottom compositions, determined reflux ratio, constant molar flow and applicable for ternary reactions: $2A \rightleftharpoons B + C$.	Combined strengths and weaknesses of both phenomena-based and reactive cascade methods.	(Almeida-Rivera et al., 2004; Kiss, 2017)

Table 2.2. Optimisation-based approaches to design reactive distillation processes

Design methods	Description	Strengths and weaknesses	References
Mixed-integer non-linear programming	This approach aims to provide fully or partially optimised solutions for design parameters of reactive distillation, such as the optimum number of theoretical stages, feed stages location, reflux ratio, condenser ad reboiler duties and liquid hold-ups. The application of this method is based on rigorous calculations with functions consisting of masters and sub-problems. The objective functions are related to annual operating cost and annualised investment. The constraints of the rigorous calculations are taken into account from the mass, equilibrium, summation and heat (MESH) equations, kinetics and thermodynamics, and/or rational connections between process parameters.	+ Applicable for multiple reactions and the systems that do not reach reactive equilibrium + Generates optimum designs concerning economics and controllability - Huge computational time for multiple optimisation scenarios and for columns with a large number of stages - Requires complicated numerical tools - The optimisation problem might be hard to solve	(Almeida-Rivera et al., 2004; Ciric and Gu, 1994; Malone and Doherty, 2000)
Orthogonal collocation on finite elements	This method converts the discrete number of stages in a RD column into a continuous variable and makes compositions and temperature as functions of position.	+ Applicable for multiple reactions and the systems that do not reach reactive equilibrium	(Almeida-Rivera et al., 2004; Seferlis and Grievink, 2001)

Design methods	Description	Strengths and weaknesses	References
Orthogonal collocation on finite elements (*continued*)	In this approach, the column is divided into several sections that is subsequently partitioned into smaller fine elements. For each fine element, a number of collocation points is determined and mass and energy balances are fulfilled. These collocation points are selected as the roots of the discrete Hahn family of orthogonal polynomials.	+ Generates optimum designs concerning economics and controllability - Huge computational time for multiple optimisation scenarios and for columns with a large number of stages - Requires complicated numerical tools - The optimisation problem might be hard to solve	
Mixed-integer dynamic optimisation	This approach control problems of reactive distillation to operate columns with the minimum economic cost and with an acceptable dynamic performance due to the existence of disturbances. It involves finding parameters that include continuous parameters, such as column diameter, reboiler, condenser and tuning parameters, and integers parameters, such as the presence of catalyst on different sections of RD columns.	+ Includes both design and controllability aspects of reactive distillation + Generates optimum designs concerning economics and controllability - The optimisation problem might be hard to solve - No assurance for obtaining convergence to a global solution	(Almeida-Rivera et al., 2004; Bansal et al., 2000; Georgiadis et al., 2002; Kiss, 2017; Russel et al., 2000)

Design methods	Description	Strengths and weaknesses	References
Memetic algorithm	This approach is a hybrid of a problem-specific evolutionary algorithm that handles discontinuous cost functions and a mathematical programming technique that solves large nonlinear and continuous sub-problems.	+ Able to provide a large numbers of local optima + Reasonable computational time - Not well proven for complex problems with large numbers of structural decisions - Requires a large number of iterations	(Lutze and Gorak, 2013; Urselmann and Engell, 2015; Urselmann et al., 2011)
Infinite dimensional state-space framework	This process synthesis methodology delivers the global optimisation of reactive distillation networks, especially in terms of minimum reactive holdup and total capacity. In a wider context, this approach offers optimal process networks by decomposing them into an operator network, such as reactors, distillation columns, heat exchangers, and a distribution network, such as mixing, splitting, recycling. Within this framework, network synthesis is prepared as an infinite dimensional linear programs problem. This process representation gives rise to a liner feasible region for RD networks.	+ Capable of identifying the potential of process intensification candidates + A systematic approach to interconnect RD networks with other unit operations - The infinite dimensional linear program cannot be solved explicitly, but it requires a series of finite linear programs - Complex calculations - Complicated schematic network	(Burri and Manousiouthakis, 2004; da Cruz and Manousiouthakis, 2017; Segovia-Hernández et al., 2015)

Design methods	Description	Strengths and weaknesses	References
Disjunctive programming approach	This approach uses rigorous models, including tray-to-tray, phase equilibrium and kinetic based models, to assess optimal designs of reactive distillation for kinetically controlled reactions. This technique employs disjunctions for conditional trays to apply the MESH and kinetics formula with an aim of minimising the size of the nonlinear programming sub-problems.	+ Reduces the size of nonlinear programming to be solved due to the applied conditional trays rule - Difficult for initialisation - Complex calculations	(Jackson and Grossmann, 2001)

Heuristics approaches suggest reactive distillation design variables based upon knowledge of conventional distillation processes and previously designed reactive distillation processes. Subawalla and Fair (1999) proposed heuristic guidelines to design reactive distillation columns, which include the use of a pre-reactor, operating pressure, location of feed location and reactive zone, reactants' ratio, catalyst mass, the number of theoretical stages, reflux ratio and column dimensions. For instance, the reactive zone should be placed where the concentration of reactants is at its maximum. The minimum catalyst loading in a reactive distillation column can be determined by simulating a series of isothermal plug-flow reactors and ideal separators in series. Shortcut methods for conventional distillation, such as the Fenske method, can give an estimation of the number of non-reactive stages in a reactive distillation column. While, the number of reactive stages is calculated by dividing the height of reactive zone—that depends on the catalyst mass, catalyst density and column diameter—over the height equivalent of a theoretical plate for catalytic section.

Overall, key strengths and weaknesses of the graphical, optimisation-based and heuristic approaches discussed in this section are reviewed and presented in Table 2.3. Graphical methods are capable of providing insights into the applicability of reactive distillation processes. However, they are usually restricted by their inherent graphical nature, which limits the number of compounds involved in a reactive distillation assessment. Optimisation-based techniques strongly consider economics in an assessment, but their application requires complex models and lengthy assessment due to the presence of multivariable and non-linear equations. Heuristic approaches are capable of estimating important design variables of reactive distillation columns, but their use demands for rigorous computations of pre-defined real processes and does not link the design variables to the generation of an optimum column design.

The three classes of methods for designing reactive distillation columns share two significant limitations. Firstly, their application requires an in-depth knowledge about reactive distillation processes. As a consequence, those methods are unsuitable for engineers in the chemical industry who have lack of time to deeply understand and screen the applicability of reactive distillation columns. Secondly, the existing methods are unable to generate multiple designs of reactive distillation columns from a single assessment. An assessment of the performance of reactive distillation usually provides a single set of

solutions, such as a reflux ratio and a number of theoretical stages, for a reactive distillation configuration. Therefore, rigorous and repetitive computations are needed to allow one to consider multiple reactive distillation configurations in a design process.

Table 2.3. Key strengths and weaknesses of existing methods for designing reactive distillation processes, developed from Almeida-Rivera et al. (2004), Malone and Doherty (2000), Segovia-Hernández et al. (2015).

	Graphical methods	Optimisation-based techniques	Heuristic approaches
Key strengths	Able to provide insights into the applicability of reactive distillation columns	Accounts for economics	Able to estimate important design variables of reactive distillation columns
Key weaknesses	Limited to their graphical nature	Complex models and lengthy assessment	Requires rigorous computations of pre-defined real processes
	• Requires an in-depth knowledge about reactive distillation processes • A single assessment cannot provide a wide range of reactive distillation designs		

2.3. Mathematical Models of Reactive Distillation Columns

Integrated reaction and separation functions in a reactive distillation column lead to complex interactions of mass transfer, chemical reaction and hydrodynamics. Different modelling approaches, which are summarised in Fig. 2.2, are used to describe reactive distillation processes. Various combinations of these approaches are selected by engineers to model simultaneous phenomena in a reactive distillation column. Note that as the complexity of the model increases, the column design becomes more realistic.
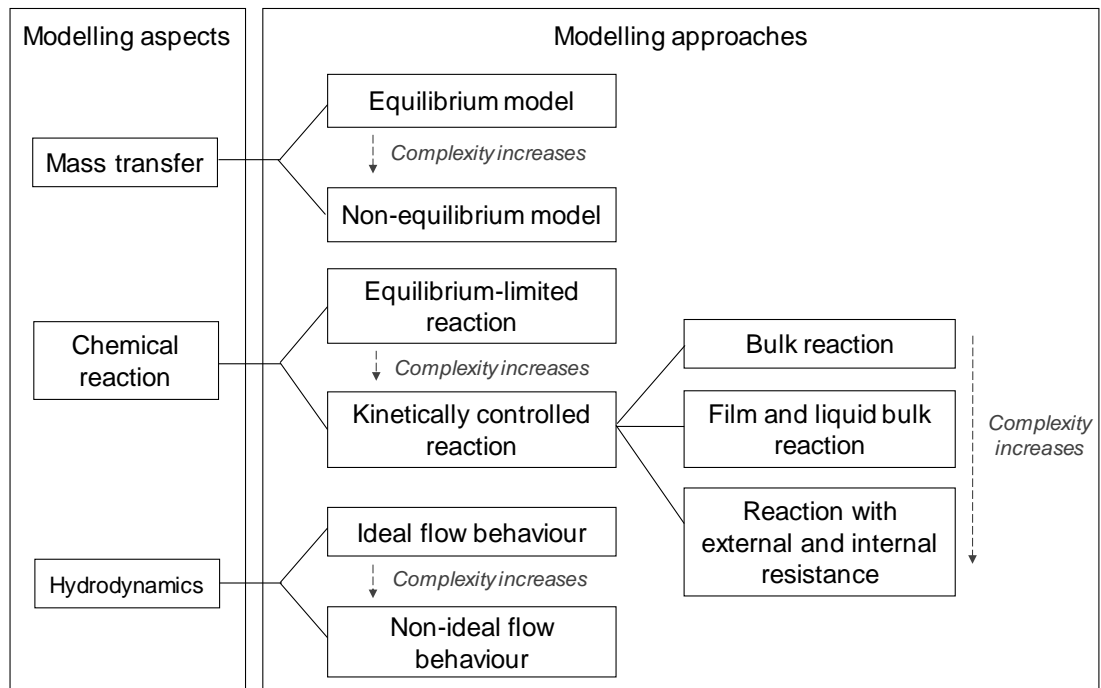
Fig. 2.2. Approaches to model mass transfer, chemical reaction and hydrodynamics in a reactive distillation column (modified from Noeres et al., 2003).

1. Mass transfer models of reactive distillation columns

In terms of liquid-vapour mass transfer, reactive distillation processes can be modelled using equilibrium and non-equilibrium approaches. The equilibrium approach assumes thermodynamic equilibrium between liquid and vapour streams that leave a stage, whereas the non-equilibrium (rate-based) approach accounts for non-equilibrium conditions, which include multicomponent mass and heat transfer rates between the liquid and vapour streams. Both models have been described in great detail elsewhere (Lee and Dudukovic, 1998; Kenig and Górak, 2007; Peng et al., 2002; Towler and Frey, 2002), and only the key explanation will be summarised here.

In the equilibrium model, the phenomena occurring in a reactive distillation column can be described using material, equilibrium, summation and heat (MESH) equations. The schematic mass transfer mechanism on each equilibrium stage is illustrated in Fig. 2.3. The given mathematical expressions of MESH in this section are based on those suggested by Taylor and Krishna (2000). The total and component material balances (M of MESH) are given as

$$\frac{dU_j}{dt} = V_{j+1} + L_{j-1} + F_j - (1+r_j^V)V_j - (1+r_j^L)L_j + \sum_{m=1}^{r}\sum_{i=1}^{c} v_{i,m}R_{m,j}\varepsilon_j \tag{1}$$

and

$$\frac{dU_j x_{i,j}}{dt} = V_{j+1}y_{i,j+1} + L_{j-1}x_{i,j-1} + F_j z_{i,j} - (1+r_j^V)V_j y_{i,j} - (1+r_j^L)L_j x_{i,j} + \sum_{m=1}^{r} v_{i,m}R_{m,j}\varepsilon_j , \tag{2}$$

respectively, where U_j is the hold-up (mole), which is usually that of liquid, on stage j, t is time (s), V_j is the vapour flow rate on stage j (mole s^{-1}), L_j is the liquid flow rate on stage j (mole s^{-1}), F_j is the liquid feed stream on stage j (mole s^{-1}), $v_{i,m}$ is the stoichiometric coefficient of component i in reaction m, R_m is the rate of reaction m on stage j (mole m^{-3} s^{-1}), ε is the reaction volume, and x_i is the mole fraction of component i in the liquid phase. All the time derivatives in Eqs. (1) and (2) equal to zero when a reactive distillation column operates under steady-state condition. r_j^V and r_j^L represent the ratios of side-stream flow to vapour and liquid streams, which are expressed as,

$$r_j^V = \frac{S_j^V}{V_j} \tag{3}$$

and

$$r_j^L = \frac{S_j^L}{L_j} , \tag{4}$$

respectively, where S_j^V is the vapour side stream (mole s^{-1}), and S_j^L is the liquid side stream (mole s^{-1}). Note that U_j accounts for both liquid and vapour hold-ups particularly when a reactive distillation column is operated at high pressure. Additionally, for reaction:

$$v_A A + v_B B + \ldots \rightleftharpoons v_P P + v_R R + \ldots \quad , \tag{5}$$

the reaction rate assuming the quasi-homogeneous non-ideal model can be described by the following expression,

$$R_j = U_j(k_f a_{A,j}^{vA} a_{B,j}^{vB} - k_b a_{P,j}^{vP} a_{R,j}^{vR}) \quad . \tag{6}$$
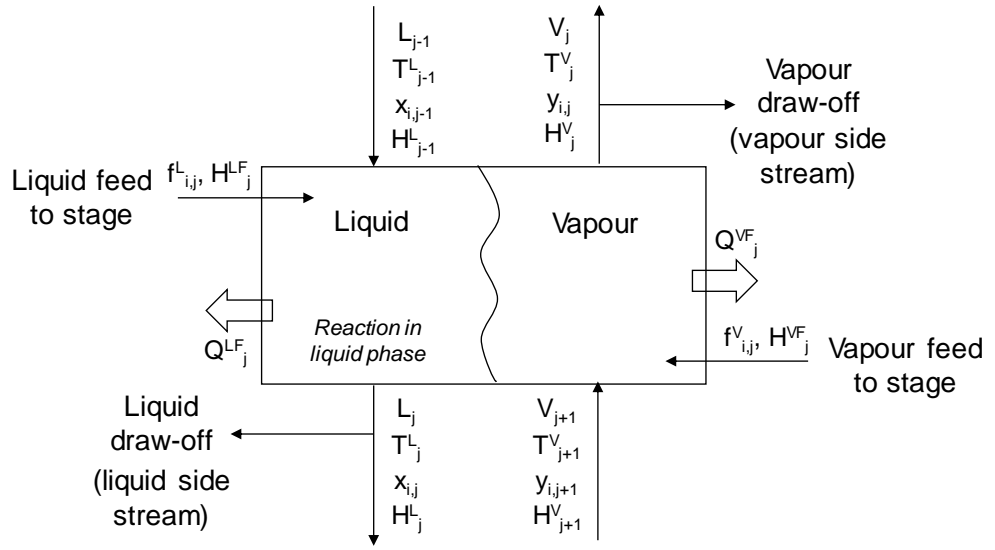
Fig. 2.3. An equilibrium model for stage *j* in a reactive distillation column (Taylor and Krishna, 2000).

The phase equilibrium relation (E of MESH) is

$$y_{i,j} = K_{i,j} x_{i,j} \ ,$$
(7)

where $y_{i,j}$ is the mole fraction of component *i* in the vapour phase on stage *j*, and $K_{i,j}$ is the vapour-liquid equilibrium constant of component *i* on stage *j*. The calculation of the vapour-liquid equilibrium constant is given as

$$K_i = \frac{\gamma_i P_i^o}{P} \ ,$$
(8)

where γ_i is liquid-phase activity coefficient, P_i^o is the vapour pressure of a pure component (Pa) and *P* is the total pressure (Pa). The pure component vapour pressure is calculated using the Antoine equation or an equation of state. Liley et al. (1999) provides the extended Antoine equation

$$\ln P_i^o = A + \frac{B}{T} + C \ln T + D T^E \ ,$$
(9)

where T is the temperature (K) and A, B, C, D and E are the regression constants. For binary mixtures, the ratio of K values of two compounds equals to the relative volatility, which is expressed as

$$\alpha_{h,i} = \frac{K_h}{K_i} \quad , \tag{10}$$

where $\alpha_{h,i}$ is the relative volatility for compounds h and i.

The summation expressions (S of MESH) are

$$\sum_{i=1}^{c} x_{i,j} = 1 \tag{11}$$

and

$$\sum_{i=1}^{c} y_{i,j} = 1 \quad . \tag{12}$$

The heat balance (H from MESH) is represented as an enthalpy equation given as

$$\frac{\mathrm{d}U_j H_j}{\mathrm{d}t} = V_{j+1} H_{j+1}^V + L_{j-1} H_{j-1}^V + F_j H_j^F - (1 + r_j^V) V_j H_j^V - (1 + r_j^L) L_j H_j^V + Q_j \quad , \tag{13}$$

where H_j and Q_j are the molar enthalpy (J mole^{-1}) and the heat duty (J s^{-1}) on stage j, respectively. Note that the enthalpies in Eq. (13) are referred to their elemental state; therefore, no separation term is required for heat of reaction (Taylor and Krishna, 2000; Venkataraman et al., 1990). The time derivative in Eq. (13) equals to zero when a reactive distillation column operates under steady-state condition.

Generating a model for a stage with a non-equilibrium condition is more difficult than that for a stage with an equilibrium condition. In a non-equilibrium model, the film, penetration and surface renewal theories are used to characterise the mass transfer phenomenon across the vapour-liquid interface (Keller, 2014). The Maxwell-Stefan equations are commonly employed to describe the vapour-liquid mass transfer in multicomponent systems, which link the diffusion fluxes of the components to their chemical potential gradients (Krishna and Wesselingh, 1997).

Fig. 2.4 illustrates a non-equilibrium stage model for a reactive distillation column in the cases of a homogeneous reaction and a heterogeneous reaction modelled as a pseudo-homogeneous system where the catalyst diffusion is lumped into the reaction term in the material balance. The transport process of a (pseudo-) homogeneous reaction includes mass transfer through the vapour film, mass transfer with reaction in the liquid film and finally reaction in the bulk liquid (Taylor and Krishna, 2003). For a slow reaction, the transport mechanism occurs only in the bulk liquid, and the material balance is

$$0 = L_j x_{i,j} - L_j x_{i,j-1} - f_{i,j}^L - \mathrm{N}_{i,j}^L - \sum_{m=1}^{r} v_{i,m} R_{m,j} \varepsilon_j \quad , \tag{14}$$

where $f_{i,j}$ and $\mathrm{N}_{i,j}$ are the component feed stream (mole s^{-1}) and the mass transfer rate (mole s^{-1}) on stage j respectively. The enthalpy balances for the phases of vapour and liquid are expressed as (Taylor and Krishna, 2000),

$$0 = V_j H_j^V - V_{j+1} H_{j+1}^V - F_j^V H_j^{VF} + \mathrm{E}_j^V + Q_j^V \tag{15}$$

and

$$0 = L_j H_j^L - L_{j-1} H_{j-1}^L - F_j^L H_j^{LF} + \mathrm{E}_j^L + Q_j^L \quad , \tag{16}$$

respectively, where H_j^V is the molar enthalpy of vapour compound on stage j (J mole^{-1}), H_j^L is the molar enthalpy of liquid compound on stage j (J mole^{-1}), F_j^V is the vapour feed stream to stage j (mole s^{-1}), F_j^L is the liquid feed stream to stage j (mole s^{-1}), H_j^{VF} is the molar enthalpy of vapour feed stream to stage j (J mole^{-1}), H_j^{LF} the molar enthalpy of liquid feed stream to stage j (J mole^{-1}), E_j^V is the interphase energy transfer rate of vapour phase on stage j (J s^{-1}), E_j^L is the interphase energy transfer rate of liquid phase on stage j (J s^{-1}), Q_j^V is the heat duty of vapour compound on stage j (J s^{-1}) and Q_j^L is the heat duty of liquid compound on stage j (J s^{-1}). Both E_j^V and E_j^L are equal in both liquid and vapour phases. For heterogeneous systems that cannot be simplified as pseudo-homogeneous reactions, characterising the mass transfer phenomenon requires more complex mathematical models. Further details on these approaches can be found elsewhere (Baur et al., 2000; Higler et al., 2000; Noeres et al., 2003).
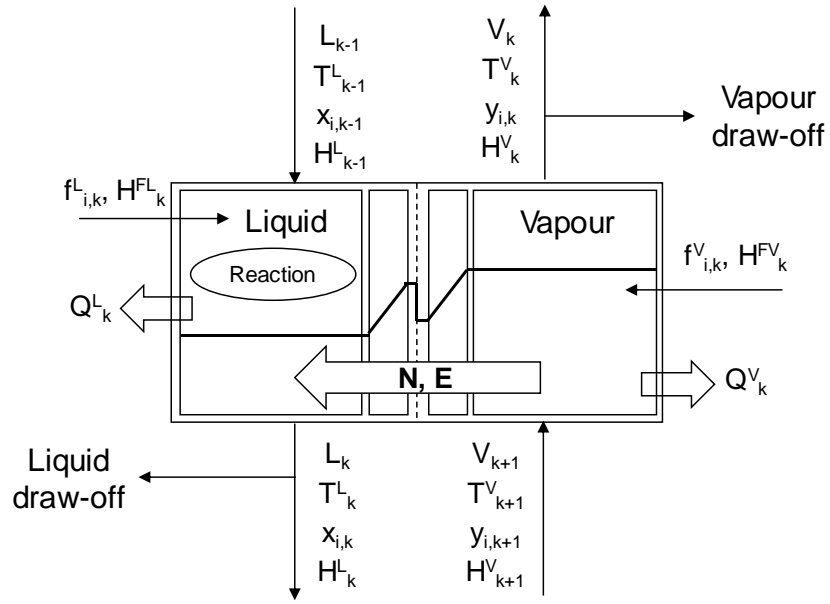
Fig. 2.4. A non-equilibrium model for stage *j* in a reactive distillation column for a homogeneous reaction and a heterogeneous reaction modelled as a pseudo-homogeneous system (Taylor and Krishna, 2000)

2. Chemical reaction models of reactive distillation columns

The equilibrium-limited reaction is driven by thermodynamics and the model may be used to represent very fast chemical reactions. In practice, the extent of reaction is strongly influenced by design parameters (e.g. liquid hold-up, liquid residence time, catalyst loading and catalyst selection) and mass transfer phenomena within the column. This type of system is known as the kinetically controlled reaction. For an equilibrium reaction,

$$v_A A + v_B B + \ldots \rightleftharpoons v_P P + v_R R + \ldots \quad , \tag{17}$$

the chemical equilibrium constant (K_{eq}) is expressed as a function of chemical activities as

$$K_{eq} = \frac{a_P^{v_P} a_R^{v_R} \ldots}{a_A^{v_A} a_B^{v_B} \ldots} = \frac{x_P^{v_P} x_R^{v_R} \ldots \gamma_P^{v_P} \gamma_R^{v_R} \ldots}{x_A^{v_A} x_B^{v_B} \ldots \gamma_A^{v_A} \gamma_B^{v_B} \ldots} \quad , \tag{18}$$

where a_i is the activity of compound *i*, v_i is the stoichiometric coefficient of compound *i*, x_i is the liquid mole fraction of compound *i* and γ_i is the liquid-phase activity coefficient of compound *i*. The chemical equilibrium constant is related to the standard Gibbs free energy by

$$K_{eq} = \exp\left(\frac{-\Delta G^o}{RT}\right) \quad . \tag{19}$$

where ΔG^o is the standard free energy (kJ mol^{-1}) and R is the gas constant (kJ mol^{-1} K^{-1}) (Levenspiel, 1999).

In autocatalysed and homogenous catalysed processes, reactions may take place both in the bulk and the film region. The chemical mechanisms are usually characterised only in the bulk phase for slow reaction systems.

More complex models accounting for external and internal mass transfer resistances may be applied for heterogeneous catalysed processes. To simplify such models, the catalyst surface is usually assumed to be fully exposed to the bulk liquid. This simplified system is called the pseudo-homogeneous chemical reaction.

When assessing and designing RD columns, dimensionless parameters, such as the Damköhler (Da) and Hatta (Ha) numbers, are used to simplify the models of a kinetically controlled reaction. The Damköhler number is the ratio of a characteristic residence time to a characteristic reaction time (Chen et al., 2002). This parameter can be expressed as

$$Da = \tau \cdot k_f \quad , \tag{20}$$

where τ is liquid residence time (s), and k_f is a pseudo-first-order reaction rate constant—with the inclusion of concentration in the rate constant (s^{-1}). The liquid residence time is defined as the ratio of liquid hold-up per stage to the incoming flow rate per stage. A low Damköhler number (Da $\leq$ 0.1) indicates a slow reaction that is driven by phase equilibrium, whereas a high Damköhler number (Da > 10) reflects a fast reaction that reaches chemical equilibrium (Venimadhavan et al., 1994). When the Damköhler number is within the two extremes, the reaction is kinetically controlled; neither phase equilibrium nor chemical equilibrium is the controlling mechanism (Shah et al., 2012c).

The Hatta (Ha) number correlates the extent of reaction to diffusion through the film (Levenspiel, 1999). This dimensionless parameter helps to differentiate between very fast, fast, average and slow reactions (Kenig and Górak, 2007). The Hatta number is formulated as (Roizard and Wild, 2002)

$$Ha^2 = \frac{k_2 C_{Bs} \delta^2}{D_A} = \frac{k_2 D_A C_{Bs}}{k_L^2} \qquad , \qquad \qquad (21)$$

where k_2 is the forward reaction rate constant (mole m^{-3} s^{-1}), C_{Bs} is the reactant concentration in the liquid bulk (mole m^{-3}), δ is the thickness of the liquid-side diffusion film (m), D_A is the diffusion coefficient (m^2 s^{-1}), and k_L is the liquid-side mass transfer coefficient (m s^{-1}). Note that other useful dimensionless numbers for modelling reactive distillation processes have also been employed, and the explanation about them can be found elsewhere (Sundmacher et al., 1994).

3. Hydrodynamic models of reactive distillation columns

In most cases, ideal plug flow patterns are assumed for both liquid and vapour phases in a reactive distillation column, where all the velocities across the column section are the same (Griskey, 2002). More complex models that takes in account, for instance, axial dispersion can be utilized to represent non-ideal flow pattern(s) (Noeres et al., 2002; van Baten et al., 2001; Shah et al., 2012a).

Although a complex model, e.g. the non-equilibrium model of mass transfer, is capable of describing more realistic phenomena in a reactive distillation process compared to that phenomena described by the equilibrium model, it always requires more sophisticated equations. A complex model does not always yield an effective assessment because of the limited availability of the model parameters (Keller, 2014). Estimating missing model parameters should be done very carefully because incorrect parameters introduce errors (Almeida-Rivera et al., 2004). Equilibrium models may be sufficient and favoured for the assessment at the conceptual design (Tuchlenski et al., 2001), whereas non-equilibrium models may expose the limitation of equilibrium models for a final design and for the development of optimisation and control strategies (Taylor and Krishna, 2000).

2.4. Process Simulation for Reactive Distillation

Process simulation software supports chemical engineers' tasks in designing and modifying process facilities. The use of process simulation tools allows the assessment of the effects of potential process changes, the estimation of capital cost expenditures, the prediction of CO_2 emissions and the evaluation of options for process optimisation and integration (Casavant and Côté, 2004).

Table 2.4 provides a list of process simulation tools that are commonly used for both industrial and educational purposes for modelling chemical processes. Commercial process simulators usually contain plentiful databases of chemicals with comprehensive thermodynamic and physical property models, which enable fast modelling of unit operations in the chemical processing.

Table 2.4. Commonly employed process simulation programs in academics and industry (Towler and Sinnott, 2012)

Name	Type	Source	Internet address http://www.–
Aspen Plus	Steady-state	Aspen Technology Inc.	Aspentech.com
CHEMCAD	Steady-state	Chemstations Inc.	Chemstations.net
DESIGN II	Steady-state	WinSim Inc.	Winsim.com
HYSYS	Steady-state and dynamic	Aspen Technology Inc.	Aspentech.com
PRO/II and DYNSIM	Steady-state and dynamic	SimSci-Esscor	Simsci.com
UniSim Design	Steady-state and dynamic	Honeywell	Honeywell.com

Based on the sequence of approaches for generating solutions, process simulation tools can be classified into two types:

1. Sequential-modular programs

   This simulation type is used to model systems under steady-state conditions. For each process unit (module), sequential-modular programs contain equations solved

sequentially using iterative techniques. The iterative procedures sometimes face difficulty in achieving converged simulations, especially when multiple recycles are present.

2. Equation-oriented (simultaneous) programs

This simulation type employs a set of equations to model the entire flowsheet potentially for both steady- and unsteady-state operations. Those equations are solved simultaneously, and hence, the programs are able to provide faster solution for flowsheets with multiple recycle streams at a computational cost that is typically higher than that of sequential-modular programs.

Aspen Plus, one of the most frequently used software for modelling chemical processes, is a process simulation program that carries out flowsheet calculations based on the sequential-modular method (Schefflan, 2011). This tool allows users to optimise processing capacity and operating conditions, monitor safety and operational issues in the plant, identify energy savings opportunities and perform economic evaluation in the process design (Dyment and Mantrala, 2015). The use of Aspen Plus is well-known particularly for modelling bulk chemicals, specialty chemicals, pharmaceutical and polymers industries (AspenTech, 2018; Ponce-Ortega and Hernández-Pérez, 2019). As a broad range of chemical reactions in those industries is considered in this PhD study, Aspen Plus is selected as the process simulation software.

Fig. 2.5 displays an example of the user interface of Aspen Plus v8.8 highlighting a "navigation pane" that gives an access to all available forms, and "environmental buttons" that allow users to perform various tasks. Environmental buttons consist of four elements (Dyment and Mantrala, 2015):

1. "Properties" environment where users assign components included in the assessed system, determine associated physical property models, regress and estimate property data and generate analytical plots, such as phase diagrams for binary mixtures and residue curves.

2. "Simulation" environment in which users create process flowsheets by selecting unit operation models that are classified into mixers and splitters, separators, heat exchangers, columns, reactors, pressure changes, manipulators, solids and user models.

3. "Safety analysis" where users carry out overpressure protection analyses in the environment.

4. "Energy analysis" environment where users identify energy savings opportunities.
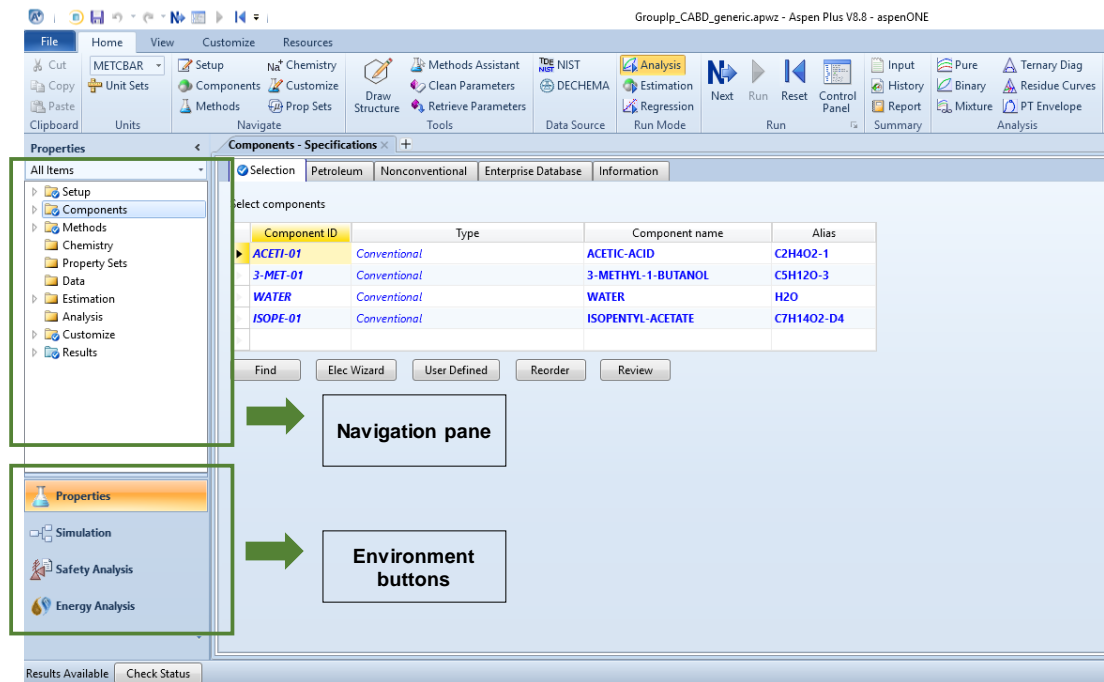
Fig. 2.5. The user interface of Aspen Plus v8.8

Through the navigation pane in the simulation environment, Aspen Plus users determine and modify streams input, unit operation blocks, reactions, convergence options and additional flowsheeting options, e.g. calculator. The navigation pane also gives access for users to find output of simulations for each unit operation, learn operating conditions, compositions and new parameter profiles inside the unit operations, and view the calculation sequences and identified problems in the control panel. In the simulation environment, users can also use sensitivity analysis and optimisation tools to investigate alternative solutions. The sensitivity analysis tool is used to gain an understanding about how a process responds to varied operating and design variables. The optimisation tool is used to maximise or minimise a user-specified objective function by manipulating decision variables, e.g. feed stream, block input based on specified constraints (AspenTech, 2000).

Among various unit operation models in Aspen Plus, RadFrac, a column model, is used to simulate multistage vapour-liquid fractionation operations including reactive distillation. RadFrac is capable of modelling equilibrium and non-equilibrium stages, two liquid phases on any stage, salt precipitation and chemical reactions in equilibrium, rate-controlled and electrolytic conditions (AspenTech, 2000). This model can include efficiency factors, such as Murphree and vaporisation efficiencies, that describe the non-ideality of mass transfer in the real processes.

2.5. Types of Reactive Distillation Configurations

The most common reactive distillation configurations are classified into four types: conventional reactive distillation, heterogeneous azeotropic reactive distillation, reactive dividing-wall column and reactive distillation column with a pre- and/or side reactors (Kiss, 2017), as pictured in Fig. 2.6. For a heterogeneously catalysed system, the vapour-liquid contact space in these configurations typically consists of rectifying, reactive and stripping zones. The structure of conventional reactive distillation is relatively less complex than the other configurations as this setup is not equipped with supporting devices, such as reactors or a decanter. Due to this relative simplicity, the development of a new method in this work focuses on the applicability of conventional reactive distillation.

To overcome heterogeneous azeotrope(s) at the top stream, a heterogeneous azeotropic RD column equipped with an overhead decanter might be applied. Examples of the application of heterogeneous azeotropic RD columns include esterification reactions to produce amyl acetate (Chiang et al., 2002), butyl acrylate (Zeng et al., 2006) and *n*-propyl propionate (Altman et al., 2010).

To deal with a highly integrated system that contains simultaneous chemical reaction(s) and multicomponent separations, reactive dividing-wall column may be advantageous (Weinfeld et al., 2018). This configuration can be considered relevant to the following reaction systems (Mueller and Kenig, 2007):

1. Reactive systems with more than two products, such as those with consecutive and side reactions;

2. Reactive systems with non-reacting components and desired separation of both products and inert compounds; and

3. Reactive systems with an excess of liquid catalyst or an excess of an extractive agent.

Reactive dividing-wall column has been proven to be promising in the production of several chemicals, such as dimethyl ether via methanol dehydration (Kiss and Suszwalak, 2012), ethyl acetate via esterification catalysed by sulphuric acid (Hernández et al., 2009) and methanol via hydrolysis of methyl acetate (Sander et al., 2007).
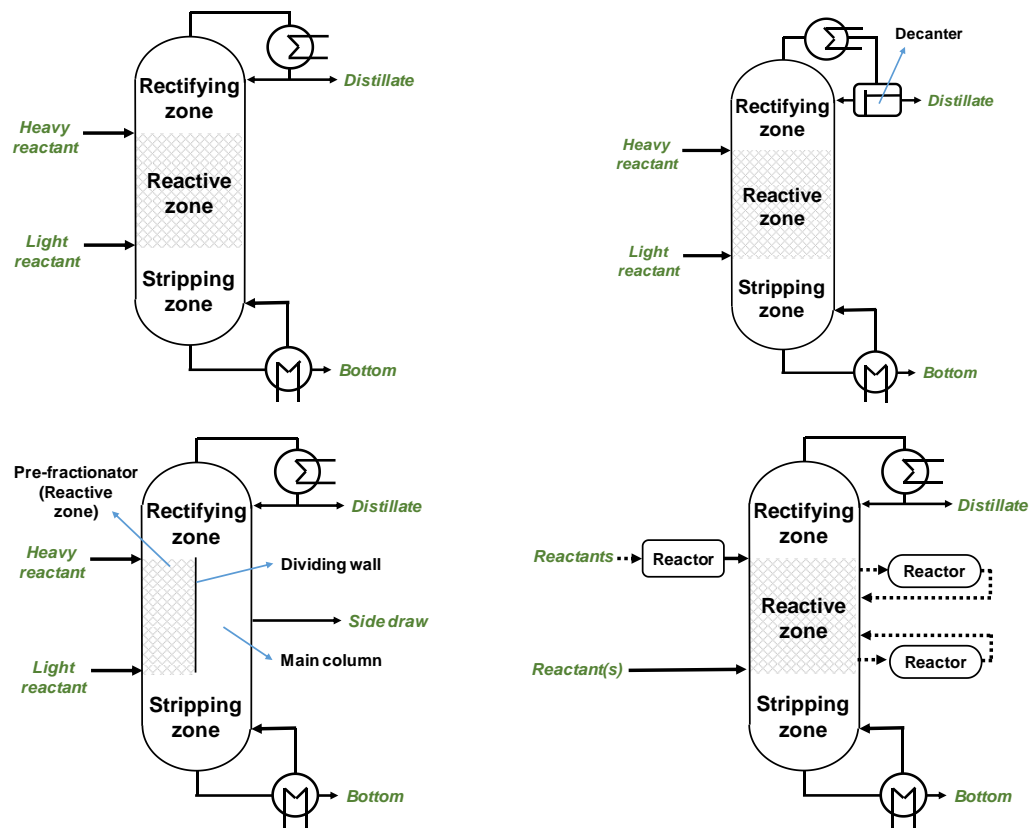
Fig. 2.6. Types of reactive distillation configurations: conventional RD (top left), heterogeneous azeotropic RD (top right), reactive dividing-wall column (bottom left) and RD with a pre- and/or side reactors (bottom right) (Kiss, 2017).

To enhance the conversion of reaction by extending residence time, reactive distillation with pre- and/or side reactors might be considered. For instance, its application is beneficial for the synthesis of unsaturated polyesters (Shah et al., 2012b) and ethyl *tert*-butyl ether (Bisowarno et al., 2004).

Among all configurations presented, the selection of the most suitable RD configuration highly depends on the characteristics of reaction systems, for instance, slow or fast reactions involved and the presence of side reaction(s). Previous studies have performed assessments to determine more beneficial reactive distillation configurations for specific reaction systems, especially in terms of cost reduction and energy saving (Bisowarno et al., 2004; Kaur and Sangal, 2017; Xu et al., 2014; Zheng et al., 2017). Nevertheless, there is plenty of room for new research to synthesise and develop general frameworks for a quick determination of the most favoured types of reactive distillation configurations.

2.6. Internals of Reactive Distillation

This section aims to extend the explanation about a design variable of reactive distillation—the type of internals—that is sometimes considered in the applicability/ feasibility assessment of reactive distillation at the conceptual level. Selecting appropriate internals of reactive distillation is essential as good internals ideally offer maximum catalyst hold-up, enhance the effectiveness of phase contacting, minimise pressure drop and avoid flooding phenomena (Keller, 2014; Towler and Frey, 2002). Although the type of internals is not a key design variable in this work as the equilibrium model is used to represent vapour-liquid mass transfer and no pressure drop along the column and ideal plug flow behaviour are assumed, this section provides readers of this PhD thesis with a wider understanding about hardware design of reactive distillation columns.

The options of RD internals consist of trays, structured and random packing, and they provide distinctive benefits. Trayed columns give high liquid hold-up and high flexibility, whereas structured packing columns are well-known for their high separation efficiencies and very low pressure drops, and random packing columns offer low investment costs (Wierschem and Górak, 2018).

For autocatalysed and homogeneously catalysed RD processes, a trayed column is usually preferred than a column with structured or random packing as it can provide higher liquid hold-up in the column. The selection of internals for heterogeneously catalysed RD processes is more challenging than that for autocatalysed and homogeneously catalysed RD processes as the internals need to serve both solid catalytic and separation functions.

Three basic concepts are usually applied to construct internals for heterogeneously catalysed RD processes: (1) immobilisation of heterogeneous catalyst inside internals, (2) immobilisation of catalysts on the surface of internals, and (3) solid catalysts shaped as packing (Richter et al., 2006).

For the purpose of catalyst immobilisation and using internals as a catalyst agent, different ways are employed for different types of RD internals. Catalyst bales or envelopes made of cotton, wire mesh, cloth, or fiberglass are placed on trays (Harmsen, 2007). The catalyst bales are stacked up on trays so that they can provide a certain height to obtain the aimed extent of reaction. Wire gauze envelopes filled with catalysts can be placed on trays and/or in the downcomer. For columns with structured packing, the internals are usually shaped as sandwiches created from corrugated wire gauze sheets that host cylinders or rectangular catalyst bags (Kiss, 2018). This packing structure comprises alternating positions between catalyst bags and open channels. Katapak-S® from Sulzer Chemtech AG and KATAMAX® from Koch-Glitsch are examples of commercial structured packing (Keller, 2014). Catalytic Raschig rings with surface-coated catalyst in a random packed column is one of the most important internals of reactive distillation (Kiss, 2017).

2.7. Concluding Remarks

Many methods for screening and designing reactive distillation processes have been developed since late 1980s and they can be classified into graphical, optimisation-based and heuristic approaches (Almeida-Rivera et al., 2004). Those methods offer particular advantages in initialising the design of reactive distillation columns: graphical methods provide insights into the applicability of reactive distillation, optimisation-based methods account for economics and heuristic approaches are able to suggest important design variables of reactive distillation columns. The existing methods are, unfortunately, less practical oriented and not easily employed by process engineers in the chemical industry, as their application demands for an in-depth knowledge that is usually possessed by reactive distillation experts. Furthermore, the use of those methods cannot yield multiple designs of reactive distillation columns from a single assessment. As the consequence, when process engineers aim to consider multiple configurations in a design process, they need to perform multi-assessments requiring many rigorous computations.

Further development needs to focus on the generation of simple methods that employ only some key process characteristics to assess the performance of reactive distillation; therefore, reducing complexities in RD design tasks at the conceptual level. Further development should aim to derive quick methods that guide process engineers in the decision making process regarding the applicability of reactive distillation prior to performing multi-assessments with many rigorous computations. The development of new methods also needs to account for the concept of process synthesis that provides engineers with hierarchical steps; therefore, the assessment of the applicability/feasibility of reactive distillation can be carried out in a systematic manner.

The knowledge gaps that are identified from the key strengths and weaknesses of the existing methods become the main drivers of this PhD thesis. A new conceptual tool is generated and developed in this study by taking into consideration the above needs.

The literature review presented in this chapter covers several subjects—mathematical models of reactive distillation columns, process simulation for modelling reactive distillation processes and types of reactive distillation configurations—that are relevant to the development of a new method in this research. Additionally, types of internals have been presented to provide readers of this thesis with a wider understanding in the design of reactive distillation columns.

In modelling reactive distillation processes, one develops models and makes assumptions to represent an interplay of mass transfer, chemical reactions and hydrodynamic phenomena in reactive distillation columns. Relatively simple models, i.e. the equilibrium models for mass transfer, chemical reactions disregarding mass transfer resistance and ideal plug flow behaviour, will be applied to develop a new method in this work. While, is important to keep in mind that more complex models, i.e. the non-equilibrium models for mass transfer, chemical reaction models accounting for mass transfer resistance and non-ideal flow behaviour, are also important, but they are required for further detailed assessment at a later stage in the development of reactive distillation processes.

Different process simulation software can be used to support process engineers' tasks in designing reactive distillation columns. All simulations required for the development of a new method in this work will be performed by using Aspen Plus because this process simulation software is capable of modelling a wide range of chemical reaction systems in

bulk chemicals, specialty chemicals, pharmaceutical and polymers industries. Note that the application of reactive distillation technology is targeted for chemical reactions in those industries.

Commonly, types of reactive distillation configurations consist of conventional reactive distillation, heterogeneous azeotropic reactive distillation, reactive dividing-wall column and reactive distillation column with a pre- and/or side reactors (Kiss, 2017). The development of a new method in this work will focus on the application of conventional reactive distillation columns because the structure of conventional reactive distillation is relatively less complex than the other configurations that are equipped with a dividing-wall column, a decanter, or pre- and/or side reactors.

The development of a new conceptual tool aiming to address the above knowledge gaps and needs by considering the selected mathematical models, process simulation tool and type of reactive distillation configurations will be presented in the next chapters.

Chapter 3

Development of a Mapping Method for (Near-) Ideal Quaternary Reaction Systems with Both Reactants as Mid-Boiling Compounds

List of publications:

- **Publication 1**

  Muthia, R., Reijneveld, A. G. T., van der Ham, A. G. J., ten Kate, A. J. B., Bargeman, G., Kersten, S. R. A. and Kiss, A. A. (2018). 'Novel method for mapping the applicability of reactive distillation', *Chemical Engineering and Processing: Process Intensification,* 128, pp. 263–275.

- **Publication 2**

  Muthia, R., Jobson, M. and Kiss, A. A. (2019). 'Innovative mapping method for screening reactive distillation designs', *Computer Aided Chemical Engineering,* 46, pp. 739–744.

3.1. Preface of Publications 1 and 2

Reactive distillation processes promise major improvements in the chemical industry over conventional reaction-separation processes, but for two decades, a critical question remains: how can one decide quickly if RD is a good process concept (Almeida-Rivera, et al., 2004; Malone and Doherty, 2000; Segovia-Hernández, et al., 2015)? Aiming to address this question, the work in Publications 1 and 2 introduce and develop a new conceptual tool, called a mapping method, to assess the applicability of reactive distillation.

The features of the novel mapping method are introduced in Publications 1 and 2. This method visualises the applicability of reactive distillation with a plot of reflux ratio vs the number of theoretical stages that is hereafter called an "applicability graph". This plot reveals achievable operations of reactive distillation with multiple combinations of reflux ratio and the number of theoretical stages. The mapping method offers simple procedures for process engineers in the chemical industry because the applicability of reactive distillation is:

- determined only by two or three constant process characteristics, namely relative volatilities of components (α_{ij}), chemical equilibrium constant (K_{eq}) and, in some cases, the Damköhler (Da) number, and
- carried out based on pre-calculated performance information for hypothetical and idealised generic cases, i.e. pre-generated applicability graphs of generic cases.

In this thesis, the strategy considered in the development of the mapping method is the complexities of the assessed reaction systems, i.e. the involvement of azeotropes and the difficult separation caused by the order of boiling points, are increased gradually. The work in Publications 1 and 2 focuses on (near-) ideal quaternary reaction systems, A + B $\rightleftharpoons$ C + D, that are not hindered by the formation of azeotropes. The assessed reactions are limited to a subset of quaternary reaction systems with both reactants as mid-boiling compounds, $T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$. With this order of boiling points, an ease of products separation is expected because product C as the most volatile compound is predominantly present at the top, while product D as the least volatile compound is largely present at the bottom part of reactive distillation columns.

The objectives of this thesis that are addressed in Publications 1 and 2 are, as follows.

1. To investigate the effects of the process characteristics considered in the mapping method—relative volatilities, chemical equilibrium constants and the Damköhler numbers—on the performance of reactive distillation (as discussed in Publication 1). As explained in Chapter 2, relative volatilities are equivalent to the ratio of vapour-liquid equilibrium constants of two compounds and they indicate the ease of separation within a reactive distillation column. A chemical equilibrium constant is proportional to the ratio of products-to-reactants compositions in an equilibrium condition, which indirectly reflects the maximum conversion attainable when a reaction reaches the equilibrium condition. A dimensionless Da number, which is solely employed in the case of a kinetically controlled reaction, characterises the influences given by residence and reaction time on the performance of reactive distillation. While relative volatilities have been used as a process characteristic in shortcut methods of conventional distillation, the interplay of relative volatilities, chemical equilibrium constants and the Damköhler numbers is newly introduced in the mapping method to characterise the operation of reactive distillation. This study aims to gain an understanding of the effects of these process characteristics by comparing RD configurations of generic cases. The challenge associated in this task is to specify multiple generic cases that can represent a wide range of the three process characteristics.

2. To assess the applicability of reactive distillation by using pre-calculated performance information for hypothetical and ideal generic cases, i.e. applicability graphs of generic cases (as discussed in Publications 1 and 2). Process engineers employ the mapping method to assess the RD applicability by overlaying representative relative volatilities, chemical equilibrium constant and the Damköhler number of the real reaction system of interest onto pre-generated applicability graphs of generic cases. Therefore, one can expect the reduction of computational effort in determining the applicability of reactive distillation in the early phase of the conceptual level. The work in Publication 1 aims to develop approaches to calculate representative relative volatilities, chemical equilibrium constant and the Damköhler number of the real reaction system, while the work in Publication 2 extends the discussion presented in Publication 1 on characterising fixed relative

volatilities of the real system. The challenge associated in this task is performing extensive simulations by considering multiple scenarios with different approaches to quantify representative relative volatilities, chemical equilibrium constant and the Damköhler number of the real reaction system.

3. To validate the proposed mapping method by performing rigorous simulations for case studies (as discussed in Publications 1 and 2).

The assessment of the applicability of reactive distillation based on generic applicability graphs is validated with two case studies representing near-ideal quaternary reaction systems with both reactants as mid-boiling compounds: transesterification of methyl benzoate with benzyl alcohol (Case 1) and hydrolysis of methyl lactate (Case 2). There is no azeotrope identified in Case 1, whereas there is a reactive azeotrope found in Case 2. The suitability of the mapping method is evaluated qualitatively by comparing pre-prepared generic applicability graphs and actual applicability graphs generated from rigorous simulations for the case studies. Besides, the validation of the method is carried out quantitatively by calculating the deviation of predicted reflux ratio and the number of theoretical stages from the actual values.

3.2. Publication 1

This section is based on the following publication:

Muthia, R., Reijneveld, A. G. T., van der Ham, A. G. J., ten Kate, A. J. B., Bargeman, G., Kersten, S. R. A. and Kiss, A. A. (2018). 'Novel method for mapping the applicability of reactive distillation', *Chemical Engineering and Processing: Process Intensification,* 128, pp. 263–275.

DOI: 10.1016/j.cep.2018.04.001.

The US English spelling in the original publication has been changed here to the UK English spelling to fulfil the requirements of the PhD theses policy regulated by the University of Manchester.

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 subsets of quaternary reversible reactions (A + B $\rightleftharpoons$ 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 (Reay et al., 2008). 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 success story of a process intensification technology for enhanced manufacturing of chemicals (Orjuela et al., 2016; Stankiewicz, 2003). RD combines a reactor and a distillation column into a single unit operation (see Fig. 1).

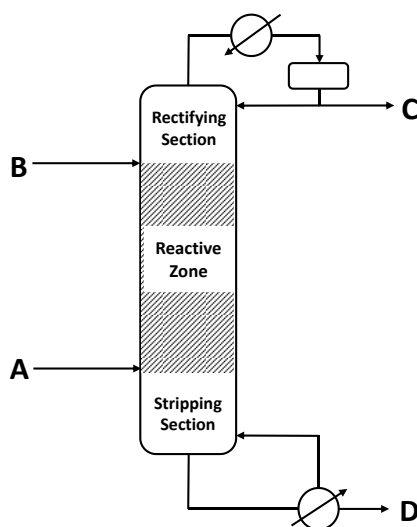Fig. 1. Schematic representation of a reactive distillation column.

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 (Kiss, 2013; Luyben and Yu, 2008; Shah et al., 2012; Taylor and

Krishna, 2000; Tuchlenski et al., 2001). 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 (Luyben and Yu, 2008):

$$A + B \rightleftharpoons C + D \text{ (quaternary systems) and } A + B \rightleftharpoons C \text{ (ternary systems)}$$
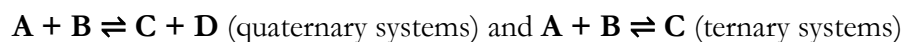
RD has been industrially used for more than 25 years, for applications with capacities up to 3000 kton/year (Harmsen, 2007). Current applications of RD are mostly for esterification reactions, with the production of methyl acetate as a prime example (Agreda et al., 1990). Other processes in which RD 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) (Luyben and Yu, 2008). Many prospective chemical systems (which are neither extremely exothermic nor endothermic) for the RD application are also listed in the open literature (Hiwale et al., 2004; Poddar et al., 2017; Sharma and Mahajani, 2003).

The available reactive distillation design methods can be classified into three main groups, based on: 1) graphical/topological considerations, 2) optimisation techniques, 3) heuristic/evolutionary approaches (Almeida-Rivera et al., 2004), which are presented in literature (Amte et al., 2013; Ciric and Gu, 1994; Damartzis and Seferlis, 2010; Fien and Liu, 1994; Giessler et al., 1998; Groemping et al., 2004; Hoyme, 2004; Shah et al., 2012; Subawalla and Fair, 1999; Thery et al., 2005; Ung and Doherty, 1995). 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 question has been raised more than a decade ago: how could anyone decide quickly (at the conceptual design stage) whether RD is a feasible process concept for a certain reversible reaction system? (Malone and Doherty, 2000). The ultimate goal would be to rapidly assess the RD applicability to various reaction systems by only using a simple model (i.e. requiring significantly less time for the evaluation than any other method available).

This paper describes the development of a novel RD mapping method - based on the KISS principle (keep it short & simple) for the end-users - that aims to provide insights into the RD operation and quickly evaluate the applicability of RD to (real) chemical systems with a rather straightforward approach. To start with, the most relevant subset of the quaternary systems with both reactants as mid-boiling components ($T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$) was investigated as it is commonly encountered in practice. A good separation of products is attainable for this boiling point order. The mapping approach uses generic cases to produce the RD applicability graphs, based on ideal thermodynamics and few specified basic data, i.e. relative volatilities (α), chemical equilibrium constants (K_{eq}) and chemical reaction kinetics. The applicability graph is presented by plotting the reflux ratio (RR) vs the number of theoretical stages (NTS), which then can easily give access to the energy requirement and the capital investment. Extensive insights into the RD operation are provided using those applicability graphs. Finally, the new RD mapping method is used to assess the applicability areas of real (non-ideal) systems by only referring to available pre-defined applicability graphs (based on the generic cases). This approach enables 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 $\rightleftharpoons$ 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 a 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 the 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 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/constraints specified, which are a bottom product purity and a 0.5 mole/mole 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 $\geq$ 99 mole% of bottom product purity was always set. By setting the B/F ratio and product purity, the minimum overall conversion is 99 mole%.
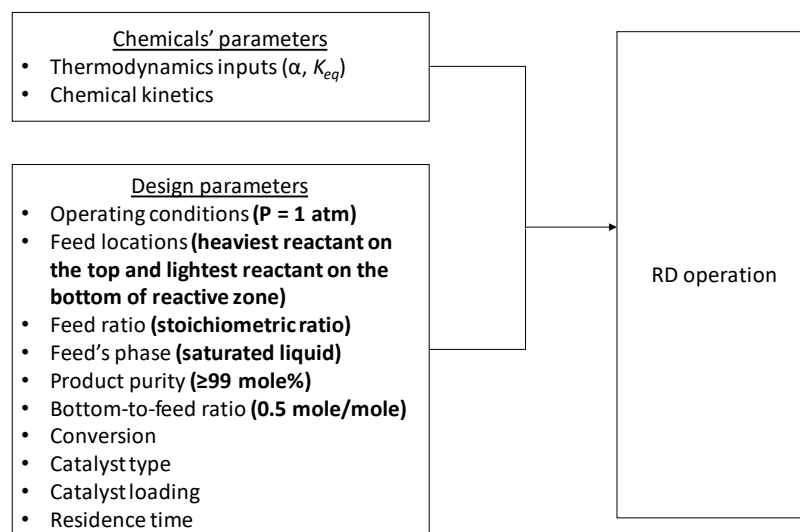
Fig. 2. Key parameters of the RD operation.

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 vapour-liquid behaviour 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).

Fig. 3. Procedure to generate an applicability graph of a generic case.

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 optimisation tool. The sensitivity analysis was utilised to vary the configurations of RD (i.e. numbers of rectifying, reactive and stripping stages) for each NTS. At the same time,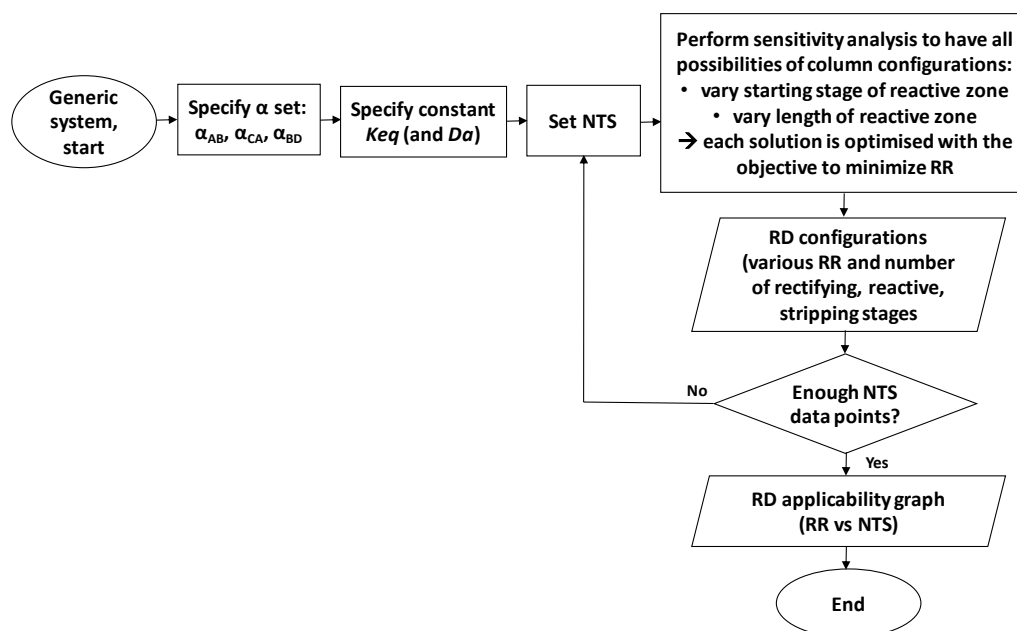 for each configuration, the optimisation tool was used to provide a solution with a minimised RR. Combining the sensitivity analysis and the optimisation tools to minimise RR for any RD configuration distinguishes the method proposed in this work from other design methods that aim to estimate the RR_{min} for an infinite NTS using short-cut methods, such as the works of Doherty et al. (Barbosa and Doherty, 1988a; 1988b; Levy and Doherty, 1986; Levy et al., 1985).

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.
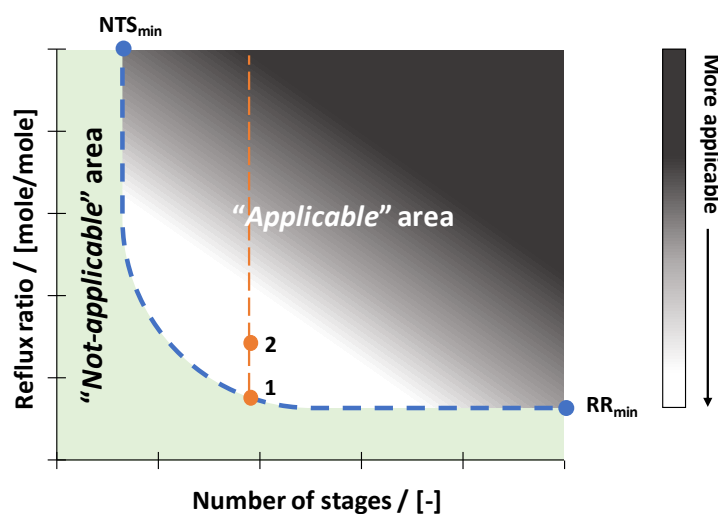
Fig. 4. Illustrative applicability graph of RD for a certain chemical system.

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 the number of rectifying, reactive and stripping sections. The vertical asymptote of the

boundary line shows the NTS_{min} which has different RD configurations by the increase of RR. Correspondingly, the horizontal asymptote of the boundary line indicates the RR_{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.

Points 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 set up 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. the 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 favourable to have a 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 colour of applicable area from the bottom-left to the top-right corner shifts from lighter to darker shading. The lighter colour 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 a maximum scale of 100. The NTS_{min} is defined as the NTS for RR = 100; the RR_{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. the ratio of height to diameter of the column. Selecting the NTS_{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_{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 performance 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 characterises 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 a RD column. The utilisation of the Da number in the kinetically controlled reactions for RD technology has been common practice in many previous research studies (Buzad and Doherty, 1994; Chen et al., 2000; Okasinski and Doherty, 1998; Venimadhavan et al., 1994).

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

$$Da = k_f \cdot \beta \cdot \tau \quad . \tag{1}$$

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 (τ) 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_f, while β 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 holdups along the column, the τ was specified as a design input to determine the Da number. Setting τ is practical and easy for the RD operation, as usually there is a maximum allowed τ of up to 4–5 min (Huang et al., 2012; Taylor and Krishna, 2003; Towler and Frey, 2002). To the best of our knowledge, based on industrial experience, τ 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 the 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 low and 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 $\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$ (K_A: K_B: K_C: K_D = 3:2:6:1) 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 = $2 \cdot NTS_{min}$ 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 a 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·NTS$_{min}$), 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 separation 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·RR$_{min}$ or any other points. Referring to NTS = 2·NTS$_{min}$ 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 the 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 mole% 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.
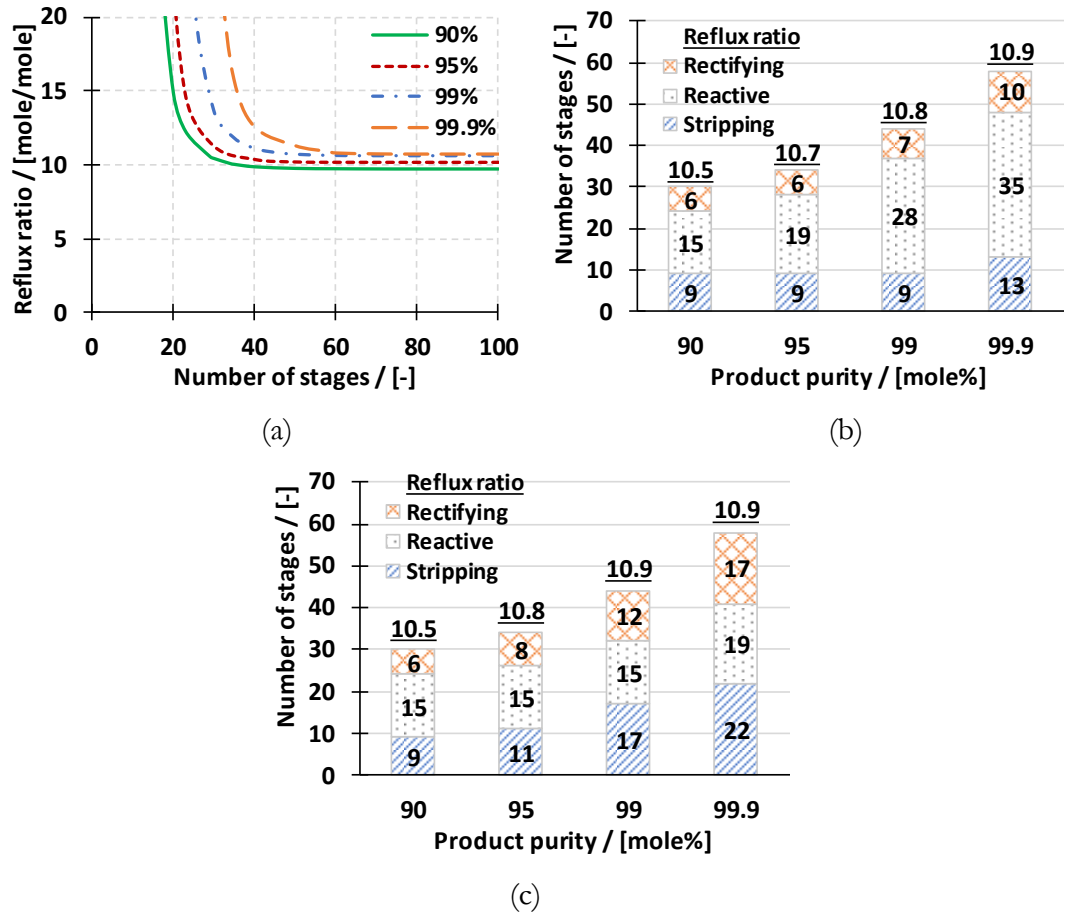
(a)

(b)

(c)

Fig. 5. (a) The applicability areas of RD for various bottom product purities on mole basis and (b and c) their configurations at NTS = 2·NTS$_{min}$ in case of equilibrium-limited reactions for α_{AB} = 1.5, α_{CA} = 2, α_{BD} = 2, considering K_{eq} = 0.01. In (b) combinations for objective of constant number of separation stages, in (c) combinations for objective of constant reactive stages.

Firstly, Fig. 5 (b) shows the selected RD configurations with (more or less) a constant number of separation 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 mole%, the addition of reactive stages alone is not sufficient, and the number of separation stages needs to be increased. Secondly, Fig. 5 (c) presents the RD configurations with (more or less) a constant number of reactive stages. As a 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 favourable 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.

3.1.2. Influence of the chemical equilibrium constant

Fig. 6 (a) shows the impact of the K_{eq} on the applicability areas of RD for the base case. For K_{eq} = 0.01, the NTS_{min} (RR $\approx$ 100) is 22, and the RR_{min} is 11, while for the most favourable case of K_{eq} = 10, the NTS_{min} (RR $\approx$ 100) and the RR_{min} both are much lower, 12 and 2, respectively. Accordingly, the RD applicability area becomes larger for a higher chemical equilibrium constant.

For the different K_{eq} values, the RD column configurations for the base case are shown graphically in Fig. 6 (b). The K_{eq} mainly influences the number of reactive stages and the RR, where a lower K_{eq} leads to more reactive stages and a higher RR. However, it is not followed by the growth of the rectifying and stripping sections. On the contrary, slightly less rectifying and stripping stages for a lower K_{eq} 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 K_{eq} values 0.1 and 1. In the case of K_{eq} = 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 K_{eq} = 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 K_{eq} = 1 are less than those with K_{eq} = 0.1. The difference in the purity level between these both cases shows the role of reactive stages in performing the separation task. Since less reactive stages are available at K_{eq} = 1 compared to the case of K_{eq} = 0.1, the simultaneous separation in the reactive stages is limited therefore requiring more rectifying and stripping stages.
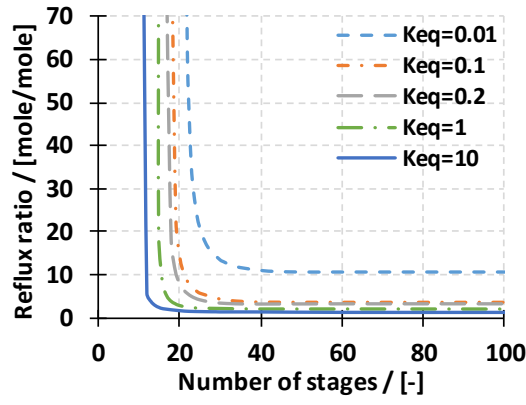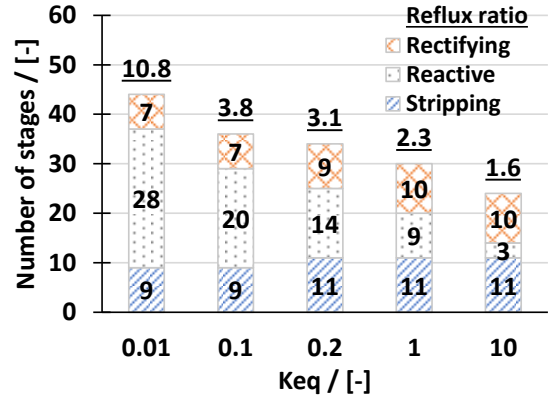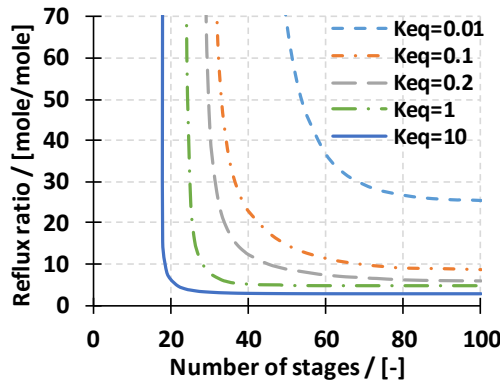
Fig. 6. The applicability areas of RD and their configurations at NTS = 2·NTS$_{min}$ in case of equilibrium-limited reactions for (a and b) α_{AB} = 1.5, α_{CA} = 2, α_{BD} = 2, (c and d) α_{AB} = 1.5, α_{CA} = 1.2, α_{BD} = 2, (e and f) α_{AB} = 1.5, α_{CA} = 2, α_{BD} = 1.2 considering K_{eq} = 10.
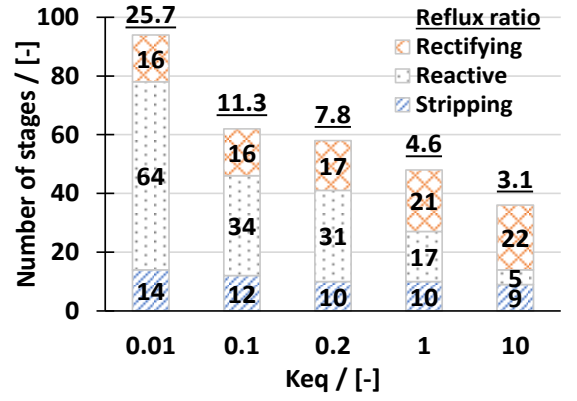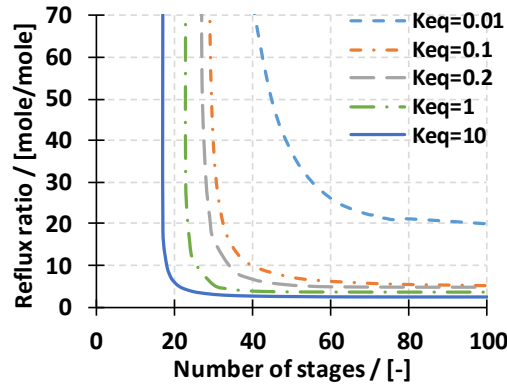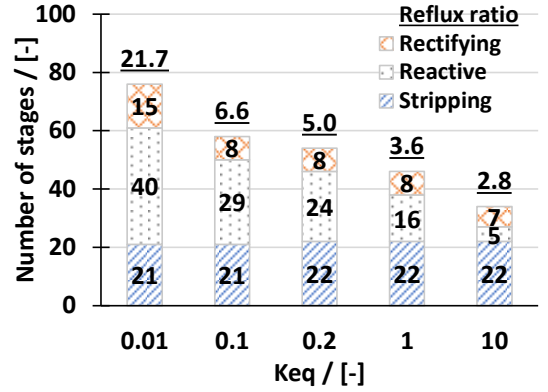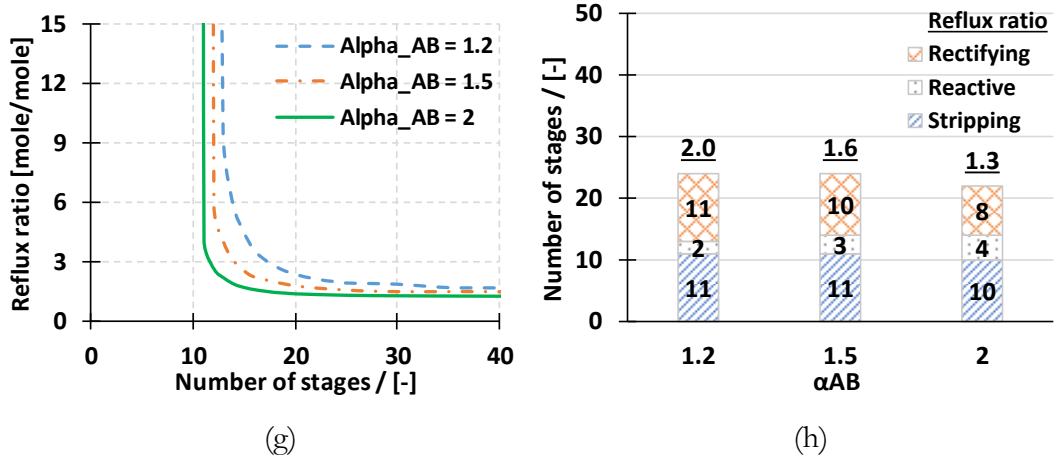
(g)   (h)

Fig. 6. The applicability areas of RD and their configurations at NTS = 2·NTS$_{min}$ in case of equilibrium-limited reactions for (g and h) varied α_{AB}, α_{CA} = 2, α_{BD} = 2 considering K_{eq} = 10.

3.1.3. Influence of the relative volatility

To investigate the influence of relative volatility on the RD performance, α_{CA}, α_{BD} and α_{AB} were varied separately. When the relative volatility for product C and reactant A is lower (α_{CA} = 1.2, K_A: K_C = 1:1.2), compared to the base case the applicability area becomes smaller for each K_{eq} (compare Fig. 6 a and c). For K_{eq} = 0.01, the NTS$_{min}$ (RR ≈ 100) and the RR$_{min}$ are 47 and 25, respectively. This is a significant increase compared to the base case, with NTS$_{min}$ (RR ≈ 100) and RR$_{min}$ 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 α_{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, α_{CB} = 3. The smaller applicability area for the case of lower α_{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 to prevent reactants from reaching the rectifying section. For instance, for K_{eq} = 0.01 the number of reactive stages is 28 in the base case, whereas it is 64 for the case of lower α_{CA}. The increase of K_{eq} in Fig. 6 (d) results in a decrease in the number of reactive stages and the RR due to higher conversion levels per stage.

The opposite effect is expected to happen when α_{CA} is increased. For instance, for $\alpha_{AB} = 1.5$, $\alpha_{CA} = 4$, $\alpha_{BD} = 2$ (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 NTS_{min} and RR_{min} decrease.

In analogy to the α_{CA} reduction, the applicability area for the system with the lower α_{BD} ($\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 1.2$, K_A: K_B: K_C: K_D = 3:2:6:1.7) is smaller compared to the base case as presented in Fig. 6 (e). For instance, for $K_{eq} = 0.2$, the NTS_{min} (RR $\approx$ 100) and the RR_{min} for the case of the lower α_{BD} are 27 and 4.6, respectively. With the same K_{eq}, the NTS_{min} (RR $\approx$ 100) for the base case (see Fig. 6, a) is much less, which is 17, with the $RR_{min} = 3.0$. A similar trend is also found for the other K_{eq} values.

Fig. 6 (f) shows the RD configurations and their RR values for the case of lower α_{BD}. In comparison to the base case in Fig. 6 (b), more stripping and reactive stages are required. The same explanation as for the case of lower α_{CA} applies here with a more difficult separation between product D and reactants ($\alpha_{BD} = 2$ and $\alpha_{AD} = 3$ for the base case and $\alpha_{BD} = 1.2$ and $\alpha_{AD} = 1.8$ for this case). To prevent reactants from reaching the stripping section, more reactive stages are required.

The applicability areas of RD in the cases of varied α_{AB} at 1.2, 1.5 and 2 are presented in Fig. 6 (g) considering $\alpha_{CA} = 2$ and $\alpha_{BD} = 2$, with $K_{eq} = 10$. With a higher α_{AB}, the boundary line shifts closer to the bottom-left of the map and the applicability area becomes larger. At the first glance, this result is seemingly caused by having a larger α_{AB} in the system. However, there is a real reason which mainly affects the size of the applicability areas. Considering the subset of quaternary systems in this study ($T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$), varying α_{AB} with fixed α_{CA} and α_{BD} gives change to α_{CB} and α_{AD}, which mostly influences the separation performance. The α_{CB} values in the case of α_{AB} of 1.2, 1.5 and 2 are 2.4, 3 and 4, respectively. The same value also applies to α_{AD} for each case. With a higher α_{AB} considering higher α_{CB} and α_{AD}, the separation becomes easier. This explanation is proven by the presented RD configurations in Fig. 6 (h) where the rectifying and stripping sections are slightly shorter and the RR is lower in the case of a higher α_{AB}. On the other hand, a higher α_{AB} slightly increases the number of reactive stages because the lighter reactant is vaporised more easily, therefore hindering the liquid interaction and reducing the reaction performance.

Observing the applicability areas and the column configurations of RD with varied α shows that the results are sensitive to the change of α.

3.2. Kinetically controlled reactions

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 area at Da = 1 is on top of the applicability area at equilibrium and the applicability area is smaller when the Da number in the reactive section of the RD column is reduced. The lower productivity by the lower Da number needs to be compensated by an increased RR and NTS, as shown in Fig. 7 (b) and (d). An increased RR which corresponds to a higher internal flow gives a better separation along the column. A larger reactive zone (more reactive stages with bigger column diameter) allows extended space for the catalyst loading which helps to improve the total conversion when the Da number is low (due to slow kinetics or short residence time).

Compared to the system with the low K_{eq} of 0.1, the applicability areas and the RD configurations for the system with $K_{eq} = 10$ change much more by the decrease of Da. This points out that although the system has a high K_{eq}, the kinetics, the catalyst hold-up and the liquid residence time give strong effects to the applicability of RD. Comparison of the results for the same Da at Da = 0.01 (see Fig. 7, b and d) for both situations shows the same configuration, as expected since the very slow kinetics is now the controlling mechanism.

In Fig. 7 (b), it seems that the applicability areas and the RD configurations become similar to the equilibrium-limited reaction for Da $\geq$ 0.05. To investigate this phenomenon, additional simulations were performed with varied K_{eq} and Da numbers. As a result, a rule of thumb connecting the kinetically controlled reactions with their equilibrium-limited reactions can be derived. Fig. S5 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 = infinite) 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.

(a)

(b)

(c)

(d)
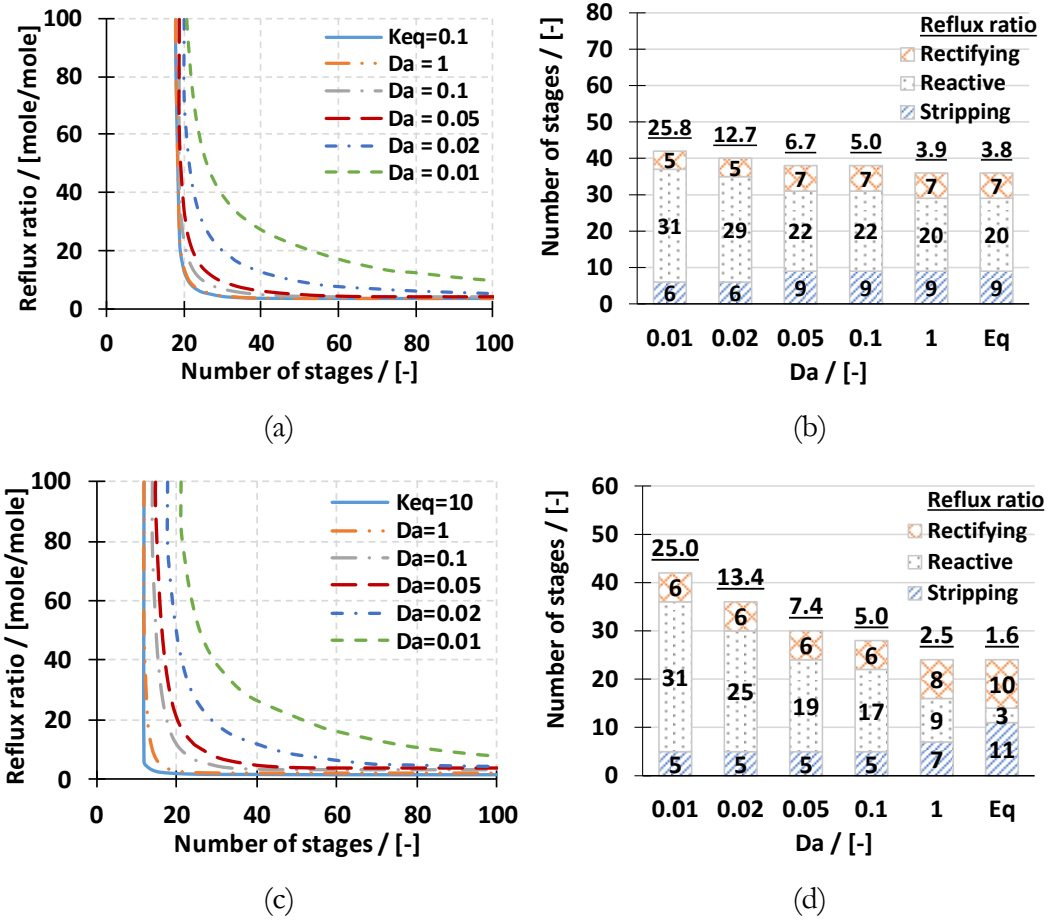
Fig. 7. The applicability areas of RD and their configurations at NTS = 2·NTS$_{min}$ in case of kinetically controlled reactions for α_{AB} = 1.5, α_{CA} = 2, α_{BD} = 2, considering (a and b) K_{eq} = 0.1 and (c and d) K_{eq} = 10.

Further study was done 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 infinite 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.

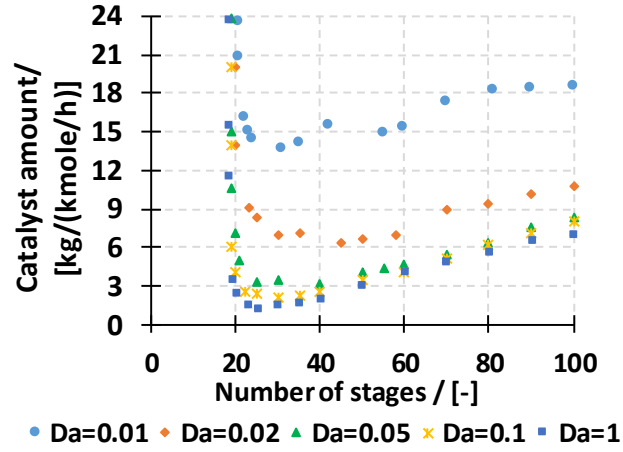Fig. 8. Catalyst amounts along the boundary lines of the applicability areas of RD in the case of $K_{eq} = 0.1$, $\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$, assuming 20 vol% of the catalyst loading per stage. The catalyst amount is based on the total molar flow rate of feed.

This investigation shows the importance of a balance between the RR and the required number of reactive stages 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 the number of reactive and separating stages, reflux ratio) of the modifying specific types of basic parameters.

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

Basic parameters		Effects*		
Type	Modification	Number of reactive stages	Number of separating stages	Reflux ratio
K_{eq} (and Da)	↓ Refer to Fig. 6 (a-b) and Fig. 7 (a-d)	More, to boost the total conversion	Less, because separation also takes place along the reactive section	Higher
α	↓ α_{CA} Refer to Fig. 6 (c-d)	More, to increase the reactants conversion to deal with difficult separation in rectifying section	More rectifying stages because α_{CA} and α_{CB} are smaller	Higher
	↓ α_{BD} Refer to Fig. 6 (e-f)	More, to increase the reactants conversion to deal with difficult separation in stripping section	More stripping section because α_{BD} and α_{AD} are smaller	Higher

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

Basic parameters	Effects*	Basic parameters	Effects*	Basic parameters
Type	Modification	Number of reactive stages	Number of separation stages	Reflux ratio
α	$\downarrow \alpha_{AB}$ Refer to Fig. 6 (g-h)	The following effects are given by fixed α_{CA} and α_{BD} with varied α_{AB}. Varying α_{AB} changes the α_{CB} and α_{AD} values which causes secondary and mixed effects (listed below).		
		Less, because reactants' ratio in liquid phase is closer to stoichiometric which results in a better conversion	More, because α_{CB} and α_{AD} are smaller which means more difficult separation	Higher

*reverse effects are obtained by increasing the value of each parameter

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 predefined maps (obtained in advance using generic systems). The new mapping method allows defining the applicability areas of real systems (i.e. non-ideal vapour–liquid behaviour and temperature-dependent basic parameters, i.e. α, K_{eq}, chemical kinetics) by only referring to the pre-defined applicability graphs of the generic cases. To
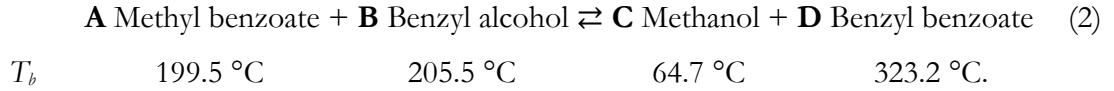
match the applicability graphs of real and generic cases, a representing set of α values of the real systems has to be specified. For that reason, the components' ratios of the real systems have been varied giving various combinations of the α set. Note that many trial simulations were carried out in order to validate the applicability graphs. After checking and validating the applicability graphs of the real and the generic cases, it is rational to estimate the set of α values of the real systems, α_{AB}, α_{CA}, α_{BD}, at 50/50, 99/1 and 1/99 mole% based mixtures, respectively. The 50/50 mole% of reactants shows an equimolar ratio of feed streams that flow through the reactive section. The 99/1 mole% of product C and reactant A gives an estimation of the mixture's composition on the top part of the rectifying section. The 1/99 mole% 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_f 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.

There are two important parameters to quantify our level of satisfaction to the developed mapping method at this initial stage: (1) the pre-defined maps can estimate the boundary lines of the applicability area of a real system, (2) the maximum acceptable deviation is ± 50% for the prediction of the NTS and RR of a real case, as this value is commonly found at the conceptual design phase (Towler and Sinnott, 2012). To calculate the deviation, linear interpolation has been performed to estimate the RD configuration of a real case based on known RD configurations of the two selected generic cases. The estimation based on the interpolation was compared with the simulation result of the real system.

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

Dimethyl terephthalate ester (DMT) is widely produced by the Witten-Hercules method (Tang and Li, 2004). 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 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):

$$\textbf{A} \text{ Methyl benzoate} + \textbf{B} \text{ Benzyl alcohol} \rightleftarrows \textbf{C} \text{ Methanol} + \textbf{D} \text{ Benzyl benzoate} \quad (2)$$

T_b 199.5 °C   205.5 °C   64.7 °C   323.2 °C.

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 behaviour of methanol and methyl benzoate in the vapour phase. There is no azeotrope present in this reaction system, and the heat of reaction (ΔH_r) is -13.79 kJ mole^{-1}.

The availability of chemical data in the literature is limited. The paper of Tang and Li (2004) provides the equilibrium conversion for an equimolar feed. In their study, the process utilised 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 142.0 °C. There is a marginal effect of the temperature on the K_{eq} constant. By assuming a batch reactor, the k_f was determined from the conversion vs time plot which is provided in the paper of Tang and Li [37]. This results in Da = 0.067 for τ = 30 s and Da = 0.133 for τ = 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 α_{AB}, α_{CA} and α_{BD} at 50/50, 99/1 and 1/99 mole% based mixtures from the real system, respectively, α_{AB} = 1.16, α_{CA} = 256 and α_{BD} = 6.5. Since the K_{eq} and α are very favourable, 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 α, 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 summarised in Table 2. The results show a good estimation of the applicability areas and satisfying accuracy. The generic cases, therefore, can be used to predict the applicability of RD to this real system in the case of an 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.
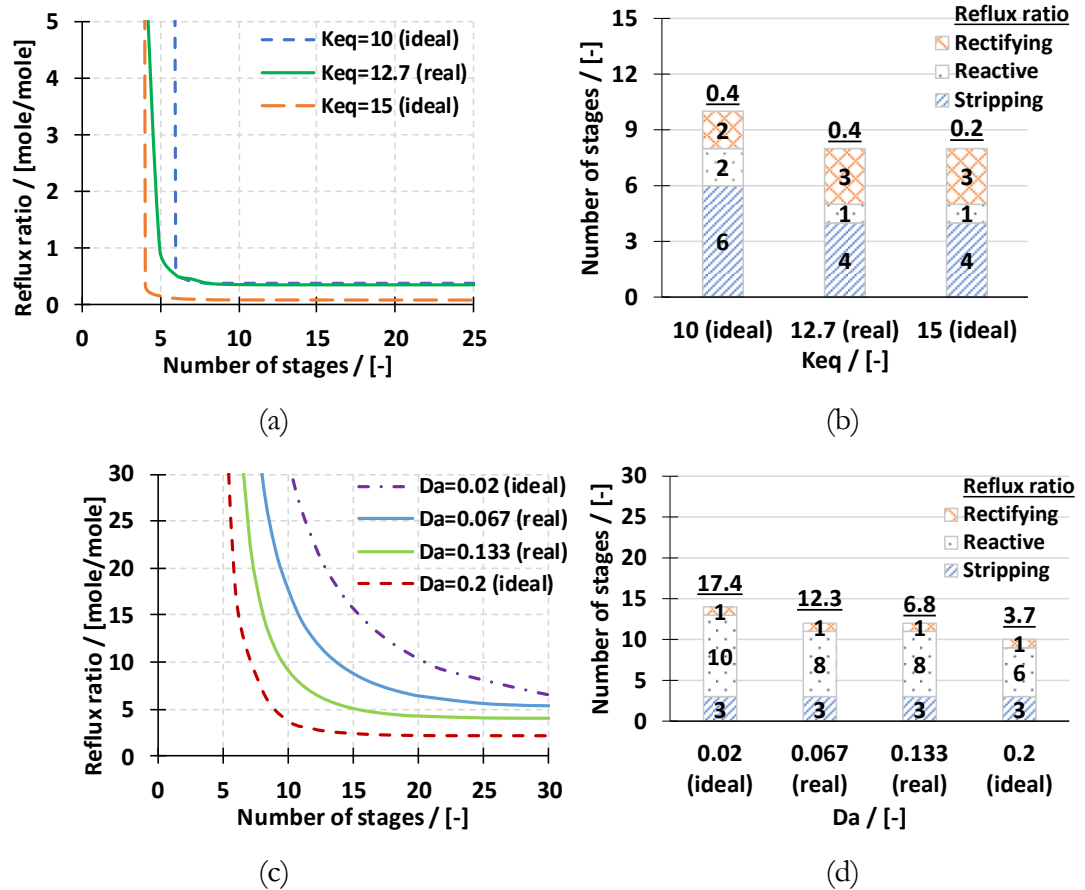

(a)

(b)

(c)

(d)

Fig. 9. The applicability areas of RD and their configurations at NTS = 2·NTS$_{min}$ for the transesterification of methyl benzoate (K_{eq} = 12.7) compared to the generic ideal case (α_{AB} = 1.16, α_{CA} = 256, α_{BD} = 6.5) for (a and b) an equilibrium-limited reaction and (c and d) kinetically controlled reactions.
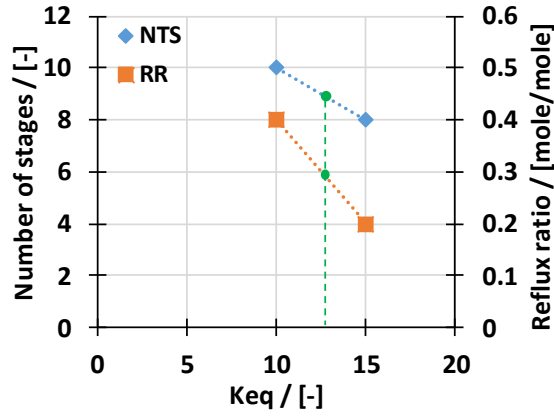
Fig. 10. Prediction of the number of theoretical stages and reflux ratio for the transesterification of methyl benzoate in the case of equilibrium-limited reaction, based on the column configurations of the generic cases.

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.

| Case | K_{eq} (and Da) | NTS | | | RR | | |
		Actual value	Interpolation result	Deviation	Actual value	Interpolation result	Deviation
Trans-esterification of methyl benzoate	K_{eq} = 12.7	8	9	+13%	0.4	0.3	-25%
	K_{eq} = 12.7, Da = 0.067	12	13	+8%	12.3	13.8	+12%
	K_{eq} = 12.7, Da = 0.133	12	11	-8%	6.8	8.8	+29%
Hydrolysis of methyl lactate	K_{eq} = 0.096	20	21	+5%	2.7	2.5	-7%
	K_{eq} = 0.096, Da = 0.16	22	22	0%	10.8	8.2	-24%
	K_{eq} = 0.096, Da = 0.62	20	21	+5%	5.2	3.9	-25%

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 α_{AB} = 1.16, α_{CA} = 256 and α_{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%.

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 hydrolysed back to methanol and lactate acid:

$$\mathbf{A}\text{ Water} + \mathbf{B}\text{ Methyl lactate} \rightleftarrows \mathbf{C}\text{ Methanol} + \mathbf{D}\text{ Lactic acid} \qquad (3)$$

T_b 100.0 °C   144.8 °C   64.7 °C   216.9 °C

ΔH_r = +33.6 kJ mole^{-1}.
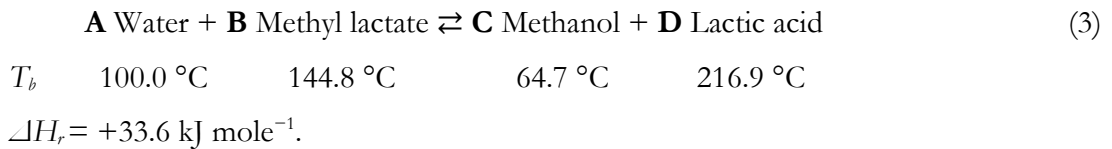
To run the simulations, the selected property model was UNIFAC-HOC since it is the most accurate model to describe the current system (Sanz et al., 2003; 2004). One azeotrope was found in this system: methyl lactate and water form an azeotrope at 97 mole% water in methyl lactate at 99.8 °C. This azeotrope 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 catalysed 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 (Levenspiel, 1999; Sanz et al., 2004). 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) and, using the given kinetic data, the forward reaction rate constant can be calculated with Eq. (5):

$$\ln\left(K_{eq}\right) = 2.6 - \frac{1954.2}{T} \qquad (4)$$

$$k_f = k_f{}^o \cdot \exp\left(-\frac{E_{a,f}}{R \cdot T}\right) \quad . \qquad (5)$$

At the average boiling point of reactants, K_{eq} is 0.096. To calculate the Da number, the k_f 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 $\alpha_{AB} = 5.5$, $\alpha_{CA} = 2.5$ and $\alpha_{BD} = 6.5$ at 50/50, 99/1 and 1/99 mole% based mixtures, respectively. Fig. 11 (a) shows the applicability area of the generic cases for $K_{eq} = 0.05$ 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 $\pm$ 5–7% 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.
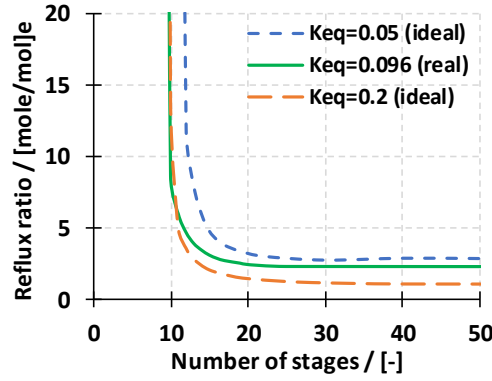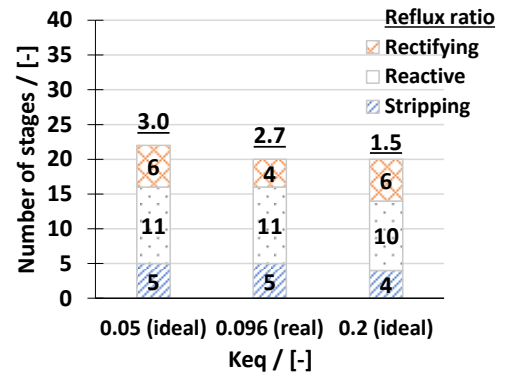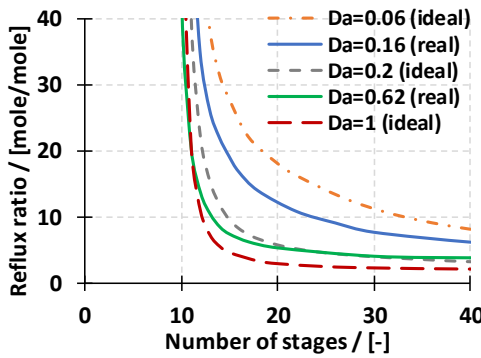
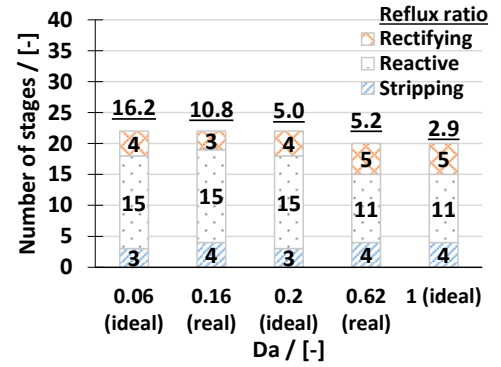Fig. 11. The applicability areas of RD and their configurations at NTS=2·NTS$_{min}$ for the hydrolysis of methyl lactate (K_{eq} = 0.096 at 122.4 °C) compared to the generic ideal case (α_{AB}=5.5, α_{CA}=2.5, α_{BD}=6.5) for (a and b) an equilibrium-limited reaction and (c and d) kinetically controlled reactions.

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. α, 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 summarised 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 analysing the predefined graphs of the generic cases. Furthermore, the method gives a quick and good prediction of the RD configurations of real systems with a deviation of less than ± 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.

Acknowledgement

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi: https://doi.org/10.1016/j.cep.2018.04.001.

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3.2.1. Appendix to Publication 1: Supporting Information

1. Basic parameters for applicability graphs of RD

The following results show the column configurations of RD considering varied vapour and total pressures with fixed α and K_{eq} values in case of equilibrium-limited reactions. Having varied vapour pressures—as presented in Table S1 (a)—and different total pressures, the column configuration (the number of rectifying, reactive and stripping sections) stays the same. The RR change is negligible for different cases. With those column configurations and RR, the targeted bottom product purity (≥ 99 mole%) can be achieved. Simulations with different NTS gave the same conclusion to these presented results. Accordingly, identical applicability graphs were obtained for the cases with varied vapour and total pressures. This concludes that the combination of basic parameters, i.e. α, K_{eq} and chemical kinetics, gives unique applicability graphs.

Table S1 (a). Varied vapour pressures and boiling points of compounds for the generic cases considering $\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$.

	$P°$ (atm)				T_b (°C) at 1 atm			
	A	B	C	D	A	B	C	D
$P°$	1.5	1.0	3.0	0.5	119.5	130.9	101.9	152.7
$0.5 \cdot P°$	0.75	0.5	1.5	0.25	139.7	152.8	119.6	178.3
$2 \cdot P°$	3.0	2.0	6.0	1.0	102.0	112.0	86.4	131.0
$3 \cdot P°$	4.5	3.0	9.0	1.5	92.6	102.0	78.0	119.6

Table S1 (b). Column configurations of RD for varied vapour pressures and total pressures for the generic cases with $\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$, in case of equilibrium-limited reactions considering $K_{eq} = 1$.

P^ν	P (atm)	NTS	Number of rectifying stages	Number of reactive stages	Number of stripping stages	RR	Bottom product purity (mole%)
P^ν	1	20	6	8	6	3.0	98.99
	5	20	6	8	6	2.9	99.00
	10	20	6	8	6	2.9	98.99
$0.5 \cdot P^\circ$	1	20	6	8	6	2.9	98.99
	5	20	6	8	6	2.9	98.99
	10	20	6	8	6	2.8	98.99
$2 \cdot P^\circ$	1	20	6	8	6	3.0	98.99
	5	20	6	8	6	2.9	98.99
	10	20	6	8	6	2.9	99.00
$3 \cdot P^\circ$	1	20	6	8	6	3.0	98.99
	5	20	6	8	6	2.9	98.99
	10	20	6	8	6	2.9	98.99

2. Multiple solutions of RD configuration in applicability graphs

Fig. S1 (a) shows the applicability graph of RD for an equilibrium-limited reaction considering $K_{eq} = 0.1$ in case of $\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$. For this case, $2 \cdot \text{NTS}_{min} = 36$. Close to the region of RR_{min} at NTS = 36, there are multiple RD configurations available with the numbers of reactive stages highlighted in Fig. S1 (b). In details, the multiple solutions of RD configurations are shown in Table S2 in which within only 3% of RR change, at least there are 17 possible RD configurations.

| (a) | (b) |

Fig. S1. (a) Applicability graph of an equilibrium-limited reaction, $\alpha_{AB}= 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$, considering $K_{eq} = 0.1$ and (b) the plot of the number of reactive stages required for different RD configurations at $2 \cdot NTS_{min} = 36$.

Table S2. Multiple solutions of RD configurations for an equilibrium-limited reaction, $\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$, considering $K_{eq} = 0.1$.

Number of theoretical stages	Reflux ratio	Number of Rectifying Stages	Number of Reactive Stages	Number of Stripping Stages	Bottom product purity (mole%)
36	3.79514	7	20	9	99.00
36	3.80197	8	18	10	99.00
36	3.80723	8	17	11	99.00
36	3.81597	7	19	10	99.00
36	3.82566	6	22	8	99.00
36	3.82650	9	15	12	99.00
36	3.83058	6	23	7	99.00
36	3.83425	9	16	11	99.00
36	3.84320	7	21	8	99.00
36	3.85541	8	16	12	99.00
36	3.86606	6	21	9	99.00
36	3.86694	9	14	13	98.99

36	3.86831	8	19	9	99.00
36	3.87449	10	13	13	99.00
36	3.87475	7	18	11	99.00
36	3.88760	10	14	12	99.00
36	3.90148	5	25	6	99.00

3. Asymptotes of applicability graph of RD

Fig. S2 presents an applicability graph of an equilibrium-limited reaction considering $K_{eq} = 1$ in case of $\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$. Table S3 (a) and (b) give column configurations of RD along vertical and horizontal asymptotes of the boundary line of the applicability graph. The vertical asymptote shows the NTS_{min} with different RD configurations by the increase of RR. The horizontal asymptote gives RR_{min} with different column configurations by the increase of NTS.
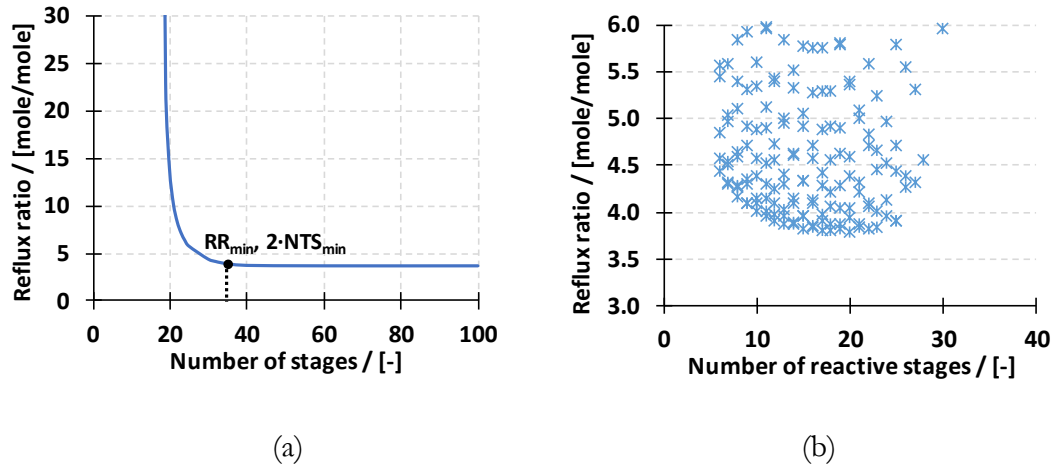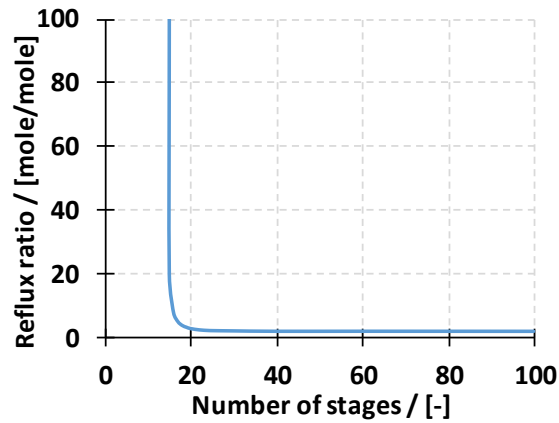

Fig. S2. Applicability graph of an equilibrium-limited reaction, $\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$, considering $K_{eq} = 1$.

Table S3 (a). RD column configurations along the vertical asymptote of the boundary line of the applicability area in case of an equilibrium-limited reaction, considering $K_{eq} = 1$, $\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$.

Number of theoretical stages	Reflux ratio	Number of Rectifying Stages	Number of Reactive Stages	Number of Stripping Stages	Bottom product purity (mole%)
15	20.00	4	6	5	99.00
15	20.69	4	7	4	99.00
15	21.62	5	5	5	99.00
15	22.42	4	5	6	99.00
15	22.87	5	6	4	99.00
15	23.02	3	8	4	99.00
15	23.83	5	4	6	98.99
15	23.85	3	7	5	99.00
15	25.03	6	4	5	99.00
15	26.50	6	5	4	98.99
15	26.68	3	6	6	99.00
15	27.15	6	3	6	99.00
15	27.33	3	9	3	99.00
15	27.88	4	4	7	99.00
15	28.66	4	8	3	98.99
15	29.15	5	3	7	99.00
15	31.45	5	7	3	98.99
15	31.65	7	3	5	99.00
15	32.49	6	2	7	98.99
15	32.58	3	5	7	99.00
15	33.60	7	2	6	98.99
15	33.60	7	4	4	98.99
15	35.57	6	6	3	98.99
15	40.65	4	3	8	99.00
15	41.41	5	2	8	99.00

15	43.71	7	5	3	98.99
15	46.81	3	4	8	99.00
15	46.93	2	9	4	99.00
15	46.93	2	10	3	98.99
15	48.45	8	2	5	98.99
15	48.55	2	8	5	99.00
15	51.26	8	3	4	98.99
15	51.72	2	7	6	99.00
15	52.13	3	10	2	98.99
15	54.59	2	11	2	99.00
15	55.48	4	9	2	98.99
15	58.55	2	6	7	99.00
15	58.69	5	8	2	98.99
15	63.39	6	7	2	98.99
15	63.71	8	4	3	98.99
15	73.17	7	6	2	98.99
15	77.01	2	5	8	99.00
15	82.43	4	2	9	99.00
15	92.69	3	3	9	99.00
15	97.65	8	5	2	98.99

Table S3 (b). RD column configurations along the horizontal asymptote of the boundary line of the applicability area in case of an equilibrium-limited reaction, considering $K_{eq} = 1$, $\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$.

Number of theoretical stages	Reflux ratio	Number of Rectifying Stages	Number of Reactive Stages	Number of Stripping Stages	Bottom product purity (mole%)
90	2.16	40	4	46	99.05
91	2.13	40	5	46	99.02
92	2.12	40	4	48	99.03

93	2.10	39	5	49	99.04
100	2.10	43	4	53	99.01

4. Conversion at equilibrium condition

There is a limit of conversion for an equilibrium reaction, which could prevent from reaching a high product purity. The limit of conversion depends on the chemical equilibrium constant and the ratio of feed. Fig. S3 displays the equilibrium conversion depending on varied chemical equilibrium constants for quaternary reaction systems with a stoichiometric feed ratio.

(a)   (b)
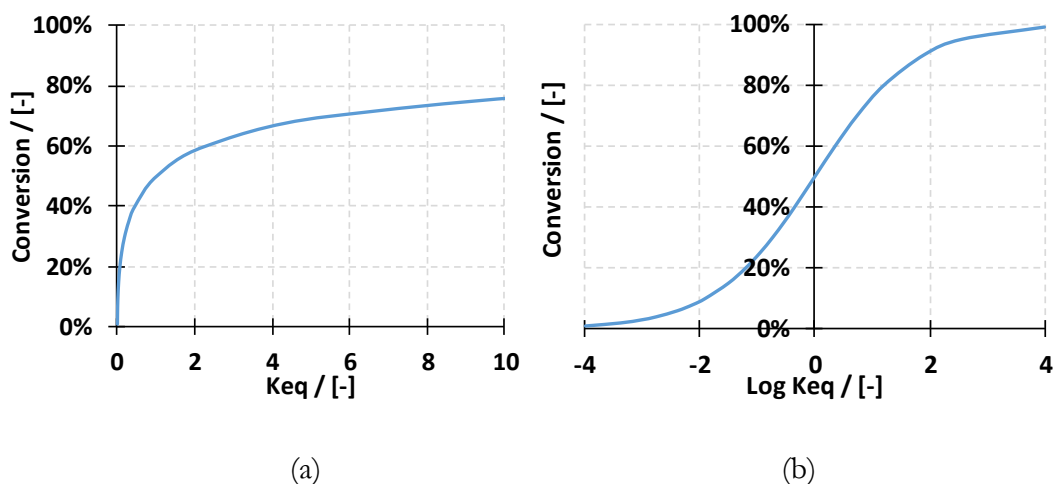
Fig. S3. The effect of chemical equilibrium constant to the equilibrium conversion for quaternary reaction systems with a stoichiometric feed ratio in (a) non-logarithmic scale and (b) logarithmic scale.

5. Liquid composition profiles

Chemical equilibrium constant gives effect to the distribution of mole fraction inside an RD column. The following graphs show the distribution of mole fraction in liquid phase for two varied K_{eq} values. In the graphs, the top and the bottom stages of the reactive zone are indicated by vertical lines. The combined stages between the vertical lines represent the reactive section.

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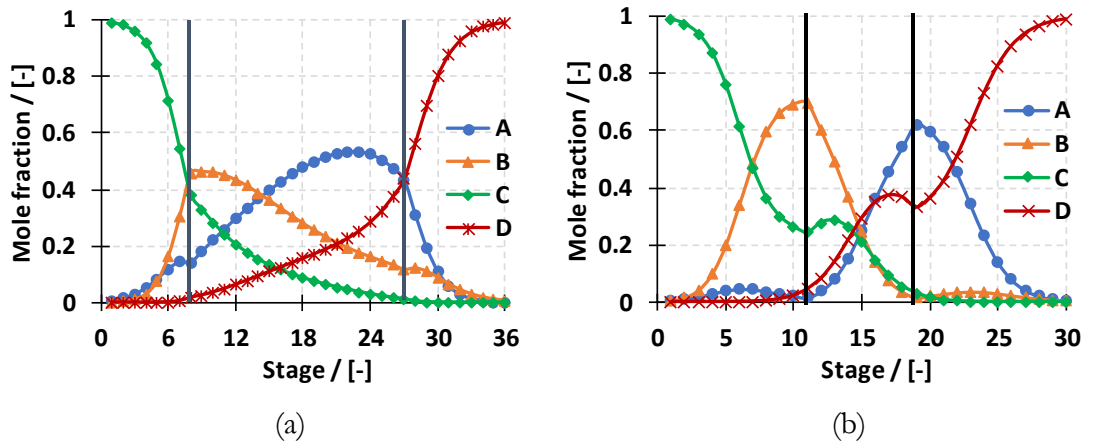
Fig. S4. Liquid composition profiles in an RD column for equilibrium limited reactions, $\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$, considering (a) $K_{eq} = 0.1$ and (b) $K_{eq} = 1$.

6. Da/K_{eq} ratio

The configuration of RD was studied in order to connect the kinetically controlled reactions with their equilibrium-limited reactions. The following figure presents the ratio of number of reactive stages in case of a kinetically controlled reaction over number of reactive stages at equilibrium as the function of Da/K_{eq}. The vertical line highlights NRS/NRS$_{eq}$=1 at Da/K_{eq} = 5. This indicates that the required RD configuration for those kinetically controlled reactions is the same with their equilibrium-limited reactions.
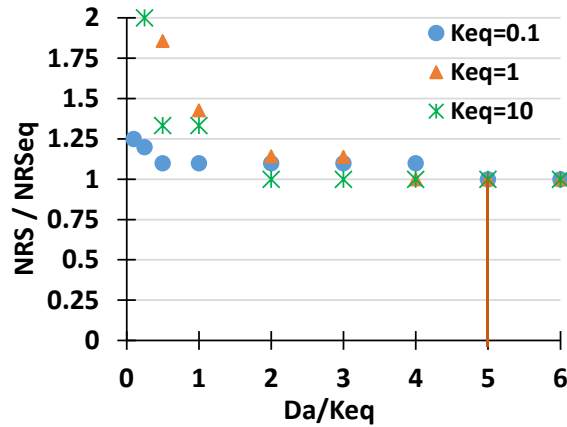
Fig. S5. The ratio of number of reactive stages in case of a kinetically controlled reaction over number of reactive stages at equilibrium condition as the function of Da number over K_{eq}, $\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$.

7. Development of the RD mapping method

The development of the RD mapping method has been through extended and exhaustive study resulting in a schematic procedure to develop the method to predict the applicability area and RD configuration of a real system from available information of generic cases (see Fig. S6).
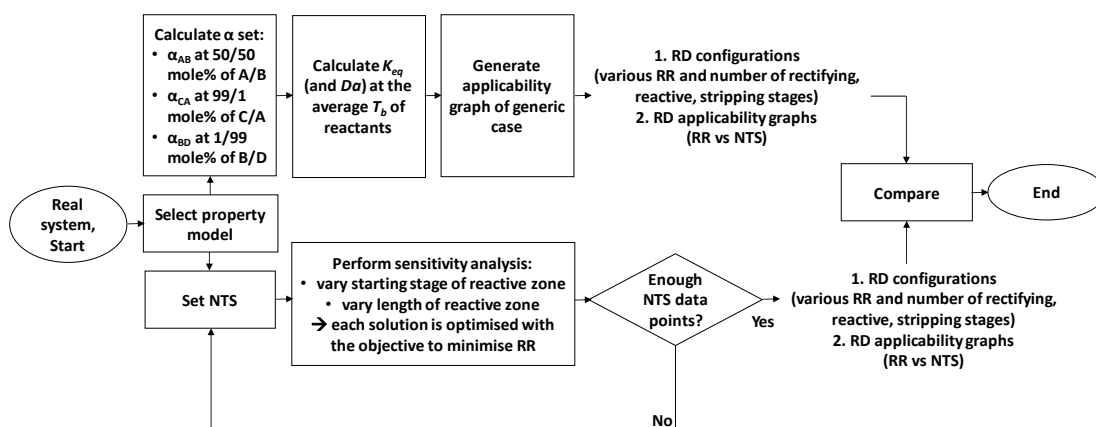
Fig. S6. Schematic methodology for the development of the RD mapping method.

Fig. S6 shows two routes:

i)   The top route represents the method with certain assumptions (e.g. the selected mixture composition for calculating α) to generate the applicability graphs of the generic systems,

ii) The bottom route represents the procedure applied for the detailed simulations. These results will be the reference values to evaluate the results of the top route in block 'compare'.

During the process of establishing the method, rigorous trial simulations have been performed. Fig. S7 and S8 show the results of simulations for the set of α values of the real systems (i.e. α_{AB}, α_{CA}, α_{BD}) at 50/50 mole% based mixtures. The base K_{eq} was calculated at the average boiling point of reactants. The results show significant deviations between the applicability areas of real systems and generic cases which indicate that the establishment of the approach has to be re-iterated with different set of α values and/or boiling point used to calculate the base K_{eq}.

(a)

(b)

(c)

(d)
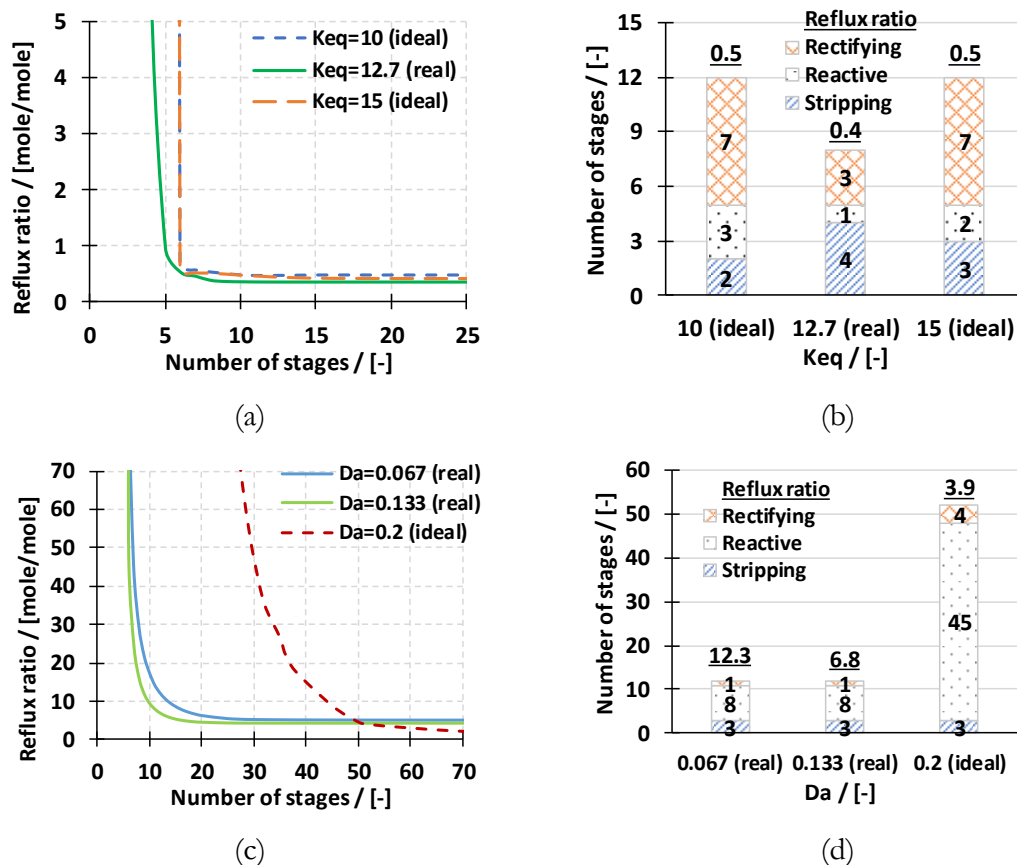
Fig. S7. The applicability areas of RD and their configurations at NTS = 2·NTS$_{min}$ for the transesterification of methyl benzoate (K_{eq} = 12.7) compared to the generic ideal case (α_{AB} = 1.16, α_{CA} = 94, α_{BD} = 17, at 50/50 mole% based mixtures) for (a-b) an equilibrium-limited reaction and (c-d) kinetically controlled reactions.
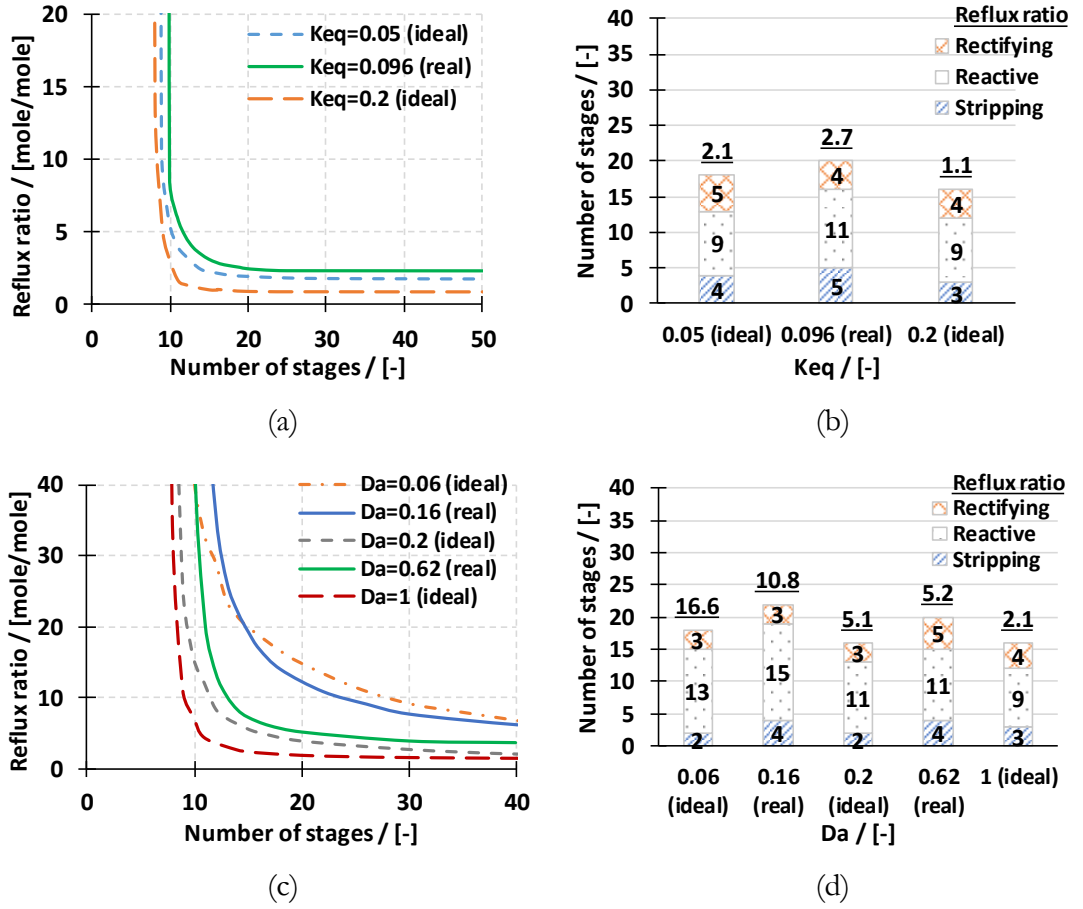
Fig. S8. The applicability areas of RD and their configurations at NTS = 2·NTS$_{min}$ for the hydrolysis of methyl lactate (K_{eq} = 0.096 at 122.4 °C) compared to the generic ideal case (α_{AB} = 5.5, α_{CA} = 3.6, α_{BD} = 11.7 at 50/50 mole% based mixtures) for (a-b) an equilibrium-limited reaction and (c-d) kinetically controlled reactions.

8. Case study: Hydrolysis of methyl lactate

The Da number has to be expressed in a dimensionless unit. For the case of hydrolysis of methyl lactate, the given unit of k_f is mol·g$_{cat}$$^{-1}$·s^{-1} (Sanz et al., 2004). The Da number is generated according to the Eq (1), with the kinetic data and calculated Da numbers are given in Table S4:

$$Da = \frac{k_f \cdot M_r \cdot \rho_{cat} \cdot \beta \cdot \tau}{\rho_{mix}} \quad . \tag{1}$$

β catalyst hold-up per stage $[m^3_{cat}\ m_{liquid\ hold-up}^{-3}]$

k_f pre-exponential forward reaction rate constant $[mole_{mix}\ g_{cat}^{-1}\ s^{-1}]$

M_r molecular weight $[g_{mix}\ mol_{mix}^{-1}]$

ρ_{cat} density of catalyst $[g_{cat}\ m_{cat}^{-3}]$

ρ_{mix} density of mixture $[g_{mix}\ m_{mix}^{-3}]$

τ liquid residence time per theoretical stage $[mole_{liquid\ hold-up}\ mole_{liquid\ flow}^{-1}\ s^{-1}]$

Table S4. Kinetic data and calculated Da numbers for the hydrolysis of methyl lactate.

Kinetic model	Value	Unit
k_f°	$2.8 \cdot 10^3$	mole g_{cat}^{-1} s^{-1}
$E_{a,f}$	50.9	kJ mol^{-1}
K_{eq} (at 122.4 °C)	0.096	-
Average molecular weight	61	g_{mix} mole^{-1}
Density of catalyst	1.7	g mL^{-1}
At 50/50 mole% of A and B:		
γ_A	1.46	-
γ_B	1.00	-
Da number (at 122.4 °C)		
$\beta = 0.071$, $\tau = 30$ s	0.16	-
$\beta = 0.146$, $\tau = 60$ s	0.62	-

References

Sanz, M. T., Murga, R., Beltrán, S., Cabezas, J. L. and Coca, J. (2004). 'Kinetic Study for the Reactive System of Lactic Acid Esterification with Methanol: Methyl Lactate Hydrolysis Reaction', *Industrial & Engineering Chemistry Research,* 43(9), pp. 2049–2053.

3.3. Publication 2

This section is based on the following publication:

The US English spelling in the original publication has been changed here to the UK English spelling to fulfil the requirements of the PhD theses policy regulated by the University of Manchester.

Innovative mapping method for screening reactive distillation designs

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Abstract

Reactive distillation (RD) technology offers key benefits in many chemical processes, including energy savings and costs reduction. Prior to its application in industry, screening, addressing technical feasibility and economic viability, must be performed at the conceptual design level. But these tasks can be challenging and time-consuming since detailed models are usually needed. To overcome this complexity, we provide a mapping method to quickly assess the applicability of RD. The mapping method overlays key parameters of a real system, i.e. relative volatilities (α) and chemical equilibrium constant (K_{eq}), onto pre-calculated graphs indicating the RD performance, i.e. the reflux ratio (RR) vs the number of theoretical stages (NTS) based on generic cases. The mapping method focuses on quaternary systems ($A + B \rightleftharpoons C + D$). A case study (methyl lactate hydrolysis) is used to demonstrate the approach. Three scenarios are presented, applying different characteristic volatility values; each scenario gives rise to a different RD applicability map for equilibrium constants in the range 0.01 to 10. The findings are validated against the results of rigorous process simulation and optimisation. The most accurate scenario is that in which α sets are calculated for mixtures with molar compositions 99% C / 1% A, 50% A / 50% B, 1% B / 99% D, respectively. The results show that the mapping approach allows the prediction of the number of theoretical stages and the reflux ratio to be estimated within 10% of the optimum values.

Keywords:

Reactive distillation, mapping method, applicability graph

1. Introduction

Reactive distillation (RD) is an important intensification technology that offers multiple advantages: 1. an improved chemical process (i.e. higher conversion and selectivity), 2. energy savings, 3. costs reduction, and 4. inherently safer designs (Shah et al., 2012). This technology has received industrial interest for over 30 years; and for example, the production of methyl acetate and ethers using RD is commercially well established (Stankiewicz, 2003). Within the same time frame, studies have been performed to intensify operation of a wider range of chemical processes, such as (trans-)esterification, hydrolysis, (de-)hydration and alkylation (Kiss, 2017).

In spite of the promising applications offered by RD, the complexity of designing RD columns has hindered the industrial application of the technology. Simpler approaches are needed to guide design engineers and support design decision making as to whether RD is an applicable unit (Segovia-Hernández et al., 2015). Recent work has aimed to provide such guidance, via a mapping approach that facilitates screening of RD application (Muthia et al., 2018a). The method uses RD applicability graphs which plot reflux ratio (RR) vs the number of theoretical stages (NTS) and aid go/no-go screening of proposed RD operations considering the maximum acceptable values for NTS and RR. The mapping method is currently limited to use in quaternary reactions (Muthia et al., 2018b). This paper presents an extended development of the method and highlights the importance of using the appropriate characterisation of the relative volatilities in the column to predict RD applicability.

2. Mapping method

Fig. 1 (left) shows the RD configuration used in this study. The column is assumed to operate at atmospheric pressure, with negligible pressure drop, and to achieve vapour-liquid and reaction equilibria at each stage. The reactive section is located between the inlets of the lighter and heavier reactants; reaction and separation occur simultaneously in this section. Further separation takes place in the rectifying and stripping sections, to achieve the targeted product purities. It is assumed that equal molar flows of the reactants are fed to the column as saturated liquids.

The RD column, with any configuration, is simulated using Aspen Plus v8.6. For a given NTS, a sensitivity analysis is carried out in which the number of stages in the rectifying, reactive and stripping sections is varied. A generic case is defined, in which the boiling order of the reactants and products and the type of reaction are defined (e.g. A + B $\rightleftharpoons$ C + D). The method assumes that the generic cases have ideal vapour-liquid equilibrium behaviour (neither azeotropes formation nor liquid split) and constant key parameters, i.e. all relative volatilities (α) and chemical equilibrium constant (K_{eq}). The optimisation tool within Aspen Plus is used in order to minimise the reflux ratio, where the purity of both products is specified as a constraint. Multiple (flat) optimal solutions are obtained for each choice of NTS which correspond to multiple column designs that can meet the specifications. For a given number of theoretical stages, the lowest value of the reflux ratio defines a boundary to the region in which RD is feasible – this is known as the applicability area, as shown in Fig. 1 (right).

Fig. 1 (right) depicts the boundary lines of two RD applicability areas, corresponding to two different K_{eq}s. Only on and above each boundary line, the RD technology is applicable, i.e. the targeted product purities are achieved. The two dashed curves are the lower bounds belonging to two generic cases, i.e. with K_{eq}s equal to 1 and 2.

Fig. 1. RD column configuration (left); RD boundary lines of generic and real systems (right)

The boundary lines of the generic cases are used to predict the RD applicability of a specific, real system. Firstly, key process parameters are calculated (a set of α values and the value of K_{eq}) for the real system. Then the user seeks the two boundary lines, one with a higher K_{eq} value and one with a lower K_{eq}. This allows the user to estimate the position of the boundary line for the real system. For example, for a real system with $1 < K_{eq} < 2$,

its boundary line is predicted to lie between the two generic boundary lines, within the shaded area shown in Fig. 1 (right). Later, rigorous simulations will be carried out to confirm that the actual boundary line of the real system – indicated by the solid line – is indeed well predicted by the neighbouring generic boundary lines.

In classic distillation, short-cut methods, such as the Fenske and Underwood methods, are used to estimate the minimum number of theoretical stages (NTS_{min}) and minimum reflux ratio (RR_{min}). The α value may be that of the feed or considered as an average α along the column based on the composition of the top and the bottom streams, and the results of the Fenske and Underwood design calculations can be relatively sensitive to which approach is adopted. The approximation quality is significantly affected by the nonideality of the mixtures involved. Greater errors are in general obtained in more nonideal systems (Smith, 2016). Therefore, it is crucial to use an appropriate representation of the set of α values in the column when applying simple distillation design methods. In the context of RD, this study evaluates different representations of α sets in the development of the mapping method. The work assumes that the characteristic value of the equilibrium constant, K_{eq}, should be calculated at the average boiling point (T_b) of the two reactants, as the temperature profile in the reactive section is typically confined to the within the range of the reactant boiling temperatures.

The generic boundaries are created by an extensive series of calculations. The vast number of possible combinations of α sets and K_{eq} values implies that an infinite number of boundary lines for generic cases can be obtained. Therefore, the range of K_{eq} is limited to a pragmatic range from 0.01 to 10 (i.e. 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10) that aims to cover the range of reactions with potential for practical RD application. In addition, the lower bound is chosen to the set of results corresponding to a number of theoretical stages that is twice the minimum ($NTS = 2 \cdot NTS_{min}$), in which the reflux ratio is up to 10% higher than the lowest reflux ratio on the boundary line. These choices are based on heuristics for estimating the optimal number of stages for classic distillation.

3. Case study

This study focuses on the quaternary reaction (A + B $\rightleftharpoons$ C + D), where $T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$), which has been explored widely for RD applications. Due to space limitations, only the case study of methyl lactate hydrolysis is presented, as shown in Eq. (2):

Water (A) + Methyl lactate (B) $\rightleftharpoons$ Methanol (C) + Lactic acid (D)   (2)

T_b 100 °C   144.8 °C   64.7 °C   216.9 °C

$\Delta H_r = +33.6$ kJ mole^{-1}.

The activity coefficients are calculated by UNIFAC-HOC and a correlation between temperature and chemical equilibrium constant is shown in Eq. (3),

$$\ln\left(K_{eq}\right) = 2.6 - (1954.2/T) \ , \tag{3}$$
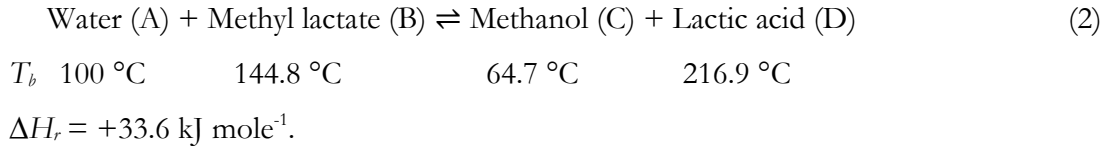
where T is in K (Sanz et al., 2004). An azeotrope exists at 99.8°C with a molar composition of 97% water and 3% methyl lactate. In this study, the targeted purity of products $\geq$ 99 mole%.

4. Method development and validation

Table 1 presents three scenarios, applying different definitions for the characteristic α sets. For all scenarios, α_{AB} is for a 50/50 mole% mixture of the reactants, corresponding to the equimolar feed of reactants. In Scenario 1 (S1), α_{CA} and α_{BD} are calculated using the compositions of the top and the bottom streams, respectively. Scenario S2 aims to consider volatilities within the column, and not just at its extremities; therefore, the characteristic α_{CA} and α_{BD} are calculated 50/50 mole% binary mixtures. Scenario S3 calculates α_{CA} and α_{BD} at compositions (1/99% CA and 99/1% BD mixtures) that are only expected to occur if K_{eq} is very low, leading to very low conversion. In this case, a single RD column is unlikely to be appropriate.

Table 1. Characterisation of α sets

Scenario	Representation of α set		
	α_{CA}	α_{AB}	α_{BD}
S1	2.5 (99/1 mole%)		6.5 (1/99 mole%)
S2	3.6 (50/50 mole%)	5.5 (50/50 mole%)	11.7 (50/50 mole%)
S3	7.5 (1/99 mole%)		14 (99/1 mole%)

The dashed boundary lines in Fig. 2, Fig. 3 and Fig. 4 (left) represent generic cases for S1, S2 and S3, respectively. Note that the solid line in each graph, which is the actual boundary line for the case study, is added later, after performing rigorous simulation for validation purposes.
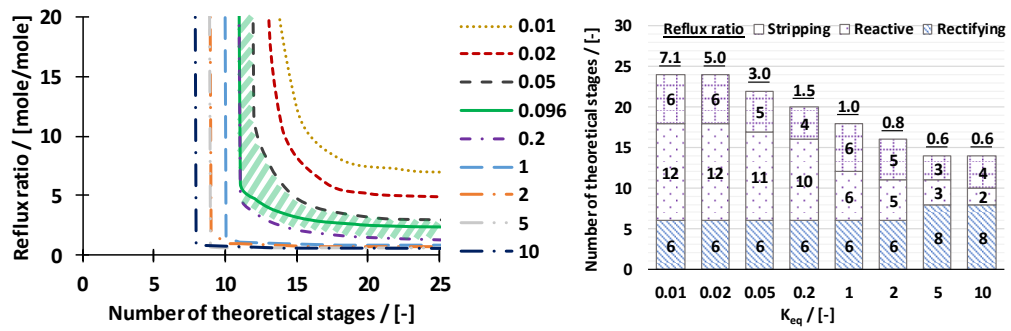

Fig. 2. RD applicability areas (left); their RD configurations at NTS = 2·NTS$_{min}$ (right) for S1
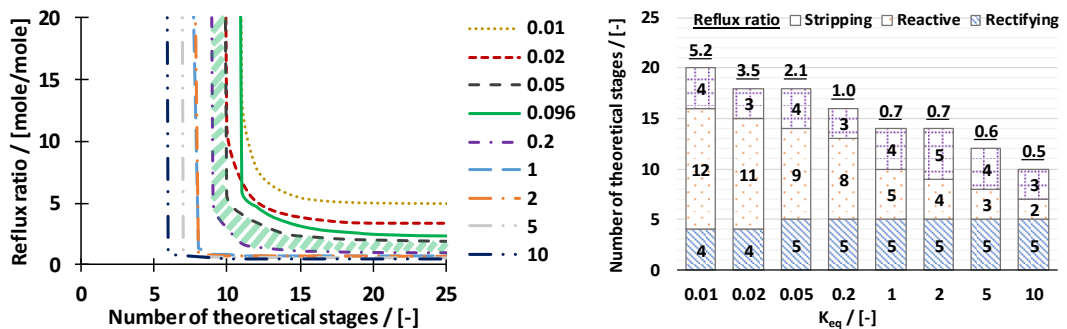
Fig. 3. RD applicability areas (left); their RD configurations at NTS = 2·NTS$_{min}$ (right) for S2

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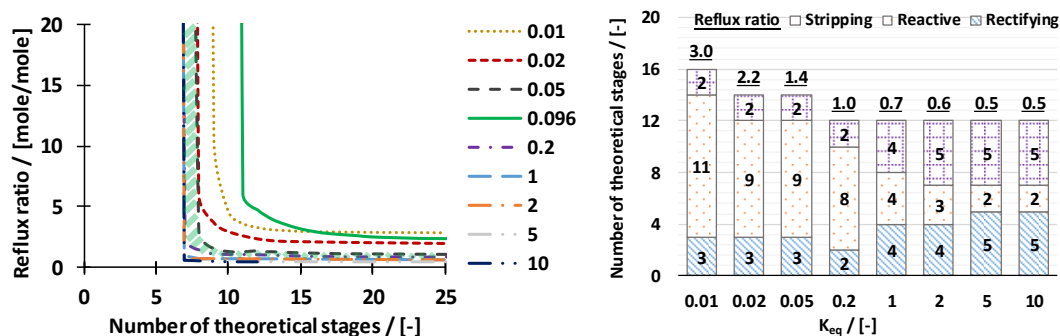
Fig. 4. RD applicability areas (left); their RD configurations at NTS = 2·NTS$_{min}$ (right) for S3

The size of RD applicability areas of the generic cases increases from S1, S2, to S3, respectively: the increasing ease of separation between reactants and products (shown in Table 1), leads to lower reflux ratios for any number of stages. This observation is in agreement with the resulting RD configurations, presented in Fig.s 2, 3 and 4 (right). In each system, fewer reactive stages are needed for higher K_{eq} values, since the reaction performance is improved. Conversely, more separation stages are needed because fewer reactive stages achieve less simultaneous separation.

For the particular conditions of the case study, K_{eq} is 0.096, calculated using Eq. (3). A premise of the mapping method is that the actual boundary line will lie between neighbouring generic boundary lines, i.e. within the shaded areas in Fig. 2, Fig. 3 and Fig. 4 (left). Rigorous simulations of the case study provide the actual boundary line, indicated by the solid line. It may be seen that the generic boundary lines predict its location well only in S1, i.e. the effectiveness of the mapping method is sensitive to the approach used to characterise volatilities in the column.

Fig. 5 (left) illustrates how the generic results can be used to design a particular RD column using linear interpolation to estimate the number of theoretical stages and reflux ratio, for $K_{eq} = 0.096$. The number of rectifying, reactive and stripping sections can be estimated using the same approach. Multiple designs configurations exist; two RD configurations of neighbouring generic cases (with K_{eq} values close to the actual value) are considered, i.e. K_{eq} values of 0.05 and 0.2. Fig. 5 (right) shows the actual (simulated) RD configuration and configurations predicted using linear interpolation for S1, S2 and S3. Table 2 quantifies the goodness of fit in terms of the differences in NTS and RR, relative

to that of the actual case. S1 is in good agreement with the generic results, with deviations below 10%.
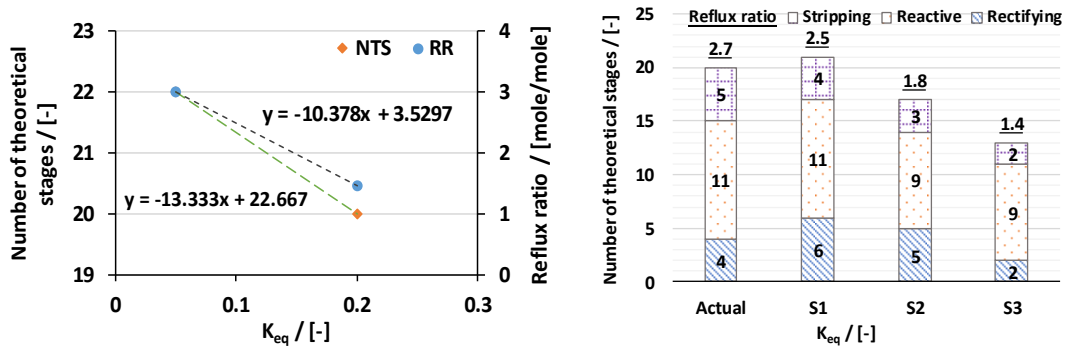
Fig. 5. NTS and RR predictions for S1 (left); Predicted and actual RD configurations (right)

Table 2. Comparison of linearly interpolated and actual NTS and RR values

Scenario	NTS			RR		
	Actual	Predicted	Deviation	Actual	Predicted	Deviation
S1	20	21	5%	2.7	2.5	8%
S2	20	17	15%	2.7	1.8	33%
S3	20	13	35%	2.7	1.4	48%

5. Conclusions

The mapping method aims to help engineers to carry out a relatively quick initial evaluation of potential RD applications. The approach uses characteristic relative volatilities and chemical equilibrium constant of a real system to screen the RD designs based on generic RD applicability graphs. This study highlights the importance of having the appropriate characterisation of relative volatilities sets to predict the RD applicability and validates the approach by comparing predictions to rigorous simulation results. The relative volatilities sets should be calculated for total feed, top product and bottom product conditions. The approach enabled the prediction of NTS and RR for the case study with deviations of less than 10%.

Acknowledgements

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Chapter 4

Development of a Mapping Method for (Near-) Ideal Quaternary Reaction Systems with Different Boiling Point Orders of Compounds

Publication in Chapter 4:

- **Publication 4**

  Muthia, R., van der Ham, A. G. J., Jobson, M. and Kiss, A. A. (2019). 'Effect of boiling point rankings and feed locations on the applicability of reactive distillation to quaternary systems', *Chemical Engineering Research and Design,* 145, pp. 184–193.

4.1. Preface of Publication 3

Reactive distillation (RD) processes have been industrially applied for more than four decades (Agreda et al., 1980; Siirola, 1996; Smith, Jr., 1980). However, the scale-up of many potential RD processes to the commercial level is hindered by difficulties in understanding complex reactive distillation processes (Chen et al., 2000; Harmsen, 2007; Segovia-Hernández et al., 2015; Li, et al., 2016). To deal with this problem, the work in Publication 3 develops and employs the mapping method to gain an understanding of the operation of reactive distillation.

The preceding chapter has shown the usefulness of the mapping method to quickly assess the applicability of reactive distillation to (near-) ideal reaction systems, $A + B \rightleftharpoons C + D$, with both reactants as mid-boiling compounds, $T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$. The application of reactive distillation, in practice, is promising for quaternary reaction systems with various orders of boiling points (Hiwale et al., 2004; Luyben and Yu, 2008; Sharma and Mahajani, 2002). Therefore, the work in Publication 3 extends the use of the mapping method for (near-) ideal reaction systems with other classes of boiling points.

Publication 3 aims to provide an understanding of the effects of boiling point orders of compounds on reactive distillation processes. In this work, quaternary reaction systems are classified according to boiling point orders of compounds, and their naming convention follows the rule specified by Luyben and Yu (2008):

- Group I_p ($T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$)
- Group I_r ($T_{b,A} < T_{b,C} < T_{b,D} < T_{b,B}$)
- Group II_p ($T_{b,C} < T_{b,D} < T_{b,A} < T_{b,B}$)
- Group II_r ($T_{b,A} < T_{b,B} < T_{b,C} < T_{b,D}$)
- Group III_p ($T_{b,C} < T_{b,A} < T_{b,D} < T_{b,B}$)
- Group III_r ($T_{b,A} < T_{b,C} < T_{b,B} < T_{b,D}$)

Out of the six groups, groups II_p and II_r are excluded from this assessment because of their unfeasibility from a thermodynamic standpoint and inconsistency with the mass-balance principle. In a quaternary reaction system where all reaction coefficients are unity, two lower-boiling reactants, which are usually characterised by lower molecular weight,

cannot convert into two higher-boiling products normally characterised by larger molecular weight.

The objectives of this thesis that are addressed in Publication 3 are:

1. To generate heuristics for the initialisation of reactive distillation designs.
   The heuristics generated in this work give benefits for process engineers to consider RD process alternatives based on a preliminary economic ranking and also to design RD columns with optimal feed stage locations. Conventionally, any knowledge related to economics and optimal configurations of RD processes is acquired in the advanced phase of a conceptual study, and one needs to perform many rigorous simulations to determine beneficial reactive distillation processes.

2. To assess the applicability of reactive distillation by using generic applicability graphs.
   To generate heuristics for a preliminary economic ranking of RD processes and optimal feed stage locations of RD columns, this work assigns hypothetical generic cases representing the four different groups of quaternary reaction systems. Comparable results for those different groups are assessed by specifying relative volatilities between reactants and products (α_{AB} and α_{CD}) in groups I_p, III_p and III_r at 2 and 6, respectively. The specified relative volatilities for group I_r are different, i.e. α_{AB} = 6 and α_{CD} = 2, as the order of boiling points of group I_r does not allow those relative volatilities to be identical with the other groups.

3. To compare the findings of this work with those of previous studies employing different conceptual approaches.
   In this work, a preliminary economic ranking is generated by taking into account the number of theoretical stages and reflux ratio as two significant variables affecting costs of reactive distillation. The results of this work are compared with those of Luyben and Yu (2008) obtained from detailed economic calculations. Furthermore, the understanding of the optimal feed stage locations is gained by varying feed stages among all possible combinations within RD columns for generic cases. Results generated in this work are compared with those obtained by Tang et al. (2005) employing rigorous simulations and detailed economic calculations for the synthesis of methyl acetate via esterification.

4.2. Publication 3

This section is based on the following publication:

Muthia, R., van der Ham, A. G. J., Jobson, M. and Kiss, A. A. (2019). 'Effect of boiling point rankings and feed locations on the applicability of reactive distillation to quaternary systems', *Chemical Engineering Research and Design,* 145, pp. 184–193.

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The US English spelling in the original publication has been changed here to the UK English spelling to fulfil the requirements of the PhD theses policy regulated by the University of Manchester.

Effect of boiling point rankings and feed location on the applicability of reactive distillation to quaternary systems

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Abstract

Reactive distillation (RD) offers major benefits such as costs reduction and energy saving, but the understanding and design of RD processes usually demand complex tasks that include extensive studies and rigorous simulations. To reduce this complexity and the time required, this study applies a novel mapping method to quickly provide insights into the RD applicability to reversible quaternary systems ($A + B \rightleftharpoons C + D$). Generic cases are used to produce applicability graphs (i.e. plots of reflux ratio vs the number of theoretical stages) and multiple RD column configurations. The systems are assumed to have ideal properties and fixed key parameters (i.e. relative volatilities and chemical equilibrium constants). This study focuses on quaternary reactions considering different boiling point rankings and feed locations. Using the mapping method, quick results are achievable regarding the preliminary economic ranking of RD processes, and the optimal feed locations with reduced energy requirement (i.e. lower reflux ratio). Ultimately, this study provides a much better understanding of the effect of boiling point orders and feed locations on the RD applicability and conceptual design, being a valuable tool in early techno-economic evaluations.

Keywords:

Reactive distillation, mapping method, applicability graph, quaternary systems

1. Introduction

Reactive distillation (RD) is a process intensification technique that allows simultaneous separation to take place when chemical reaction occurs. RD gives benefits to equilibrium-limited reactions by pulling the chemical equilibrium towards complete conversion and allowing high selectivity (e.g. avoiding potential consecutive reactions) due to the continuous removal of products from the RD column (Baur et al., 2000). Among others, RD offers great advantages in costs reduction by simplifying complex processes and integrating the reaction and separation functions into a single unit with reduced requirements (Kiss, 2019). The use of exothermic heat of reaction to drive the liquid vaporisation reduces the energy requirement (Kaur and Sangal, 2017). There are also health, safety and environmental improvements mainly because of less emissions from plants, lower levels of reactive hold-up and decreased risks of runaway reactions (Shah et al., 2012; Taylor and Krishna, 2000).

The commercialisation of reactive distillation has expanded for over 30 years (Stankiewicz, 2003). The most well-known RD process is in the methyl acetate production via esterification, which has been established since 1984 by Eastman Kodak Company (Agreda et al., 1990). The syntheses of ethers, i.e. methyl *tert*-butyl ether, ethyl *tert*-butyl ether and *tert*-amyl methyl ether, are other remarkable examples where RD technology is applied (Sharma and Mahajani, 2002). Furthermore, the implementation of RD is very appealing to other reactions involving reversible quaternary systems ($A + B \rightleftharpoons C + D$) and ternary systems ($A + B \rightleftharpoons C$ and $A \rightleftharpoons B + C$). Some examples include the hydration of cyclohexene to obtain cyclohexanol (Chen et al., 2014), dehydration of glycerol to acetol (Chiu et al., 2006), isoamyl acetate production via esterification of isoamyl alcohol and acetic acid (González et al., 2017) and diethyl carbonate synthesis via trans-esterification of propylene carbonate and ethanol (Wang et al., 2014).

Studies related to RD technology provide various methods to design and control the column operation, specify and modify its physical structures and/or evaluate the economic aspect. For example, a set of equations can be used to calculate the minimum reflux ratio (RR_{min}) for both single- and double-feeds RD columns (Barbosa and Doherty, 1988a; 1988b). The location of the reactive zone in binary reactions can be visualised by using the McCabe-Thiele and Ponchon Savarit methods (Lee et al., 2000). Other studies

determined heuristic approaches by considering basic knowledge and industrial experience, to specify the operating conditions and the physical aspects of RD (Subawalla and Fair, 1999). Other RD design methods have been also reported in literature (Almeida-Rivera et al., 2004; Buzad and Doherty, 1994; Ciric and Gu, 1994; Groemping et al., 2004; Jantharasuk et al., 2011; Thery et al., 2005). However, in contrast to much information available, the complexity of designing and understanding RD processes remained a strong barrier that has hindered the rapid commercialisation of RD for over 15 years (Chen et al., 2000; Harmsen, 2007; Li et al., 2016; Malone and Doherty, 2000; Segovia-Hernández et al., 2015). In other words, simplicity is strongly needed in the assessment of RD design at early stages of industrial R&D.

The present study aims to provide insights into RD processes by using a mapping method that was initially developed to quickly assess the applicability of RD based on pre-defined maps (i.e. applicability graphs) obtained from generic cases (Muthia et al., 2018). In that initial work, we validated the approach using two case studies, i.e. hydrolysis of methyl lactate and transesterification of methyl benzoate and benzyl alcohol, and showed that one can successfully use the generic cases to predict the applicability of RD to real systems. The following assumptions for the generic cases are applied in this study: ideal thermodynamics (neither azeotropes nor liquid split); fixed values of key parameters, i.e. relative volatility (α) and chemical equilibrium constant (K_{eq}); and vapour-liquid and chemical equilibria on each stage. The key feature of the mapping method is RD applicability graphs produced from the generic cases, which are the plots of reflux ratio (RR) vs the number of theoretical stages (NTS).

This study focuses on quaternary systems, as they are the most encountered reactions for the operation of RD in the chemical industry. Beyond the scope of this paper, the mapping method is promising for applications to ternary systems, but further studies are required to further develop the method for those systems. The application of RD to quaternary systems investigated in this study considers different boiling point (T_b) rankings and feed locations. Insights into the RD applicability related to economics and conceptual design are provided early on. This is in contrast to the conventional way, where knowledge about these aspects usually requires rigorous simulations and/or detailed calculations and at such level that understanding can be obtained only at the final stage of conceptual design studies (Seider et al., 2003; Towler and Sinnott, 2012). Firstly, the

mapping method is used to obtain a preliminary economic ranking, thus providing an overview of the most beneficial RD configurations in chemical processes. Secondly, the mapping method is used to investigate the possibilities of reducing the energy requirement (i.e. operating RD with lower reflux ratios) by finding the optimal feed locations. A recent review revealed that extensive studies about the design of RD are available in literature, but there is still a lack of understanding in terms of process optimisation (Segovia-Hernández et al., 2015).

Prior studies investigating the effect of volatilities on the RD performance are available in literature with different focuses and approaches. Luyben and Yu (2008) ranked quaternary reactions with various boiling point orders by using detailed economic calculations but considering only a fixed equilibrium constant. In this work, we use a range of chemical equilibrium constants and rank the quaternary reactions with a simpler approach, based on the number of theoretical stages and reflux ratio that provide an indication of the capital investment and energy requirement. Chen and Yu (2008) used the same approach as that in Luyben and Yu (2008) to study the effect of relative volatility ranking on RD configurations, but to ternary decomposition reactions only. In this study, we focus on quaternary reactions, which are more complex by the presence of more components in the systems. Our previous work (2018) focused on a single set of quaternary systems with both reactants as mid-boiling components and products as lightest and heaviest components ($T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$), and fixed feed locations at both end sides of the reactive section. That work provided valuable insights into RD performance considering low or high relative volatilities between product-reactant (α_{CA} and α_{BD}) and both reactants (α_{AB}). In our current study, we include all quaternary systems with different boiling point rankings and obtain the optimal feed locations considering varied feed stages.

Summing it up, this work gives useful knowledge regarding industrial RD processes, covering two aspects related to essential assessment in conceptual design studies: economic ranking of process alternatives, and optimal process configurations. Furthermore, this study provides a valuable understanding of the effect of boiling point rankings on the RD processes.

2. Approach and methodology

A novel mapping method—described in our previous work—has been employed to predict the applicability of RD based on the applicability graphs of generic cases and to study the effect of relative volatilities, chemical equilibrium and kinetics (represented by Damköhler number) on RD processes (Muthia et al., 2018). This method was also used to determine the optimal RD configurations that can operate at the lowest costs (Muthia et al., 2018a).

The key feature of the mapping method is the RD applicability graph, illustrated in Fig. 1. A boundary line in the applicability graph splits the plot into applicable and not-applicable areas. On that line, each NTS has a RD configuration with the lowest reflux ratio possible. On the boundary line and inside the applicability area at any NTS, the operation of reactive distillation is conceivable. Multiple RD configurations are available inside the applicability area, which give flat-optimum solutions (Muthia et al., 2018). For the sake of clarity, the applicability graphs shown in this work have a maximum scale of 100 for both x- and y-axes.
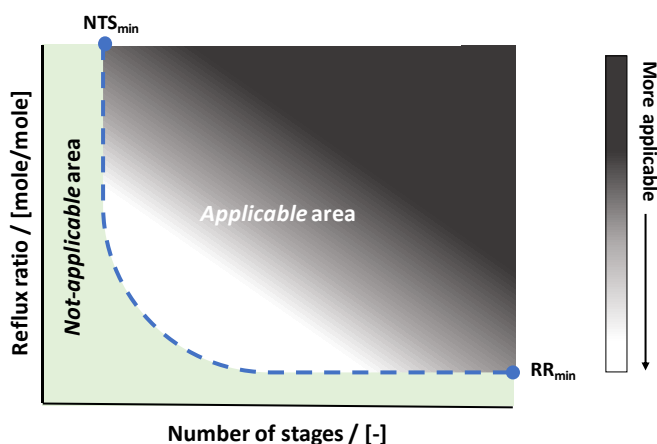
Fig. 1. An illustrative applicability graph for reactive distillation (Muthia et al., 2018).

Each RD applicability graph is coupled with a representation of column configurations within the applicable area. The selection of that representation can be based on various consideration, e.g. at a fixed NTS, at NTS = $2 \cdot \text{NTS}_{min}$, at NTS with RR = $1.2 \cdot \text{RR}_{min}$, or at any other points. In this study, each representation of RD configurations is at NTS = $2 \cdot \text{NTS}_{min}$ which is only based on the well-known rule of thumb in conventional distillation regarding the prediction of the optimum configuration. That representation is selected by

considering the availability of multiple RD configurations with reflux ratios up to 10% larger than the lowest RR. This consideration is logically accepted as that marginal reflux ratios difference is commonly negligible in the RD application.

Considering the flat-optimum solutions in the applicability graphs, various trends of RD configurations can be obtained when different applicability graphs are studied and compared. The representations of RD columns are selected based on the decrease of the number of reactive stages for a higher K_{eq} when applicability graphs of various equilibrium constants are compared. This selection criterion is logical since a better reaction performance is achieved for a higher K_{eq}.

The schematic procedure to generate an applicability graph is given in Fig. 2. It might be preferred to specify relative volatilities of components following the boiling point rankings of the quaternary systems. For instance, with the order of $T_{b,C} < T_{b,A} < T_{b,D} < T_{b,B}$, specifying α_{CA}, α_{AD} and α_{DB} might be preferred. This study only focuses on equilibrium-limited reactions as similar knowledge is expected to be the outcome for the study of their kinetically controlled reactions, as proven in our previous work (2018). Since vapour-liquid and chemical equilibria are reached on each stage of the column, specifying liquid hold-up or residence time (resulting in the Damköhler number) is not required as an input for the simulation in this work.
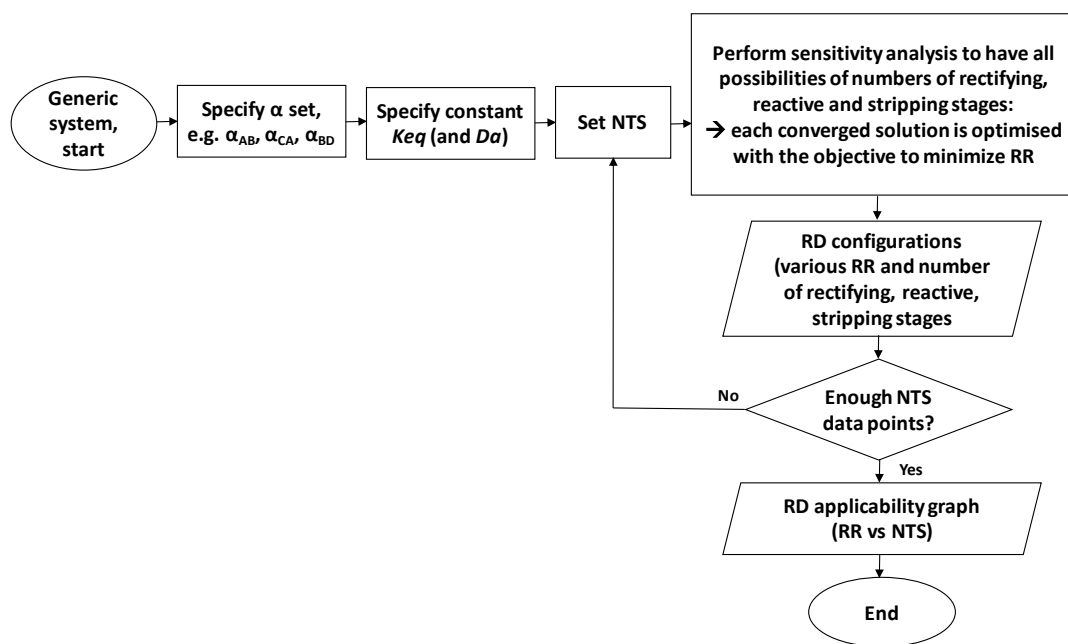

Fig. 2. Schematic procedure to generate RD applicability graph (Muthia et al., 2018).

The quaternary reactions are classified into six groups based on the boiling point rankings, as shown in Table 1. For consistency reasons, the naming convention of the groups follows the rule defined by Luyben and Yu (2008). To deliver comparable results for different groups, several key relative volatilities have to be specified uniformly. In this study, α_{AB} and α_{CD} are specified at 2 and 6, respectively (see Table 1). Only group I_r has different specified α_{AB} and α_{CD} since its boiling point order does not allow defining those relative volatilities at 2 and 6, respectively. Both groups II_p and II_r are disregarded from the investigation since from a thermodynamic point of view, it is unfeasible to obtain two heaviest / lightest products from two lightest / heaviest reactants (in stoichiometric systems).

Table 1. Groups of quaternary systems based on boiling point (T_b) orders.

Group	Boiling point ranking	Specified variables		Set variables		α set following T_b order
		α_{AB}	α_{CD}	α_{CA}	α_{BD}	
I_p	C < A < B < D	2	6	2	1.5	$\alpha_{CA} = 2$, $\alpha_{AB} = 2$, $\alpha_{BD} = 1.5$
I_r	A < C < D < B	6	2	0.6	0.6	$\alpha_{AC} = 1.7$, $\alpha_{CD} = 2$, $\alpha_{DB} = 1.7$
II_p	C < D < A < B	disregarded from consideration, for thermodynamic reasons				
II_r	A < B < C < D					
III_p	C < A < D < B	2.1	6	4	0.7	$\alpha_{CA} = 4$, $\alpha_{AD} = 1.5$, $\alpha_{DB} = 1.4$
III_r	A < C < B < D	2.1	6	0.7	4	$\alpha_{AC} = 1.4$, $\alpha_{CB} = 1.5$, $\alpha_{BD} = 4$

Using the mapping method, a preliminary economic ranking of RD is obtained here by considering the number of theoretical stages and reflux ratio as two main variables, which give the first economic assessment. NTS indicates the height of column which is proportional to the capital investment and RR affects the column diameter and is directly proportional to the amount of hot utility required (energy usage), respectively (Kiss, 2013). To perform this assessment comprehensively, the chemical equilibrium constants are

varied at values of: 0.01, 0.1, 0.2, 1 and 10. These values cover the practical range of reactions in terms of the RD application.

All simulations are performed in Aspen Plus v8.6. The RD scheme is presented in Fig. 3 (a). The RD column operates at atmospheric pressure, assuming negligible pressure drop. The reactants are fed as saturated liquid, in an equimolar ratio. The lighter reactant is fed on the bottom of the reactive zone and the heavier reactant is introduced to the top of the reactive zone, therefore a counter-current flow occurs which allows reaction to take place along the reactive stages. Sensitivity analysis is carried out by varying the position and the length of rectifying, reactive and stripping sections. The optimisation tool is used to minimise the reflux ratio for any converged solutions by considering product purity at top and bottom (min. 99 mole%) as a hard constraint. Next, the optimal feed locations are assessed for the quaternary systems as given in the study of preliminary economic ranking. Any configurations in RD applicability graphs can be selected for this investigation. The resulting representations of column configurations in the previous section are used as base cases, in terms of numbers of rectifying, reactive and stripping stages. Sensitivity analysis is carried out by varying both positions of feed stages, as shown in Fig. 3 (b). The optimisation tool is used to minimise the reflux ratio by considering the same constraint as in the study of preliminary economic ranking.
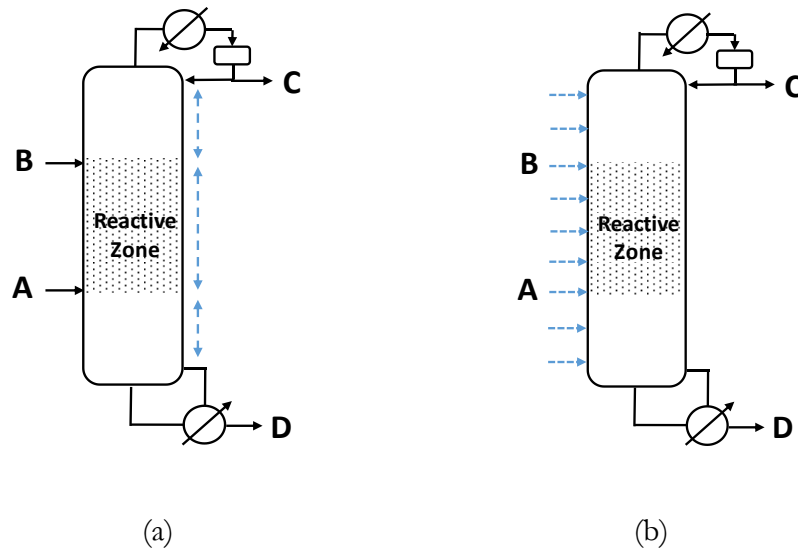

(a)   (b)

Fig. 3. RD columns with (a) fixed feed inlets on the top and the bottom parts of reactive zone and (b) varied feed inlets along the RD column.

# 3. Results and discussion

3.1. Preliminary economic ranking of RD processes

Simulations in Aspen Plus v8.6 were performed for groups I_p, I_r, III_p and III_r to obtain their applicability areas accounting for various equilibrium constants (from 0.01 to 10). There is no applicability graph available in group I_r for any specified K_{eq} which indicates that the required product purity cannot be achieved, hence a single RD column is not applicable. An advanced RD configuration (involving two columns) might be used for this group. The RD setup might be adjusted by adding side-draw product stream(s) to the column as both desired products are mid-boiling compounds (Luyben and Yu, 2008). At least an additional conventional distillation is needed to obtain the products at high purity. Besides, the application of reactive dividing wall column (R-DWC) could be considered as another option. As the application of a single column is aimed in this study, group I_r is disregarded from our further consideration.

Fig. 4 (a), (c) and (e) depict the RD applicability graphs for groups I_p, III_p and III_r, respectively. In group III_r, the applicability area of the system with $K_{eq} = 0.01$ could not be obtained for both NTS and RR up to 100. For these groups, the applicability area becomes larger when K_{eq} is higher due to a higher conversion which gives the possibilities of having RD configurations with lower capital investments and reduced energy requirements (i.e. lower NTS and RR), which is as expected.

The representations of RD configurations, at various equilibrium constants, is shown in Fig. 4 (b), (d) and (f) for groups I_p, III_p, III_r, respectively. As observed earlier, the increase of K_{eq} leads to a better reaction performance, therefore the NTS and RR decrease for each group. In comparison between different groups, at a fixed K_{eq}, the number of theoretical stages and reflux ratio increase from group I_p, III_p to III_r, respectively. This trend indicates the cost ranking of these three groups – I_p, III_p, III_r – from the lowest to the highest cost, respectively. Having obtained the RD configurations for all groups in Fig. 4 (b), (d) and (f), the column schemes are shown in Fig. 5.
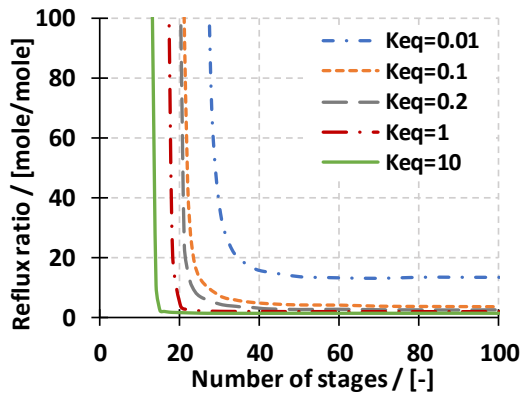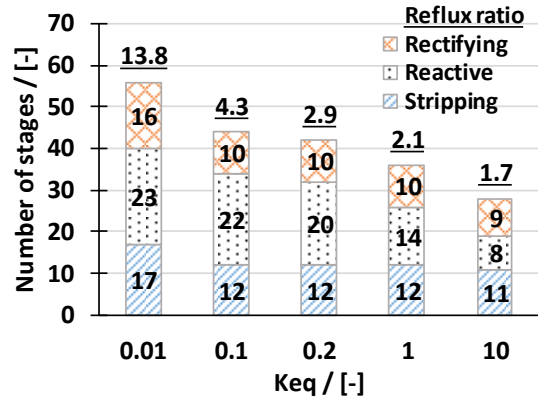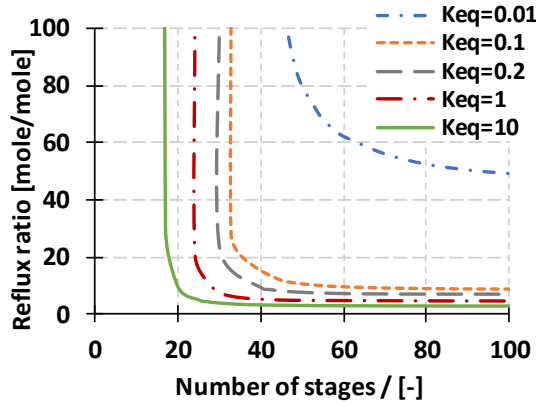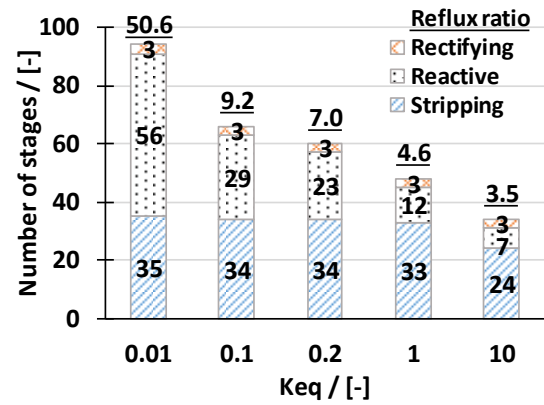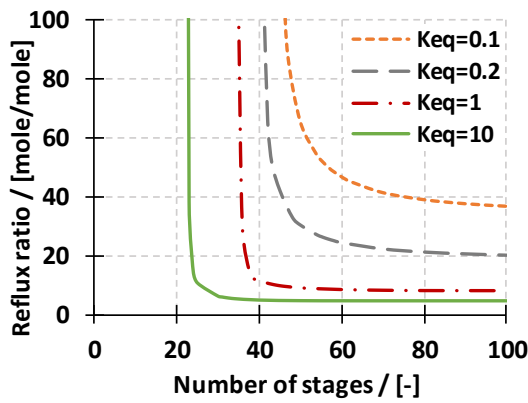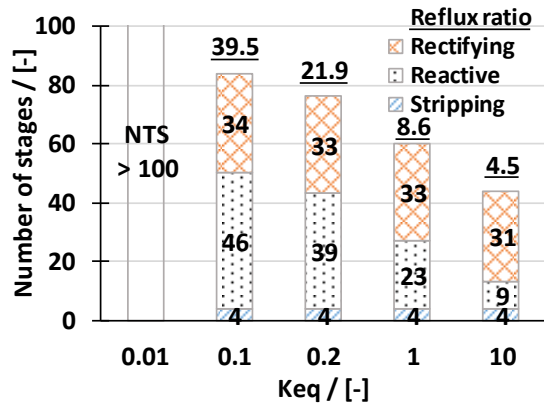
Fig. 4. RD applicability graphs and their configurations at NTS = 2·NTS_min for (a) group I_p, (b) group III_p, (c) group III_r. All the relative volatilities are according to Table 1 (Muthia et al., 2018b).
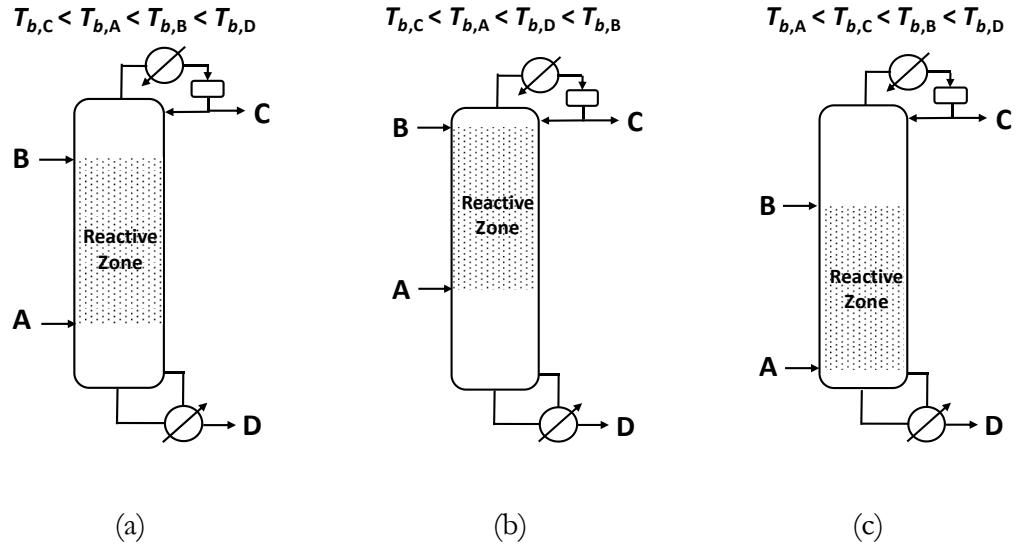
Fig. 5. RD column schemes for (a) group I_p, (b) group III_p, (c) group III_r (Muthia et al., 2018b).

Considering the volatility order of group III_p ($T_{b,C} < T_{b,A} < T_{b,D} < T_{b,B}$), it is very important to fully convert component B before it reaches the stripping section, otherwise its presence becomes a hindrance to a high purity of product D at the bottom stream. Therefore, if group III_p is compared to group I_p, a larger number of reactive stages is required. For any fixed equilibrium constant - see Fig. 4 (b) and (d) - the rectifying section of group III_p is smaller than that of group I_p because of the larger relative volatilities of compounds ($\alpha_{CA} = 4$ and $\alpha_{CB} = 8.4$ in group III_p, $\alpha_{CA} = 2$ and $\alpha_{CB} = 4$ in group I_p) which lead to an easier separation. Besides, the stripping section of the RD column for group III_p is larger than that of group I_p as the separation between reactant A and product D is more challenging ($\alpha_{AD} = 3$ in group I_p and $\alpha_{AD} = 1.5$ in group III_p). Regarding the relative volatility sets listed in Table 1, the configurations of group III_r are expected to be mirror images of the RD columns of group III_p, shown in Fig. 5 (b) and (c). However, it is observed that a higher number of theoretical stages and a larger reflux ratio are required for group III_r at various K_{eq}s, see Fig. 4 (d) and (f). In contrast to group III_p, group III_r needs a larger reactive section to fully convert the reactant A before it reaches the rectifying section. This task is more difficult than that in group III_p because the reactant A is the lightest; therefore, it is easily vaporised and enter the upper level of the column. A higher reflux ratio is required mainly because of more difficult separation in the rectifying section ($\alpha_{CB} = 1.5$ in group III_r, $\alpha_{CA} = 4$ and $\alpha_{CB} = 8.4$ in group III_p).

To gain more understanding about the effect of chemical equilibrium constants on the reaction and separation processes in the different groups, the liquid composition profiles are provided in Fig. 6. A low and a high K_{eq}s (0.1 and 10) are evaluated for each group. For all groups with K_{eq} = 0.1 - see Fig. 6 (a), (c) and (e) - there is always an accumulation of a reactant along the reactive zone because it helps to push the conversion of reaction to the products side. Commonly, reactant A is the accumulated compound because it is more easily vaporised than reactant B and the condensation process at the upper part of the column changes its phase back to liquid. However, in group III$_r$ having abundant reactant A will inhibit the desired RD process as it interferes with the high purity of product C. Therefore, in this group at a low K_{eq}, B is the reactant that is accumulated.

If the systems with an equilibrium constant K_{eq} = 10 are compared to those with K_{eq} = 0.1, the accumulation in the reactive zone of any reactant is then replaced by the product(s) due to a better reaction performance. In group I$_p$ - see Fig. 6 (b) - the accumulation of products C and D in the reactive zone can be observed, with a higher mole fraction of D present. Less accumulated C is detected, because overall the separation of product C from any reactants is easier (α_{CA} = 2, α_{CB} = 4, α_{AD} = 3, α_{BD} = 1.5). In group III$_p$—see Fig. 6 (d)—component D is the accumulated product because its separation from reactant A is more challenging than that of product C considering their relative volatilities (α_{AD} = 1.5, α_{CA} = 4). The opposite difficulty occurs in group III$_r$, see Fig. 6 (f), in which the separation between reactant B and product C is more challenging than the separation between reactant B and product D (α_{CB} = 1.5, α_{BD} = 4); therefore, C is the accumulated product in the column.

3.2. Optimal feed locations for RD units

The optimisation of feed locations has been carried out by taking the RD configurations as given in Fig. 4 (b), (d) and (f) with K_{eq} = 1 as the base cases. For all combinations of feed locations, the numbers of rectifying, reactive and stripping stages remain the same as those in the base cases, which limit the varied design parameters and give clarity to the presented results.
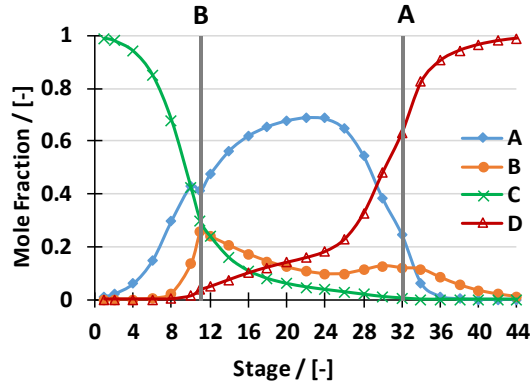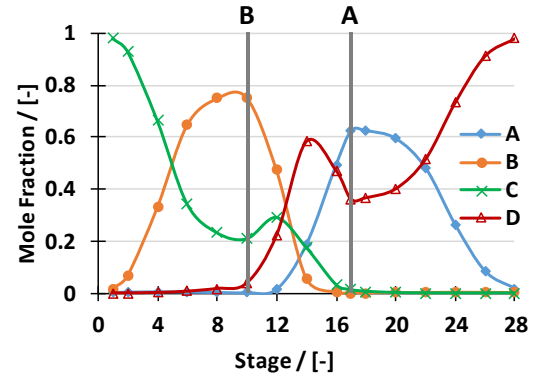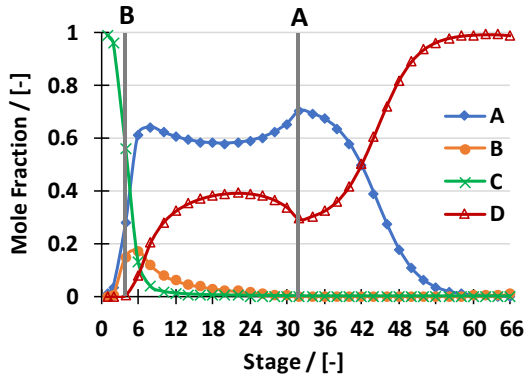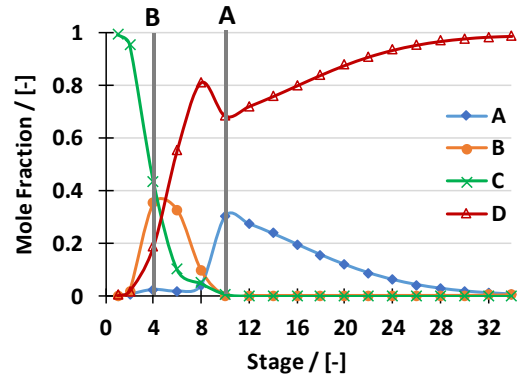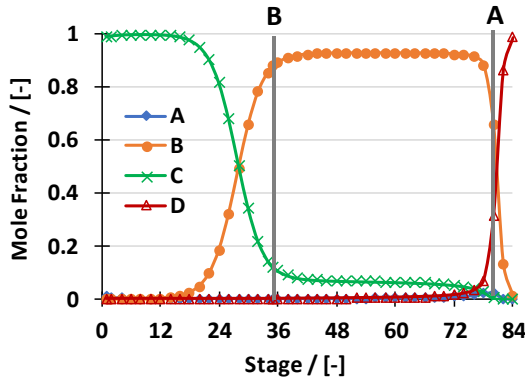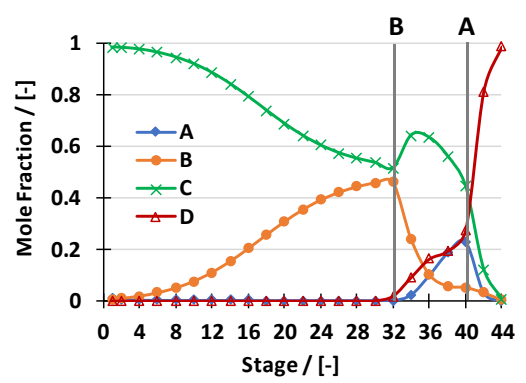
Fig. 6. The composition profiles of RD configurations at NTS = 2·NTS$_{min}$ for group I$_p$ considering (a) K_{eq} = 0.1 and (b) K_{eq} = 10, group III$_p$ considering (c) K_{eq} = 0.1 and (d) K_{eq} = 10, group III$_r$ considering (e) K_{eq} = 0.1 and (f) K_{eq} = 10. All relative volatilities are according to Table 1.

Fig. 7 (a), (b) and (c) show reflux ratios as a contour plot for varied feed locations of both reactants A and B for groups I_p, III_p and III_r, respectively, at $K_{eq} = 1$. Cross and square marks in each plot indicate the base case and a RD configuration with the most optimal feed locations (i.e. with the lowest reflux ratio reducing energy requirements), respectively. Moving from the crosses to the squares, the reflux ratios of the base cases decrease from 2.1 to 1.7 for group I_p (19% reduction), from 4.6 to 2.9 for group III_p (37% reduction), and from 8.6 to 6.6 for group III_r (23% reduction), by adjusting the feed locations.

To clearly distinguish the RR changes, each plot in Fig. 7 is partitioned based on certain RD ranges and marked with distributed colours. The optimal region (the darkest zone) in each plot is achieved by RD configurations with reflux ratios up to 3% higher than the lowest RR. For all groups, it is always beneficial to have a shorter distance between the two feed stages; therefore, an immediate contact between two reactants occur before separation takes place. Besides, it is essential to set the feed stage of reactant B (as the higher boiling reactant) above that of reactant A in order to enhance the direct contact of both reactants in the liquid phase, therefore enhancing the reaction performance. Placing the feed inlets on a reverse order causes a significant increase in reflux ratios. For instance, in group I_p, the feed stages of reactants A and B at 24 and 11 require RR = 2.1, while the reverse order gives RR = 8.1. In group III_p, RR = 3.8 is needed when the feed inlets of reactants A and B are at stages 12 and 4, while the reverse order requires RR = 10.9. In group III_r, RR = 6.9 is needed when the feed inlets of reactants A and B are at stages 56 and 44, while the reverse order requires RR = 44.3.

Moving from the crosses to the squares in Fig. 7, the optimisation pattern for different groups are identified. In group I_p, the RD process is optimised by positioning the two feed stages close to the centre part of the reactive zone. In group III_p, bringing the inlet of reactant A up within the reactive zone reduces the energy requirements (lower RR). On the contrary, lowering the feed stage of reactant B closer to the bottom section of reactive stages decreases the energy requirements (lower RR) in group III_r. For a better insight, the representations of RD configurations with lowest reflux ratios inside the darkest zone in Fig. 8 (b), (d) and (f) are coupled with the corresponding column configurations of the base cases, as shown in Fig. 8 (a), (c) and (e).
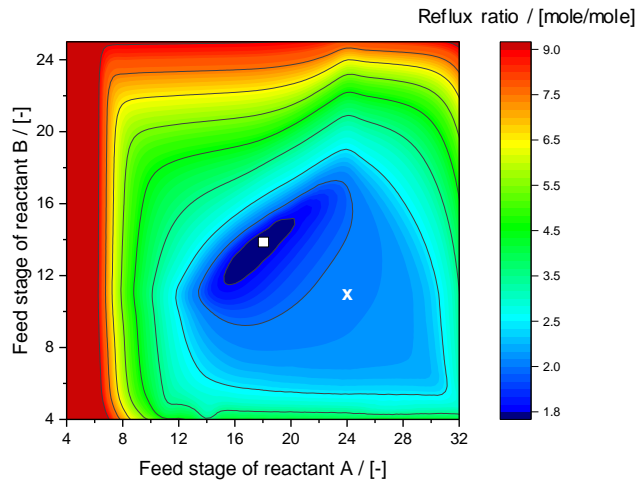
(a)
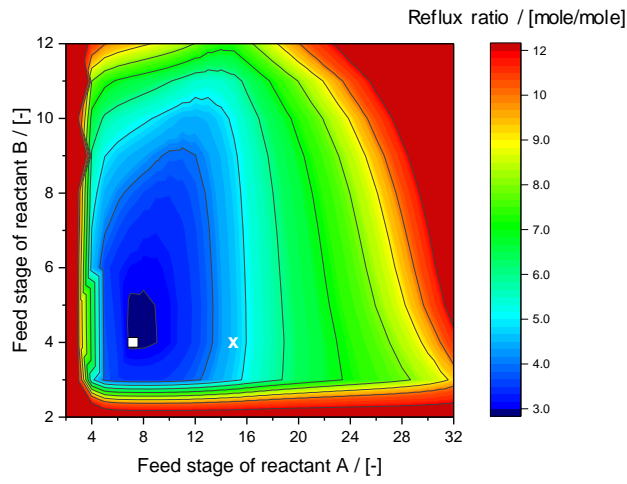
(b)
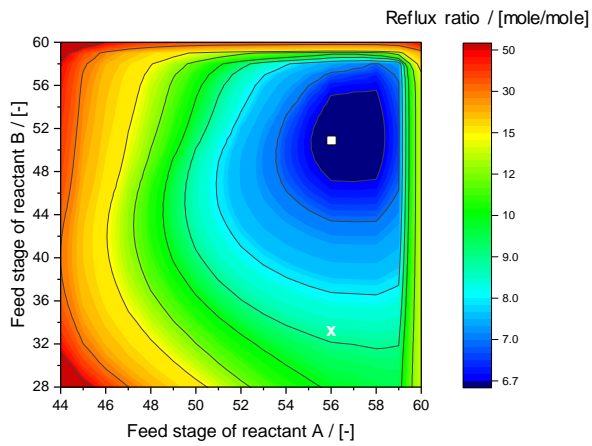
(c)

Fig. 7. Varied feed locations of both reactants A and B and their corresponding RRs at $K_{eq} = 1$ for (a) group I_p, (b) group III_p and (c) group III_r. Cross and square indicate the base cases and the RD configurations with the most optimal feed locations, respectively.
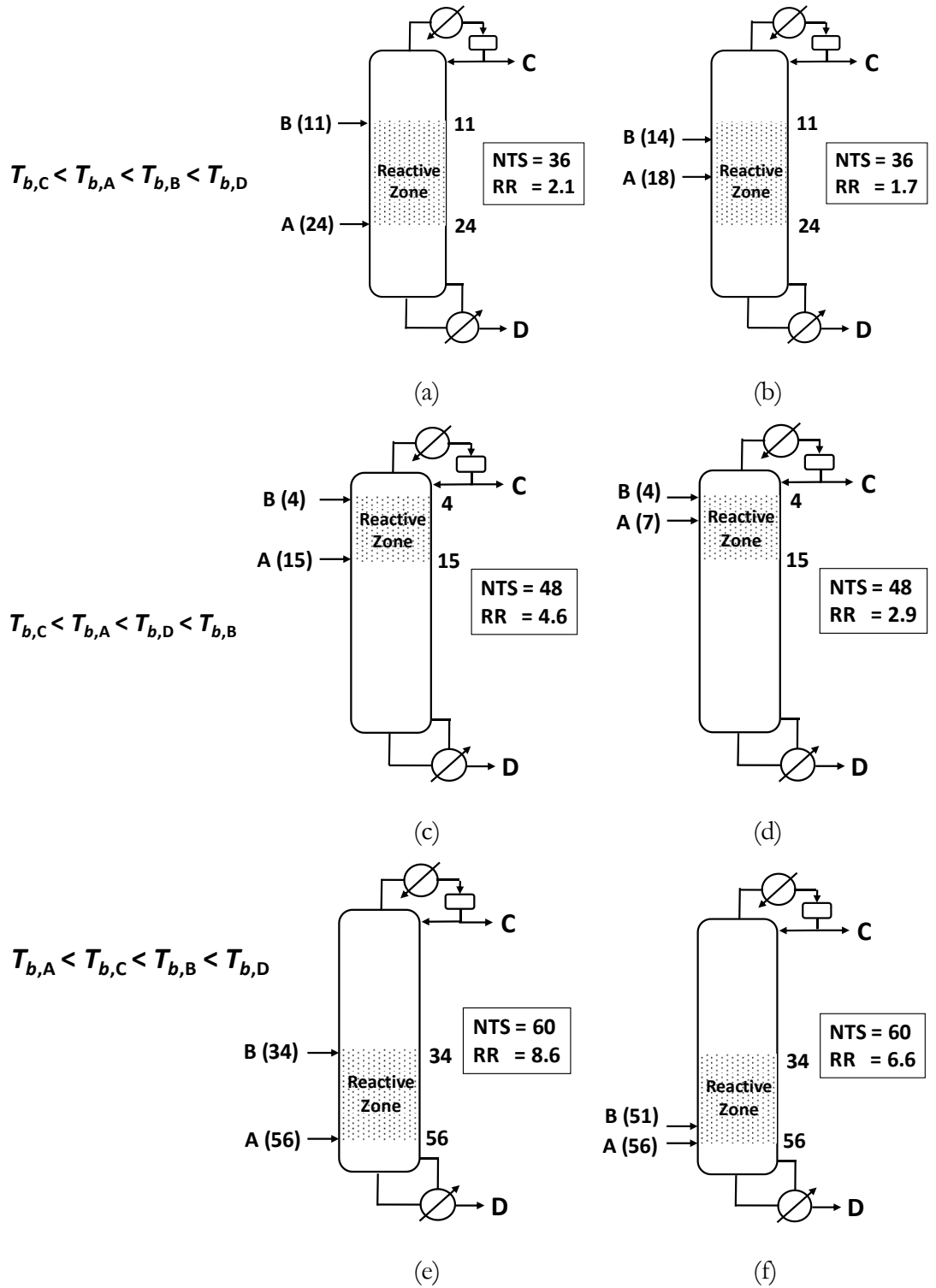
Fig. 8. RD column schemes in case of fixed feed inlets at the top and the bottom parts of reactive zone for (a) group I_p, (c) group III_p, (e) group III_r and in case of varied feed inlets to obtain the lowest RR possible for (b) group I_p, (d) group III_p, (f) group III_r. The presented numbers next to the column show the RD stages. All RD column configurations are at NTS = 2·NTS$_{min}$ in the applicability graph considering $K_{eq} = 1$.

Further investigation is performed by observing the liquid composition profiles of different groups, as given in Fig. 9. In comparison to the base case of group I_p, see Fig. 9 (a) and (b), the immediate contact of reactants for the optimised feed stages has reduced their accumulation along the RD column. As a consequence, there are less unreacted compounds found in the rectifying and stripping sections which result in less difficulty in the separation. In group III_p—see Fig. 9 (c) and (d)—the improved reaction condition in the reactive zone with modified feed locations significantly helps to eliminate reactant B (i.e. the heaviest compound in this group). The average concentration of A in the reaction zone has increased with at the same time a lower concentration of A at the bottom part of the reactive zone compare Fig. 9 (c) and (d)—which reduces the concentration of B even further and improves the separation performance (lower reflux ratio) for A/D. In the base case of group III_r, the accumulation of reactant B—see Fig. 9 (e)—is needed to enhance the reaction performance and to prevent reactant A from reaching the upper part of the column. In the improved RD process, the distribution of accumulated reactant B in the reactive zone has been optimised which is implied by the shift of the peak of its mole fraction and the increase in the average concentration of B in the reactive zone, as shown in Fig. 9 (f). This shift reduces the amount of B going up the rectifying section; therefore, the separation of product C is easier.

Although a closer distance between the two feed stages is preferred in each group, introducing reactants A and B at the same stage potentially increases the energy requirements (higher RR) because reactant A is partially vaporised at the same time when reactant B moves down to the lower level of the column prior to reaching the reaction conditions. This observation indicates the competition between reaction and separation on a reactive stage.

(a)

(b)

(c)

(d)

(e)

(f)
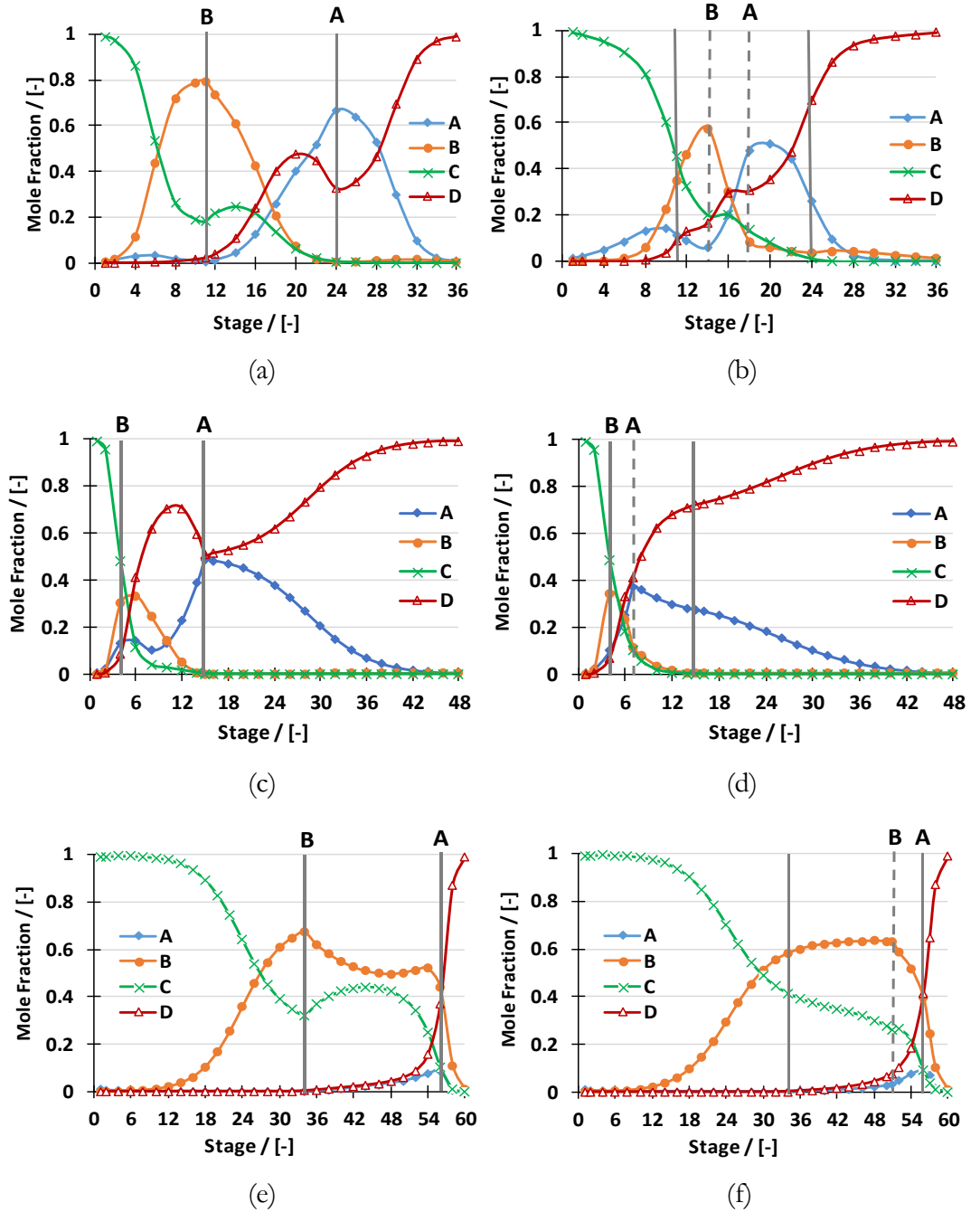
Fig. 9. The composition profiles of RD column configurations in case of fixed feed inlets at the top and the bottom parts of reactive zone for (a) group I_p, (c) group III_p, (e) group III_r and in case of varied feed inlets to obtain the lowest RR possible for (b) group I_p, (d) group III_p, (f) group III_r. The vertical solid lines always show the top and the bottom parts of the reactive zone, and also the feed inlets in (a), (c), (e). The vertical dash lines in (b), (d), (f) present the feed inlets. All RD column configurations are at NTS = 2·NTS$_{min}$ in the applicability graph considering $K_{eq} = 1$, and relative volatilities according to Table 1.

For the validation of our findings, we refer to a RD configuration with the optimal feed locations for the methyl acetate production, as provided by Tang et al. (2005) by performing rigorous simulations and detailed economic calculations. The synthesis of methyl acetate via esterification is given in Eq. (1), and, based on its boiling points ranking, this reaction is classified into group III_p ($T_{b,C} < T_{b,A} < T_{b,D} < T_{b,B}$):

$$\text{Methanol (}\mathbf{A}\text{)} + \text{Acetic acid (}\mathbf{B}\text{)} \rightleftharpoons \text{Methyl acetate (}\mathbf{C}\text{)} + \text{Water (}\mathbf{D}\text{)} \qquad (1)$$

T_b 64.7 °C   118.0 °C   56.9 °C   100.0 °C

ΔH_r = -15.85 kJ/mole.
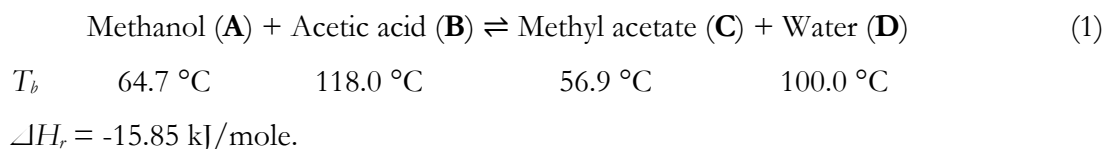
The optimal RD configuration reported by Tang et al. (2005) consists of 1 rectifying, 34 reactive and 4 stripping stages, including reboiler. The feed locations of acetic acid (the heavier reactant) and methanol (the lighter reactant) are at stage 3 and 26, respectively, counted from the top down, which matches the predicted region of the optimal feed locations of group III_p as suggested by this work, see Fig. 7 (b) and Fig. 8 (c), (d). This example confirms the promising application of the mapping method. Besides the methyl acetate production, Tang et al. (2005) assessed the optimal RD designs for other acetic acid esterification reactions producing ethyl acetate, isopropyl acetate, n-butyl acetate and amyl acetate. Due to the higher level of complexity in those systems (i.e. the presence of ternary and heterogeneous azeotropes), it was reported that the operation of a single RD column is not feasible and therefore RD columns with decanter and/or additional stripper are required. For these different RD setups, the approach provided by this work is not applicable.

4. Conclusions

This work successfully demonstrates the use of the mapping method for obtaining insightful knowledge of RD processes by using generic cases. Two essential aspects in conceptual design (i.e. economic ranking of configurations and process optimisation) can be investigated at an early stage, instead of being assessed at the final stage of conventional studies.

The boiling point rankings of components have significant effects on RD configurations. In the case of comparable chemical equilibrium constants and relative volatilities, the

preliminary cost ranking of quaternary systems for the application of a single RD column is: group I_p < III_p < III_r (from the lowest to the highest cost). A single RD column setup cannot be applied to group I_r considering the challenging separation of both mid-boiling products from the lightest and the heaviest boiling reactants. The presented approach can be used to assess other equilibrium constants and relative volatility sets, significantly improving the understanding of RD processes for different cases.

The mapping method is also useful to determine the regions where the optimal feed locations are obtained. In group I_p, it is more beneficial to position both feed inlets closer to the centre of the reactive zone. In group III_p, lower energy usage (reflux ratios) can be obtained by putting the inlet of reactant A within the reactive zone, while the inlet of reactant B is kept at the top of the reactive zone. In contrast, for group III_r, it is more beneficial to feed reactant B within the reactive zone, while keeping the inlet of reactant A at the bottom of the reactive zone. For all groups, a shorter distance between two feed inlets gives benefits, with the inlet of the heavier reactant always above the inlet of the lighter reactant. However, feeding both reactants at the same stage is detrimental for energy usage since the competition between reaction and separation phenomena hinders the RD performance.

Acknowledgement

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Chapter 5

Development of a Mapping Method for Non-Ideal Quaternary Reaction Systems with Different Boiling Point Orders of Compounds

List of publications:

- **Publication 4**

  Muthia, R., Jobson, M. and Kiss, A. A. (2020). 'A systematic framework for assessing the applicability of reactive distillation for quaternary mixtures using a mapping method', *Computers & Chemical Engineering*, 136, 106804.

- **Publication 5**

  Muthia, R., Jobson, M. and Kiss, A. A. (2020). 'Determining the design parameters of reactive distillation processes by a quick mapping method', accepted for publication in *Computer Aided Chemical Engineering*.

5.1. Preface of Publications 4 and 5

This chapter aims to fully address the main research question of this thesis: how can one perform the assessment of the applicability of reactive distillation (RD) with less computational effort? Aiming to answer this question, the work in Chapters 3 and 4 has developed the mapping method to some extent, which shows that the mapping method is suitable for near-ideal quaternary reaction systems and it is capable of generating multiple solutions of column configurations and providing heuristics for designing reactive distillation columns. This chapter aims to demonstrate that the mapping method is suitable for industrially relevant non-ideal reaction systems and can provide process engineers with (semi)quantitative information about the applicability of reactive distillation.

The work in Publications 4 and 5 extends the scope of the mapping method for non-ideal quaternary reaction systems considering different boiling point orders of compounds. Herein, non-ideal is defined as a condition where homogeneous and/or heterogeneous azeotropes exist in a reaction system and potentially hinders the separation of components within a reactive distillation column. The objectives of this thesis addressed in Publications 4 and 5 are:

1. to synthesise a systematic framework based on the use of the mapping method for assessing the applicability of reactive distillation,
2. to generate heuristics for the initialisation of reactive distillation designs,
3. to assess the applicability of reactive distillation by using pre-calculated performance information for hypothetical and generic cases, i.e. generic applicability graphs, and
4. to validate the proposed method by performing rigorous simulations for case studies representing real reaction systems.

A new systematic framework in Publication 4 offers an aid for process engineers to make a go-/no-go decision regarding the application of reactive distillation before performing any rigorous simulations of RD processes. To synthesise the framework, this work includes heuristics and knowledge, which are obtained from the development of the mapping in Chapters 3–5 of this thesis.

The proposed method is validated by using five case studies representing different separation challenges due to azeotropic mixtures. Those case studies are selected to involve three groups of boiling point orders of compounds in quaternary systems, which are shown in Chapter 4 to offer the most promising applications of reactive distillation technology. The validation step using case studies aims to demonstrate the advantages proposed by the method, along with its limitation. The suitability of the method is mainly assessed by comparing the predicted applicability graphs based on pre-generated generic applicability graphs and the actual applicability graphs generated from rigorous simulations of case studies. Next to that qualitative assessment, the work in Publication 4 provides a quantitative comparison by calculating the deviation between the predicted and the actual reflux ratios and numbers of theoretical stages.

The work in Publication 5 develops of a rule of thumb to quickly determine the design parameters of reactive distillation processes, namely liquid residence time, catalyst selection and catalyst loading. The development of such rule of thumb narrows the range of possible RD design parameters, thus, saving time when assessing the applicability of reactive distillation at the conceptual design level. The new rule of thumb is included in the novel framework proposed in Publication 4 as it supports process engineers to make a go/no-go decision for the RD operation. Chemical equilibrium constants and the Damköhler numbers are taken into consideration as two parameters for indicating the RD performance. This study aims to show the correlation of the performance of reactive distillation in both equilibrium-limited and kinetically controlled reactions by assessing their applicability graphs.

5.2. Publication 4

This section is based on the following publication:

Muthia, R., Jobson, M. and Kiss, A. A. (2020). 'A systematic framework for assessing the applicability of reactive distillation for quaternary mixtures using a mapping method', *Computers & Chemical Engineering*, 136, 106804.

The US English spelling in the original publication has been changed here to the UK English spelling to fulfil the requirements of the PhD theses policy regulated by the University of Manchester.

A systematic framework for assessing the applicability of reactive distillation for quaternary mixtures using a mapping method

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Abstract

Reactive distillation (RD) is a useful process intensification technique used in the chemical process industries as it offers important advantages such as energy and cost savings, relative to conventional technologies. However, industrial application of RD is still limited by the complexity of designing and understanding such a complex process. While simple, robust shortcut design methods that require only basic information (such as the relative volatility of components) exist for conventional distillation, such methods for evaluating the applicability of RD are not yet established. This work fills this gap by presenting a new systematic framework for assessing the RD applicability based on a mapping method. The method enables RD designs to be screened using only relative volatilities and chemical equilibrium constant as input data. The evaluation focuses on reactions involving four components (A + B $\rightleftharpoons$ C + D) with various boiling point orders, which are of most industrial importance. The proposed systematic framework is validated through its application to five case studies, (trans-)esterification presenting various separation challenges due to the formation of azeotropes. This novel approach offers a valuable aid for engineers in taking an educated go/no-go decision in the very initial stages of conceptual design, before performing any rigorous simulations of RD flowsheets.

1. Introduction

Process intensification—comprising the development of apparatus and techniques in the chemical industries—is crucial for delivering cheaper, smaller, more energy-efficient, safer and sustainable technologies (Stankiewicz and Moulijn, 2000). It also paves the way to fulfil the chemical industry demands, especially in the context of globalisation and sustainability (Charpentier, 2007). Among the available process intensification units, reactive distillation (RD), which integrates reaction and separation in a single column, as illustrated in Fig. 1, has demonstrated significant contribution to process efficiency (Kiss et al., 2019).
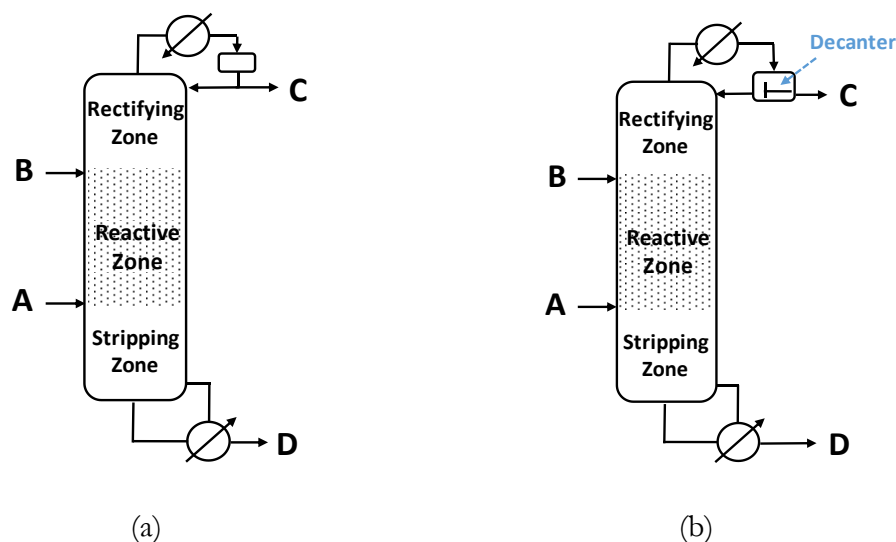
Fig. 1. Schematic representation of (a) a single reactive distillation column and (b) a heterogeneous reactive distillation column.

The benefits of reactive distillation, compared to conventional technologies involving a sequence of reaction and separation units, include: 1) increased conversion and selectivity, 2) lower capital investment due to the reduced number of the process units, 3) significant energy savings, by utilising the heat of exothermic reactions for vaporisation, and 4) reduced health, safety and environmental risks because of lower emissions, avoidance of reactor hot spots and reduces risk of runaway reactions (Harmsen, 2007; Kiss, 2016, 2017; Shah et al., 2012; Tuchlenski et al., 2001).

Over the past decade, over 1,000 research manuscripts explored the development of reactive distillation (Kiss, 2019; Wierschem and Górak, 2018), considering modelling of RD for specific systems (Khan and Adewuyi, 2019), process optimisation and control (Sharma and Singh, 2010; Sneesby et al., 1997), pilot-scale experiments (Keller et al., 2012), the selection of catalysts and operating parameters for desired reactions (Chiu et al., 2006; Kiss et al., 2008) and column internals (Götze et al., 2001; Subawalla et al., 1997).

Nevertheless, commercial application of reactive distillation remains challenging due to the complexities in the synthesis, design, and operation of RD columns (Chen et al., 2000; Li et al., 2012; Li et al., 2016). Multiple interactions between vapour-liquid equilibrium, mass transfer, intra-catalyst diffusion in heterogeneous-catalysed processes and chemical kinetics inhibit the rapid assessment of reactive distillation designs (Taylor and Krishna, 2000).

Various methods for designing RD systems have emerged since the late 1980s; these can be classified as graphical, optimisation and heuristic approaches (Almeida-Rivera et al., 2004; Barbosa and Doherty, 1988a; Barbosa and Doherty, 1988b; Kiss, 2016, 2017). For example, Lee et al. (2000) developed a graphical approach, based on the modified Ponchon-Savarit and McCabe-Thiele methods, to assess the location of reactive zones in reactive distillation for binary reactions. Urselmann et al. (2011) introduced a memetic algorithm to optimise the design of reactive distillation for the production of methyl *tert*-butyl ether, concerning the total annual cost. Subawalla and Fair (1999) suggested guidelines, based on a generic standpoint and heuristic approaches, for determining the design parameters of reactive distillation in solid-catalysed systems. Other design methods are reported in the open literature (including Amte et al., 2013; Damartzis and Seferlis, 2010; Giessler et al., 1998; Jantharasuk et al., 2011; Kiss, 2016, 2017; Thery et al., 2005; Ung and Doherty, 1995). However, the results of rigorous calculations and simulations in those methods are usually only applied to a certain reaction system; repetitive calculations are required to evaluate reactive distillation for other chemical systems. Therefore, designing a reactive distillation process can be time-consuming and complex (Segovia-Hernández et al., 2015).

In conventional distillation processes, shortcut models are used to initialise column designs. Models, such as the Fenske-Underwood-Gilliland method, determine the minimum number of theoretical stages, minimum reflux ratio and number of theoretical

stages required for a given reflux ratio. The models employ relative volatility of compounds (α) to characterise the separation performance in the column. The relative volatility can be quantified from the feed composition. Alternatively, it can be taken as an average value at the top and bottom streams based on their compositions. Non-ideal vapour-liquid equilibrium behaviour in the system reduces the accuracy of the shortcut models' predictions; greater errors are generally observed in more non-ideal systems (Smith, 2016). However, the shortcut models are robust and can be solved quickly (Towler and Sinnott, 2012), and hence, are a good basis for generating initial column designs and for initialising rigorous models. To the best of our knowledge, unlike for conventional distillation, methods that use some key parameters to evaluate reactive distillation designs are not well established. Rigorous simulations and calculations are usually needed to investigate the applicability of reactive distillation to each reaction system.

The present work proposes a new systematic framework for assessing the applicability of reactive distillation to azeotropic (non-ideal) quaternary reaction systems, $A + B \rightleftharpoons C + D$, with various rankings of boiling points, only based on hypothetical and ideal cases using few key parameters, namely relative volatilities of compounds, chemical equilibrium constants and Damköhler number. The approach is called the mapping method, and it was introduced by our prior study (Muthia et al., 2018a), but the scope of that study was limited to ideal quaternary reaction systems for only a subset of boiling point orders, $T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$.

The mapping method features a plot of reflux ratio vs the number of theoretical stages to define an 'applicable region', in which reactive distillation could potentially be employed for a certain chemical system. The applicability of reactive distillation is assessed using pre-prepared applicability graphs of 'generic' cases, corresponding to hypothetical components and ideal reaction systems. To assess a 'real' system, the user needs basic information, i.e. characteristic values of relative volatilities and the chemical equilibrium constant of the real system of interest.

Previous studies, such as Barbosa and Doherty (1988a, 1988b) have developed a set of transformed composition variables to calculate the minimum reflux ratios for single- and double-feeds reactive distillation columns. Giessler et al. (1998) proposed a method called static analysis that enables the calculation of the number of theoretical stages based on

thermodynamic-topological analysis of distillation diagrams. However, those methods only provide reflux ratio and the number of theoretical stages for a single configuration. This novel work provides a systematic approach to generate applicability graphs of reactive distillation (for any system of interest), which contain all possible RD configurations with various number of theoretical stages and reflux ratios. Note that only one applicability graph is generated for each chemical system and that graph can be used multiple times by end-users (engineers) to design different RD configurations.

The present work demonstrates the new framework by applying it to five case studies exhibiting different separation challenges arising due to the presence of azeotropes. These case studies serve to validate the proposed framework, in terms of its ability to estimate the applicable region for RD in a given quaternary system with non-ideal behaviour.

2. Mapping method overview

This work presents a systematic framework that applies our novel mapping method, for screening and initialisation of reactive distillation column designs. The mapping method (Muthia et al., 2018a, 2019a) has been introduced and demonstrated in near-ideal quaternary systems with the reaction $A + B \rightleftharpoons C + D$. Initially the approach was demonstrated for systems with boiling point order $T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$ (Muthia et al., 2018a), where the two products are the lightest (C) and heaviest (D) components in the system and so are readily separated from each other. A subsequent study demonstrated the approach for systems with other boiling point orders (Muthia et al., 2019b) and provided some insights into the optimal feed locations of reactive distillation columns.

The main feature of the mapping method is the applicability graph of reactive distillation designs, which is a plot of reflux ratio vs the number of theoretical stages, as illustrated in Fig. 2(a). A boundary line in an applicability graph identifies the lowest reflux ratios possible for various numbers of theoretical stages. The 'applicable area' represents multiple column configurations each with a certain number of rectifying, reactive and stripping stages, where some very dissimilar configurations may have very similar reflux ratios for an identical number of theoretical stages. For example, see Fig. S1 and Table S1 in the Supporting Information.
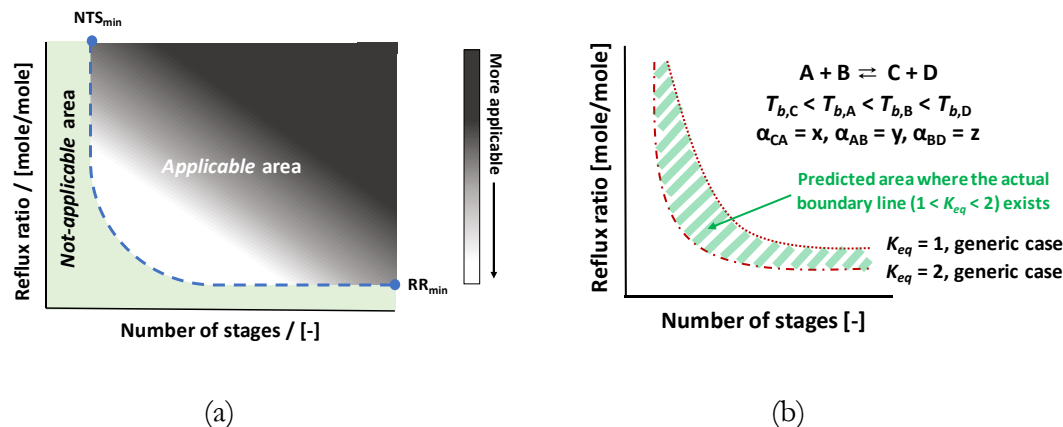
Fig. 2. (a) An illustrative applicability graph of reactive distillation and (b) an illustrative prediction of the applicability of reactive distillation to a reaction system, based on generic cases—the actual boundary line is predicted to be within the shaded area.

As demonstrated for near-ideal quaternary systems (Muthia et al., 2018a), the method is capable of predicting the applicability area for reactive distillation of real systems based only on pre-prepared applicability graphs of generic cases. In these idealised, hypothetical generic cases, the relative volatilities and chemical equilibrium constants are fixed and independent of process temperatures. This work aims to demonstrate that real (non-ideal) systems can also be addressed by the method, in particular for cases involving the presence of azeotropes, as these systems are industrially important.

Fig. 2(b) illustrates application of the method: the user must select the most relevant generic cases, i.e. where the representative relative volatilities and chemical equilibrium constant are similar to those of the real system being assessed. The shaded area in Fig. 2(b) represents the location in which the actual boundary line is expected to lie. Thus, the user can read from the plot approximate values of the reflux ratio and numbers of stages required in the reactive distillation column. Note that the mapping method predicts the number of theoretical stages and reflux ratio, but not the column configuration. The multiple possible configurations represent an opportunity for reactive distillation column design.

Fig. 3 summarises the methodology developed in this work, which has three directions for: (1) the generation of applicability maps, (2) the validation of the maps using case studies, and (3) the actual use of the generic maps by end-users to determine the applicability of reactive distillation for new cases. For the purpose of the validation of the

proposed method, in this study, the generation of generic applicability graphs is only performed for relevant generic cases with the representative relative volatilities and chemical equilibrium constants that are similar to those of case studies.
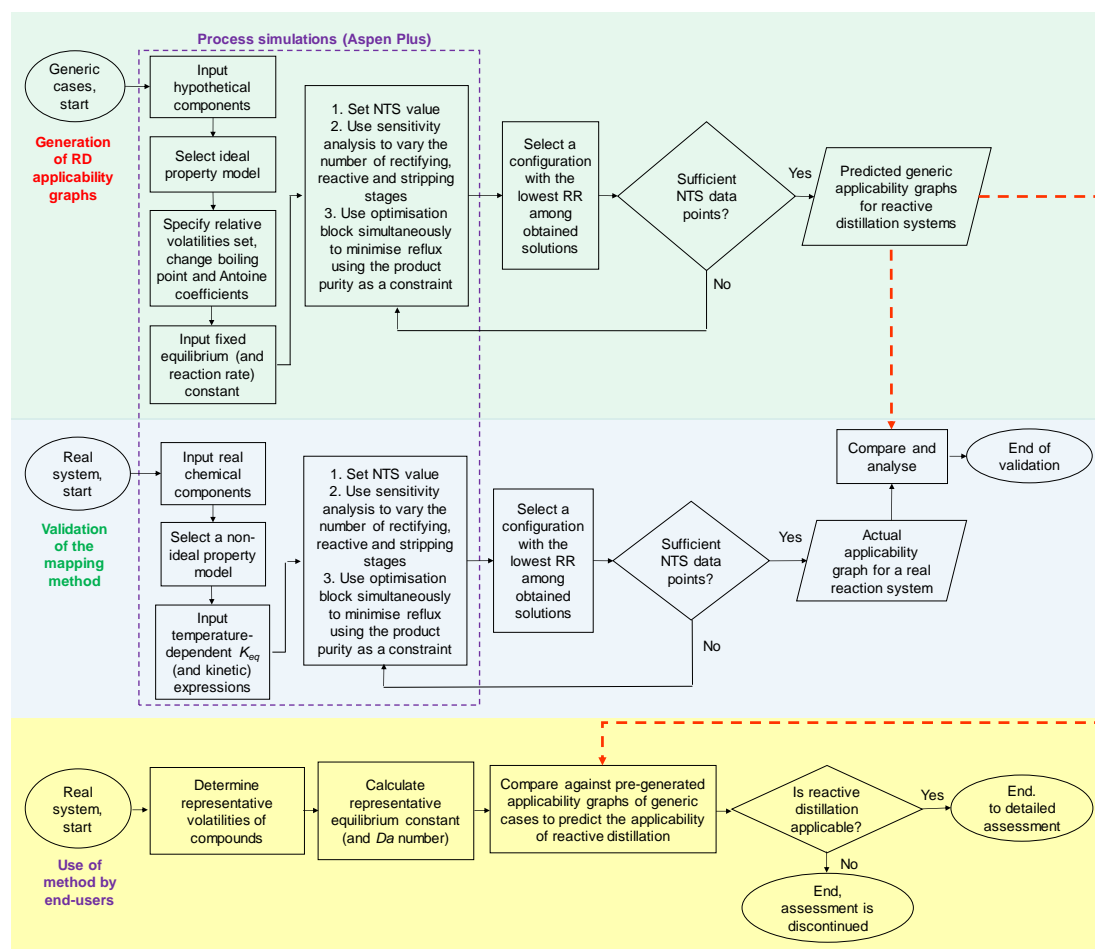
Fig. 3. Methodology developed for the generation of the applicability graphs of reactive distillation, the validation of the mapping method and the use of the method by end-users.

The generation of generic applicability graphs and the validation of the mapping method in this study require extensive simulations for both generic cases and case studies, in which reactive distillation configurations are generated in Aspen Plus process simulation software using the RadFrac model. In the simulations for the generation of generic maps, hypothetical chemical components A, B, C and D are defined, the ideal property model

is selected, and the boiling points and the Antoine coefficients of defined hypothetical components are changed for the specified relative volatilities set. Next, fixed equilibrium (and reaction rate) constants are input to the simulation software. An equimolar feed of the reactants (A and B) is fed to a reactive distillation column in which each separation stage is assumed to reach phase equilibrium and each reactive stage is assumed to reach both reaction and phase equilibria. The purity of the product streams is specified (99 mole%), i.e. the overall material balance is fixed. The mixture is modelled as an ideal mixture, but the column is modelled rigorously—material and energy balances are carried out on each stage, informed by equilibrium calculations.

Note that the simulations are all carried out for a 'simple' reactive distillation, with a structure such as that shown in Fig. 1(a). The column operates at atmospheric pressure with fixed feed inlets at the top and the bottom stages of the reactive section. To obtain multiple configurations, the numbers of rectifying, reactive and stripping stages are varied for each number of theoretical stages by using the sensitivity analysis block. For each configuration, the optimisation tool in Aspen Plus is simultaneously employed to minimise the reflux ratio under the constraint of product purity ≥ 99 mole%. Among all possible configurations, the lowest reflux ratio is manually selected for each number of theoretical stages. The lowest energy for all numbers of theoretical stages forms a boundary line of an applicability area.

To validate the method, in this study, the predictions of the applicability graph are compared with the results of rigorous simulations for the case studies. These simulations, carried out in Aspen Plus, take into account real chemical components, the phase equilibrium behaviour (i.e. constant relative volatility is not assumed) and reaction behaviour (e.g. reaction kinetics or dependence of equilibrium conversion with temperature and composition are accounted for).

Similar to that conducted for the generic case, sensitivity and optimisation blocks are employed for the case study, in which various column configurations—with various numbers of rectifying, stripping and reactive stages—are modelled for different numbers of theoretical stages. Once again, the feed is assumed to be an equimolar mixture of the reactants (A and B) and the purity of the products is fixed at 99 mole%. Depending on the properties of the mixture, various configurations may be explored. For example, feed stages at other locations than the top and bottom of the reactive zone may be selected

and a liquid-liquid phase separator may be included, as shown in Fig. 1(b), if it is anticipated that the overhead product is a low-boiling heterogeneous azeotrope. These validation simulations aim to identify the minimum reflux ratio required to achieve the desired material balance for a given total number of stages. The result is then compared to the boundary of the applicability region for a generic system with similar characteristic parameters (relative volatilities and reaction equilibrium constant). If the required reflux ratio for a given number of stages is similar (e.g. within 50%) for the two cases, then it is argued that the applicability map is valid—i.e. that it is sufficiently useful for process screening to allow informed go/no-go decision-making.

Prior to the use of the mapping method by end-users, a team of researchers or engineers, who act as map generators, produce a bundle of many generic applicability maps with different sets of fixed relative volatilities, chemical equilibrium constants and reaction rates. Once those graphs have been created through multiple simulations in Aspen Plus, further rigorous simulations are not needed to allow the graph to be used for process screening. Note that an applicability graph of a generic case prepared once by map generators can be used afterwards multiple times by process engineers to assess the applicability of reactive distillation and design different column configurations.

End-users employ the mapping method in a similar way to a global positioning system (GPS), where determined representative relative volatilities of compounds and calculated equilibrium constant (and the Damköhler number for a kinetically controlled reaction) are overlaid onto generic applicability graphs that are pre-generated by map generators. The graphs may then be used to quantify the reflux ratio – number of stages relationship for a real system, without requiring any detailed simulation of the real system or associated reactive distillation column. In principle, the fixed parameters of the generic system should be similar to those of the real system, to get the most useful predictions.

3. Results and discussion

This section focuses on formulating and testing the systematic framework, by outlining the new systematic framework developed for assessing the applicability of reactive distillation columns and exploring the effectiveness of the framework for five case studies.

3.1. A systematic framework for assessing the applicability of reactive distillation

Fig. 4 summarises the workflow of the framework, showing the sequence of steps followed to obtain multiple reactive distillation configurations and to conduct a preliminary economic evaluation of a proposed reactive distillation application. The users of the systematic framework are expected to be process engineers in the chemical industries involved in the very early stages of conceptual process design, and who wish to explore the potential benefits of reactive distillation, while minimising the engineering time required to assess options and identify potentially attractive design solutions. That is, the framework aims to help engineers support decision making, while avoiding time-consuming rigorous process simulations.

The framework is designed to consider equimolar quaternary reactions (A + B $\rightleftharpoons$ C + D) —industrial applications have already shown reactive distillation to be an attractive technology for systems of this nature (Hiwale et al., 2004; Sharma and Mahajani, 2003). At the beginning of the applicability assessment, it is crucial to identify the boiling points of the four species and to classify the quaternary mixture according to their ranking, using an established convention (Luyben and Yu, 2008). Prior studies have shown a significant impact of boiling point order on the performance of reactive distillation (Chen and Yu, 2008; Luyben and Yu, 2008). In those studies, they conducted rigorous simulations and performed detailed economic calculation concerning only a fixed chemical equilibrium constant.

Our previous work considered a range of chemical equilibrium constants and employed a simpler approach, based on the mapping method, taking the number of theoretical stages and reflux ratio as important performance indicators for the capital investment and the energy requirement (Muthia et al., 2019b). These studies found that, in general, the likelihood of a quaternary system (A + B $\rightleftharpoons$ C + D) being well suited to RD increases in the following order:

- Group I_r ($T_{b,A} < T_{b,C} < T_{b,D} < T_{b,B}$)
- Group III_r ($T_{b,A} < T_{b,C} < T_{b,B} < T_{b,D}$)
- Group III_p ($T_{b,C} < T_{b,A} < T_{b,D} < T_{b,B}$)
- Group I_p ($T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$).

In the most suitable class of mixtures (I$_p$), the boiling point order facilitates separation of the products C and D because they have the most extreme boiling points in the mixture.
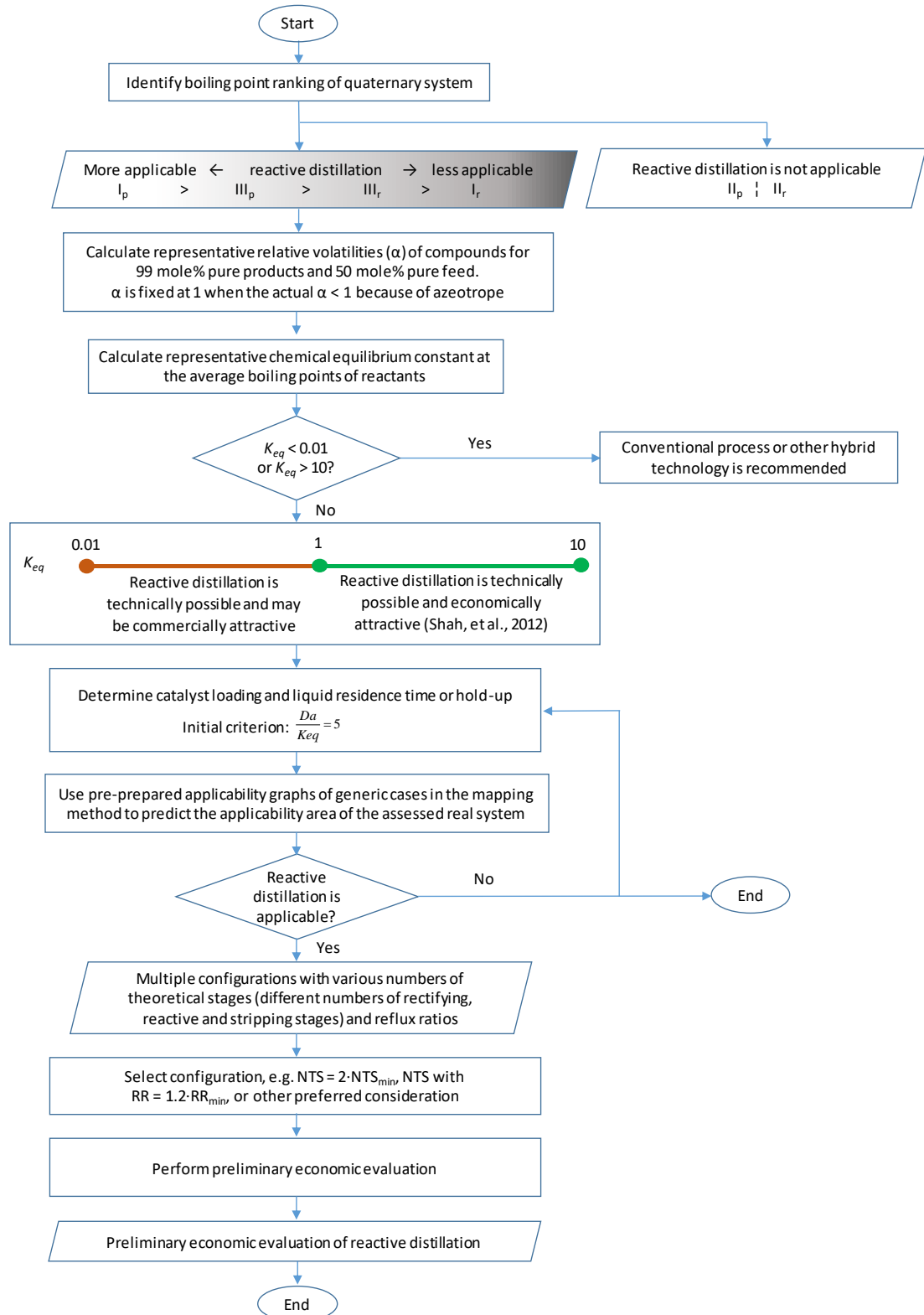
Fig. 6. Systematic framework for assessing the applicability of reactive distillation.

Note that reactive distillation technology is not possible for equimolar reactions in groups II_p ($T_{b,C} < T_{b,D} < T_{b,A} < T_{b,B}$) and II_r ($T_{b,A} < T_{b,B} < T_{b,C} < T_{b,D}$), as, in these cases, the reactants (A and B) are both lighter than or both heavier than the products (C and D). As shown in Fig. 4, the first step of the framework, therefore, is to identify the extent to which reactive distillation is applicable to the mixture of interest by considering the class of mixture. For mixtures in classes I and III, the user proceeds to the next step of the flowchart.

Next, the user determines characteristic values of the relative volatilities, assuming the purities of products C and D are 99 mole% (where the main impurity of product C is the lighter reactant, A, and the main impurity in product D is the heavier reactant, B) and an equimolar feed (50 mole% A and B). That is, volatilities of the products and feed α_{CA}, α_{AB} and α_{BD} need to be calculated in group I_p, for mixtures containing 99% C/1% A, 50% A/50% B and 1% B/99% D (Muthia et al., 2018a, 2019a).

Table 1 summarises which volatilities need to be calculated for each class of mixture. In all cases, the volatility between reactants A and B is determined at saturated liquid conditions of the feed (with composition 50 mole% A, 50 mole% B) and the volatility between each product and the closest-boiling reactant is determined at saturated liquid condition of the product (with composition 99% product, 1% reactant). Note that the method (described so far) does not account for the formation of azeotropes.

Table 1. Summary of characteristic volatilities for quaternary mixtures of groups I and III

Group	Boiling point order	Volatility order	Characteristic product volatilities
I_p	$T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$	C > A > B > D	Distillate: α_{CA} (99% C, 1% A) Bottoms: α_{BD} (1% B, 99% D)
III_p	$T_{b,C} < T_{b,A} < T_{b,D} < T_{b,B}$	C > A > D > B	Distillate: α_{CA} (99% C, 1% A) Bottoms: α_{DB} (99% D, 1% B)
III_r	$T_{b,A} < T_{b,C} < T_{b,B} < T_{b,D}$	A > C > B > D	Distillate: α_{AC} (1% A, 99% C) Bottoms: α_{BD} (1% B, 99% D)
I_r	$T_{b,A} < T_{b,C} < T_{b,D} < T_{b,B}$	A > C > D > B	Distillate: α_{AC} (1% A, 99% C) Bottoms: α_{DB} (99% D, 1% B)

This paper significantly expands the scope of the mapping method to include non-ideal quaternary systems, with various boiling point orders. The presence of an azeotrope between two compounds with the closest boiling points is significant, as it may correspond to a change of volatility order, i.e. the characteristic relative volatility may be less than 1. In order to represent the difficulty (or impossibility) of separating the azeotrope-forming mixture, this work sets the relative volatility to 1.

As in conventional distillation, representative relative volatilities in the shortcut models may not accurately account for the significant non-ideality of the systems. Based on this knowledge, this work assumes that the mapping method is unsuitable for quaternary mixtures forming more than one azeotrope between any two components influencing the value of any representative relative volatility. Specifying multiple representative relative volatilities at 1, due to the presence of azeotropes, might result in over-/underestimation of the applicability of reactive distillation. Therefore, Fig. 6 shows that the flowchart rejects systems of this type as unsuitable.

The next step is to characterise the chemical equilibrium constant of the system. As chemical equilibrium is typically temperature dependent, a characteristic temperature needs to be selected; the method is then applied assuming that the equilibrium constant applies throughout the column. This work suggests that the equilibrium constant is calculated at the average boiling points of reactants. The logic for this is that the mixture in the reactive zone of the column will predominantly comprise the reactants, i.e. the boiling point of the mixture will lie between the boiling points of the two pure-component reactants.

A reaction will only achieve a low conversion if its chemical equilibrium constant is small. A low conversion in a reactive distillation column could cause reactants to accumulate in the column, thus promoting the reverse reaction(s) as well as inhibiting separation and/or requiring large reflux ratios to purify the products satisfactorily. Therefore, this work applies the heuristic that reactive distillation is not likely to be an attractive technology for systems with a very low reaction equilibrium constant, i.e. $K_{eq} < 0.01$ (Shah et al., 2012). In these cases, conventional reaction processes or other types of hybrid processes may be more suitable. On the other hand, systems with a very high chemical equilibrium constant ($K_{eq} > 10$) strongly favour high conversion in the reactor, and therefore simultaneous separation in a distillation column may not bring a significant advantage (Shah et al., 2012).

In these cases, conventional reaction–separation–recycle flowsheets are likely to perform satisfactorily. Therefore, the next step of the framework suggests the range of chemical equilibrium constants that is practically relevant for reactive distillation processes, as shown in Fig. 4. In spite of that recommendation, evaluating the feasibility of reactive distillation might still be useful for the system with a high chemical equilibrium constant, if a slow kinetically controlled reaction most likely occurs.

In real processes, the assumption of reaction equilibrium may be highly unrealistic. For example, parameters that control the reaction and separation performance of a reactive distillation column, relate to reaction kinetics and residence time. The dimensionless Damköhler (Da) number relates key parameters—the reaction rate constant (k_f), liquid residence time (τ) and catalyst loading (β):

$$Da = k_f \cdot \beta \cdot \tau \qquad . \qquad (4)$$

For the calculation of the Damköhler number this method takes into account the liquid residence time per stage, which is actually the ratio of the liquid hold-up per stage to the flow rate per stage. The maximum liquid residence time per stage considered is 120 seconds to enable realistic column designs, i.e. the liquid and catalyst occupy maximum 50% of the stage hold-up volume. The catalyst loading per stage (β) is the volumetric ratio of the amount of catalyst to the liquid hold-up per stage. A large Da number implies fast kinetics, a long liquid residence time, a high liquid hold-up and/or a high catalyst loading, which could benefit the performance of a reactive distillation process.

A higher Da number increases the size of the applicability region for a given reaction, until the applicability region is effectively identical to that when it is assumed that reaction equilibrium is achieved. Overestimation of the liquid residence time, liquid hold-up or catalyst loading, however, may result in an ineffective column operation or even an unfeasible process. Determining appropriate values of those parameters is essential for realistic design of the process. Therefore, the next step in the flowchart uses the ratio of the Da number to the equilibrium constant when applying the generic applicability graphs.

At $Da/K_{eq} \geq 5$, Muthia et al. (2018a) observed that for a defined generic case with various chemical equilibrium constant values (K_{eq} values = 0.1, 1, 10) the reactive distillation configuration of a kinetically controlled reaction is similar to that of its equilibrium-limited case, in terms of reflux ratio and the number of separation and reactive stages. Additionally, Fig. S2 in the Supporting Information shows that the applicability areas of both equilibrium-limited and kinetically controlled reactions are identical for two cases representing real reaction systems – synthesis of methyl acetate and hydrolysis of methyl lactate. This proves that Da/K_{eq} ratios exceeding 5 can be used practically as an initial criterion for initialising the design parameters of reactive distillation column.

The applicability assessment is conducted using pre-prepared graphs of a relevant generic case, i.e. with the same boiling point order and relevant values of the volatilities and equilibrium constant. Further assessment is required to obtain a preliminary economic evaluation of alternative designs. Cost estimation for reactive distillation columns can be obtained by adapting the economic evaluation procedures for conventional distillation, which are explained by Douglas (1988), Seider et al. (2010), Towler and Sinnott (2012). The Supporting Information presents some important equations used to calculating the total annual cost for conventional column.

Our previous work (Muthia et al., 2018b) presents the cost estimation of a reactive distillation process for amyl acetate production, using two assumptions affecting the economic aspect of the column design: 1) the cost of reactive trays is 20% higher than the cost of separation trays because of its non-standard features, and 2) the height of reactive stages is 20 to 30% larger than that of separation trays to avoid flooding or entrainment because of the presence of catalyst. The study found that the most cost-effective reactive distillation configurations lie close to the boundary line of the applicability graph of the assessed reaction system (i.e. the configurations with the lowest reflux ratios). Furthermore, it suggested that the cost of reactive distillation is more sensitive to the change of reflux ratio than the increase of number of reactive stages; a slight increase of reflux ratio could significantly affect both capital investment and energy requirement.

As described above, the framework presented in Fig. 4 provides a systematic approach for screening a quaternary system for its suitability for reactive distillation, for estimating key design parameters, including number of stages, reflux ratio and hold-up on reactive

stages, and for preliminary cost estimation of the reactive distillation column. The method is based on some very strongly simplifying assumptions. In our previous work, elements of the method were developed and demonstrated. The next section aims to explore the extent to which the method is useful for screening quaternary mixtures with non-ideal phase equilibrium behaviour.

3.2. Case studies: validation of the design framework

This section presents five case studies for the validation of the proposed framework presented in Fig. 4, where these case studies involve non-ideal phase equilibrium behaviour, i.e. the formation of homogeneous and heterogeneous azeotropes. The case studies also aim to demonstrate the advantages offered by the method, along with its limitation. The validation steps consist of: (1) preparing the applicability graph of the generic case corresponding to the key parameters of the case study (characteristic relative volatilities and chemical equilibrium constant), and (2) performing rigorous simulations for the case to evaluate the performance predicted by the methodology with that predicted using rigorous simulation.

The case studies belong to groups I_p ($T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$), III_p ($T_{b,C} < T_{b,A} < T_{b,D} < T_{b,B}$) and III_r ($T_{b,A} < T_{b,C} < T_{b,B} < T_{b,D}$), which offer the promising reactive distillation applications. While reactive distillation might be applicable to group I_r ($T_{b,A} < T_{b,C} < T_{b,D} < T_{b,B}$), additional equipment for purifying the products is typically needed (Luyben and Yu, 2008; Muthia et al., 2018c). Therefore, reaction systems in class I_r are not explored in this work. The case studies are limited to equilibrium-limited reactions. As shown previously (Muthia et al., 2018a), the results for kinetically-controlled reactions are expected to be similar to those for equilibrium-limited reactions.

The suitability of the mapping method to assess quaternary systems is mainly assessed by comparing the predictions from the pre-prepared applicability graphs for generic cases and the rigorous simulation results of corresponding column configurations for real systems. The deviation between the predicted and the actual reflux ratios and numbers of theoretical stages is calculated, to provide a quantitative comparison. Note that: 1) the purpose of the framework is to accelerate the initial assessment of the suitability of reactive distillation for a given reactive system; 2) the purpose of the economic evaluation

is to provide a very approximate estimate of costs to assist with decision-making about whether to continue to explore the design option in more detail. Based on our experience of working in and with industrial practitioners, we argue that there is a need for a method that provides qualitative guidance, not necessarily quantitative agreement, to evaluating the RD applicability at an early conceptual design stage in order to support a go/no-go decision.

3.1.1. Case 1: Methyl acetate synthesis by esterification

Methyl acetate is widely used as a solvent for producing resins and oils. The production of methyl acetate via esterification is a prime example of the successful application of reactive distillation in the chemical industries. Many researchers have used this reaction as a case study for developing models and design approaches (e.g. Al-Arfaj and Luyben, 2002; Bangga et al., 2019; Bessling et al., 1998; Huss et al., 2003; Kreul et al., 1998; Song et al., 1998). This system is selected as a case study for validating our method because it is industrially important and key data are available in the literature. Methyl acetate (C) and water (D) are produced by esterification of methanol (A) and acetic acid (B), as shown in Eq. (5):

$$\text{Methanol } \textbf{(A)} + \text{acetic acid } \textbf{(B)} \rightleftharpoons \text{methyl acetate } \textbf{(C)} + \text{water } \textbf{(D)}$$

| T_b (°C) | 64.7 | 118.0 | 56.9 | 100.0. |

(5)
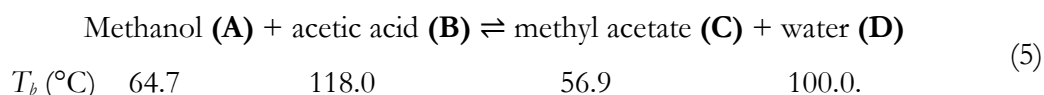
The mixture is in class III_p. The UNIQUAC-Hayden-O'Connell property model represents the non-ideality of this system (Pöpken et al., 2000). Methyl acetate–methanol and methyl acetate–water form homogeneous binary azeotropes; Table 2 presents their compositions and boiling points. Table S2 in the Supporting Information provides the liquid and equilibrium vapour-phase compositions of the feed and products. The representative relative volatilities for 99 mole% pure products are $\alpha_{CA} = 0.52$ and $\alpha_{DB} = 1.6$ and the feed volatility, $\alpha_{AB} = 6.3$. Following the systematic framework, α_{CA} is then set as 1.

Table 2. Molar composition of the azeotropes and corresponding boiling points in the system containing methanol, acetic acid, methyl acetate and water at 1 atm

No.	Type	Boiling point (°C)	Methanol (A)	Acetic acid (B)	Methyl acetate (C)	Water (D)
1	Homogeneous	53.7	0.341	-	0.659	-
2	Homogeneous	56.4	-	-	0.890	0.110

Eq. (6) gives the chemical equilibrium expression provided by Popken et al. (2000); $K_{eq} = 16.3$ at the average boiling points of the reactants (91.4 °C):

$$\ln(K_{eq}) = -3.82 + \frac{2408.65}{T} \qquad (6)$$

.

Based on the representative key parameters of the case study, applicability graphs of generic cases were prepared for values of K_{eq} of 10 and 20, with $\alpha_{CA} = 1.0$, $\alpha_{AB} = 6.3$, $\alpha_{DB} = 1.6$, as depicted in Fig. 5(a). The shaded area represents the region in which the 'real' boundary line is expected to lie.

Fig. 5 shows that the simulation results are in reasonably good agreement with the predictions of the generic applicability graph, in which the concept of using a single reactive distillation is identified as achievable. Fig. S3 in the Supporting Information presents applicability graphs for feed stage locations. It is found that locating the feed stages within the reactive zone improves the column performance, as indicated by the increased size of the applicable region. Placing the feeds within the reactive zone supports immediate reaction, therefore lowering the chance of forming an azeotrope between methyl acetate (product C) and methanol (reactant A). The solid line in Fig. 5(a) shows the real boundary line for Case 1, where both feed stages are within the reactive zone.
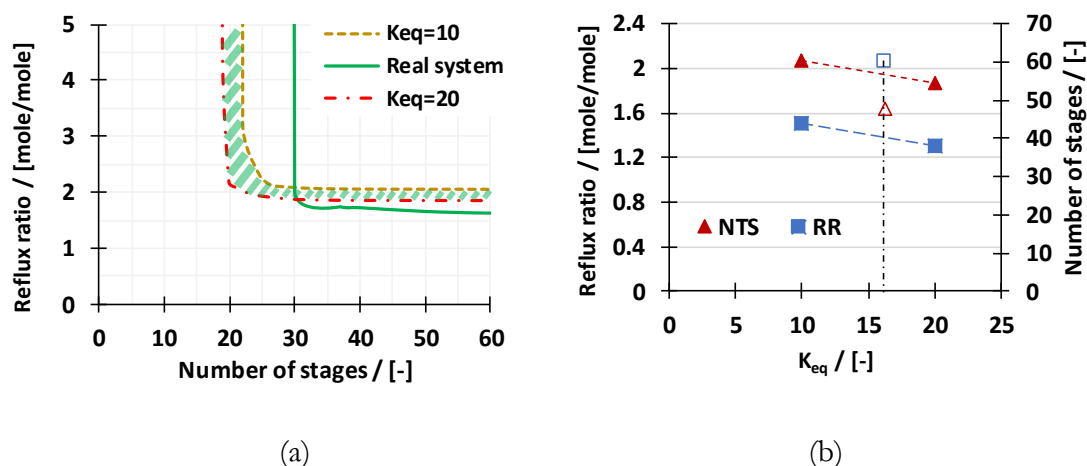
Fig. 5. Case 1—methyl acetate production via esterification (a) The predicted boundary line of the RD applicability within the shaded area and the actual boundary line of the RD applicability indicated by the solid line; (b) Reflux ratio and the number of theoretical stages: solid points = estimate; open points = rigorous simulation results.

In spite of the formation of azeotropes, and the assumption in the applicability graph of constant relative volatility, the graph indicates that reactive distillation is applicable. In this system, classified as group III_p ($T_{b,C} < T_{b,A} < T_{b,D} < T_{b,B}$), product C—the lightest compound—is readily removed as the top product. The high chemical equilibrium constant enables reactant B—the heaviest compound—to be almost completely consumed before it reaches the stripping section. For example, the composition profile of a column configuration with NTS = 2·NTS$_{min}$ (2 rectifying, 51 reactive and 7 stripping stages) and reflux ratio of 1.8 is given in Fig. S4 in the Supporting Information.

3.1.2. Case 2: 2-Ethylhexyl acrylate production via esterification

2-Ethylhexyl acrylate (2-EHA) is used in the chemical process industries as a precursor of various homopolymers and copolymers. They are frequently used for the production of coatings, printing inks and adhesives (Komoń et al., 2013). The esterification reaction at the core of the 2-EHA production is shown in Eq. (7):

Acrylic acid **(A)** + 2-ethylhexanol **(B)** ⇌ water **(C)** + 2-ethylhexyl acrylate **(D)**

T_b (°C)   141.0   184.0   100.0   216.0.

(7)
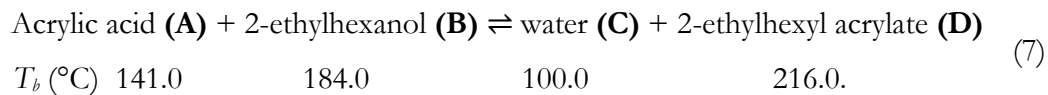
The UNIQUAC-Hayden-O'Connell property model describes the non-ideality of the mixtures (Moraru and Bildea, 2018). The mixtures of water/2-ethylhexanol and water/2-EHA compose two heterogeneous binary azeotropes at specific temperatures and compositions, as listed in Table 3. The production of 2-EHA was selected as the second case study because it represents group I_p ($T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$) that has the most favoured boiling point ranking of quaternary systems. The presence of two azeotropes in this system adds further complexities and challenges compared to the near-ideal quaternary systems in group I_p that we have assessed previously (Muthia et al., 2018a, 2019a).

Table 3. Molar composition of the azeotropes and corresponding in the system containing acrylic acid, 2-ethylhexanol, water and 2-ethylhexyl acrylate at 1 atm

No.	Type	Boiling point (°C)	Acrylic acid (A)	2-ethylhexanol (B)	Water (C)	2-ethylhexyl acrylate (D)
1	Heterogeneous	99.1	-	0.032	0.968	-
2	Heterogeneous	99.6	-	-	0.984	0.016

The representative relative volatilities for this case study are $\alpha_{CA} = 1.6$, $\alpha_{AB} = 4$ and $\alpha_{BD} = 5.3$—see Table S3 in the Supporting Information for more details. Eq. (8) provides the correlation between the temperature change and chemical equilibrium constant; the representative chemical equilibrium constant is 19.7, at the average boiling points of reactants (162.5 °C):

$$\ln(K_{eq}) = 8.58 - \frac{2438.50}{T}$$
.

(8)

Fig. 6 (a) presents the applicability graphs of the generic cases for values of K_{eq} of 15 and 25, with $\alpha_{CA} = 1.6$, $\alpha_{AB} = 4$ and $\alpha_{DB} = 5.3$. Those applicability graphs are relevant to the applicability of a single RD column. The shaded area depicts the expected region where the boundary line for the case study should exist. Rigorous simulation for the case study, however, shows that there is no applicability area for the operation of a single column. The presence of a heterogeneous azeotrope between 2-ethylhexanol (reactant B) and water (product C) with a high fraction of product C ($x_C = 0.968$) hinders the separation of 99 mole% pure product C. Further investigation was performed resulting in the applicable heterogeneous reactive distillation configurations, as a decanter deals with the liquid-phase separation. The boundary line of the applicability graph for this setup is highlighted by the solid line in Fig. 6(a).

(a)   (b)
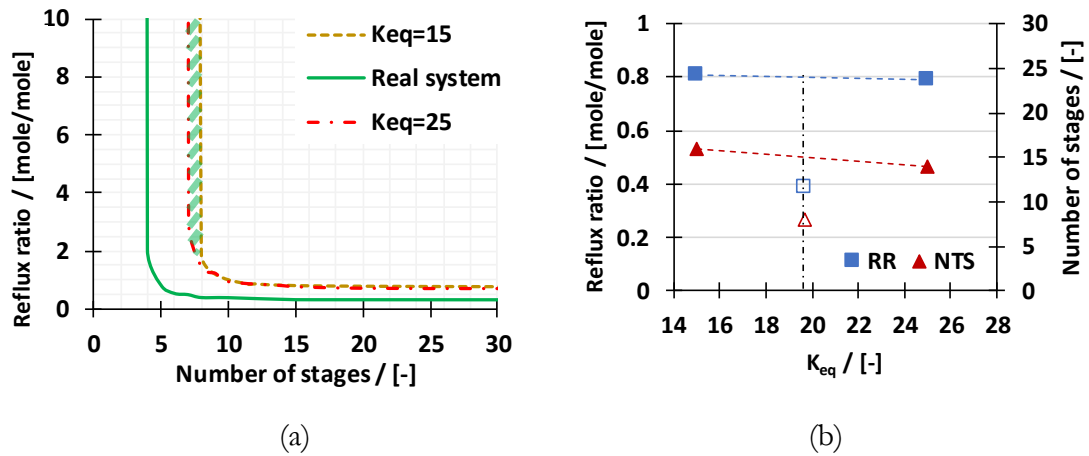
Fig. 6. Case 2—2-ethylhexyl acetate synthesis via esterification (a) The predicted boundary line of the RD applicability within the shaded area and the actual boundary line of the RD applicability indicated by the solid line; (b) Reflux ratio and the number of theoretical stages: solid points = estimate; open points = rigorous simulation results.

The assessment of this case study suggests that the mapping method is capable of predicting the applicability of RD for the systems with heterogeneous azeotrope(s) by disregarding specific types of column setup. The scope is limited in such cases, because the representative relative volatilities of the real system do not distinguish the non-ideality caused by homo- and/or heterogeneous azeotropes. In most cases, RD with a decanter is needed to overcome the heterogeneous azeotrope.

3.1.3. Case 3: Amyl acetate synthesis by esterification

Amyl acetate is mainly used as an organic solvent, a flavouring agent and an extractant. The most common route of amyl acetate production is via esterification, as shown in Eq. (9):

$$\text{Acetic acid } \textbf{(A)} + \text{amyl alcohol } \textbf{(B)} \rightleftharpoons \text{water } \textbf{(C)} + \text{amyl acetate } \textbf{(D)}$$

$$T_b \text{ (°C)} \quad 117.9 \qquad\qquad 138.0 \qquad\qquad 100.0 \qquad\qquad 147.7. \tag{9}$$
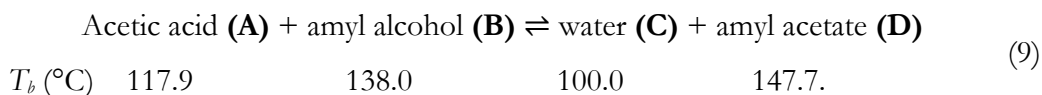
The non-random two-liquid (NRTL) property model describes adequately the non-ideality of this system (Chiang et al., 2002). The Hayden-O'Connell second virial coefficient model was used to account for the dimerisation of carboxylic acids in the vapour phase. This system also belongs to group I_p (just as case study 2), but it demonstrates further complexity with an increased number of azeotropes. This system contains one homogeneous binary, two heterogeneous binary, one homogeneous ternary and one heterogeneous ternary azeotropes, as presented in Table 4.

Table 4. Molar composition of the azeotropes and corresponding in the system containing acetic acid, amyl alcohol, water and amyl acetate at 1 atm

No.	Type	Boiling point (°C)	Acetic acid (A)	Amyl alcohol (B)	Water (C)	Amyl acetate (D)
1	Heterogeneous	94.7	-	0.044	0.823	0.133
2	Heterogeneous	94.9	-	-	0.830	0.170
3	Heterogeneous	95.9	-	0.148	0.852	-
4	Homogeneous	139.9	0.218	0.585	-	0.197
5	Homogeneous	140.3	0.260	0.740	-	-

The representative relative volatilities for this case study are $\alpha_{CA} = 2$, $\alpha_{AB} = 1.7$ and $\alpha_{BD} = 1.8$—see Table S4 in the Supporting Information for details. Eq. (10) shows the formula

of the chemical equilibrium constant (Tang et al., 2005); $K_{eq} = 2$ at the average boiling points of both reactants (128.0 °C):

$$\ln(K_{eq}) = 2.63 - \frac{777.00}{T} \qquad .$$

(10)

Fig. 7(a) gives the applicability graphs of the generic cases for chemical equilibrium constants of 1 and 5, with $\alpha_{CA} = 2$, $\alpha_{AB} = 1.7$ and $\alpha_{BD} = 1.8$. The predicted boundary line of the applicability area is expected to be within the shaded area and the actual boundary line of the applicability area is indicated by the solid line. The actual and predicted applicability areas include regions on and above their corresponding boundary lines. As observed in case study 2, due to heterogeneous azeotropes, the simulation result for this case study reveals that there is no applicability graph for a single reactive distillation column. In this reaction, obtaining product C with the purity $\geq$ 99 mole% is much more difficult than in the previous case study, as the reactive distillation operation is hindered by three potential heterogeneous azeotropes between product C and other compounds that are composed by high fractions of product C ($x_C > 0.82$). Instead, the operation of heterogeneous reactive distillation is attainable—see (a) for the actual boundary line of this setup – because a decanter takes advantage of the liquid-liquid split.
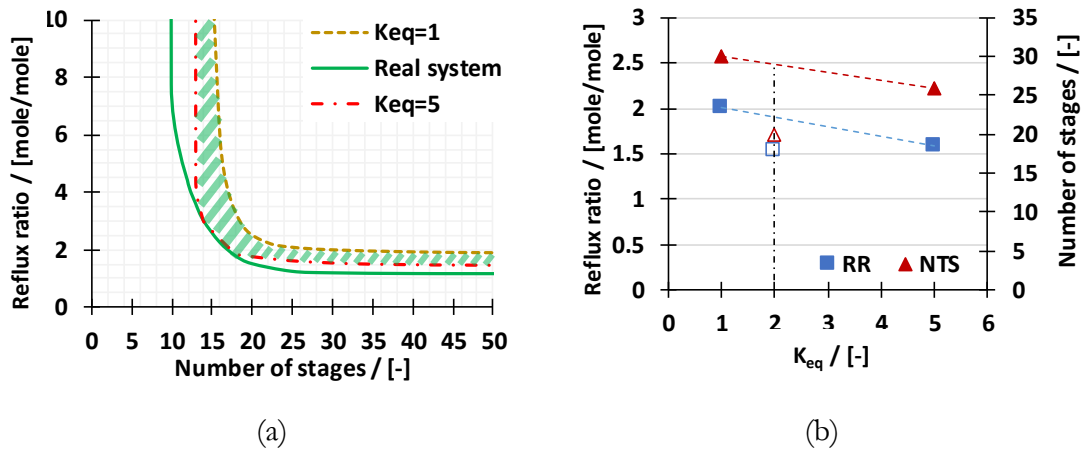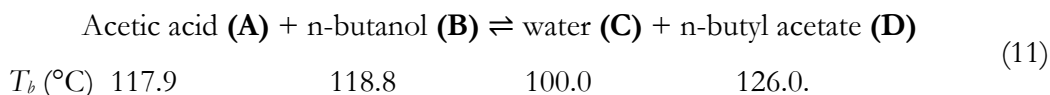

(a)   (b)

Fig. 7. Case 3—amyl acetate production via esterification (a) The predicted boundary line of the RD applicability within the shaded area and the actual boundary line of the RD applicability indicated by the solid line; (b) Reflux ratio and the number of theoretical stages: solid points = estimate; open points = rigorous simulation results.

3.1.4. Case 4: n-Butyl acetate production via esterification

Butyl acetate is used as a synthetic fruit flavouring in foods (e.g. candy, ice cream, cheese, and baked goods) as well as a high-boiling solvent of moderate polarity. The production of n-butyl acetate is common via the esterification route, as shown in Eq. (11):

$$\text{Acetic acid (A)} + \text{n-butanol (B)} \rightleftharpoons \text{water (C)} + \text{n-butyl acetate (D)}$$

$$T_b \text{ (°C)} \quad 117.9 \qquad\qquad 118.8 \qquad\qquad 100.0 \qquad\qquad 126.0. \tag{11}$$

The UNIQUAC property model represents well the non-ideality of the system (Venimadhavan et al., 1999), and it is associated with the Hayden-O'Connell second virial coefficient model. Similar to case studies 1 and 2, this system also belongs to group I_P. However, this case study possesses very non-ideal interactions between the compounds. There are six azeotropes identified in the system, including one heterogeneous ternary, two heterogeneous binary, two homogeneous binary and one homogeneous ternary azeotropes, as listed in Table 5. This case study provides more than one azeotrope between two compounds representing 99 mole% pure products and 50 mole% pure reactants. Therefore, according to the systematic framework proposed in this paper, the mapping method should not be suitable to characterise properly the relative volatilities of compounds.

Table 5. Molar composition of the azeotropes and corresponding in the system containing methyl acetate, n-butanol, methanol and n-butyl acetate at 1 atm

No.	Type	Boiling point (°C)	Acetic acid (A)	n-Butanol (B)	Water (C)	n-Butyl acetate (D)
1	Heterogeneous	90.1	-	0.107	0.690	0.203
2	Heterogeneous	90.9	-	-	0.715	0.285
3	Heterogeneous	92.7	-	0.243	0.757	-
4	Homogeneous	114.7	-	0.647	-	0.353
5	Homogeneous	120.8	0.537	0.150	-	0.313
6	Homogeneous	123.4	0.537	0.463	-	-

Rigorous simulations were performed for further validation. The representative relative volatilities for this system are $\alpha_{CA} = 1.4$, $\alpha_{AB} = 1$ and $\alpha_{BD} = 1$—see Table S5 in the Supporting Information for the details. The actual α_{AB} for 50 mole% pure reactants and the actual α_{CA} for 99 mole% pure products are 0.95 and 0.57, respectively. These variables are then set as 1, following the systematic framework. Gangadwala et al. (2003) suggested the formula of the chemical equilibrium constant, as written in Eq. (12); $K_{eq} = 11.5$ at the average boiling points of both reactants (118.4 °C):

$$\ln(K_{eq}) = 1.3404 + \frac{430.804}{T} \quad .$$
(12)

The simulation of the generic cases for K_{eq}s of 10, 15 and 20 with $\alpha_{CA} = 1.4$, $\alpha_{AB} = 1$ and $\alpha_{BD} = 1$ generated no applicability graphs. The finding is acceptable considering the separation difficulty with very strict relative volatilities of compounds.

A set of simulation carried out for the case study confirmed that there is no applicability graph obtained for a single RD column. On the other hand, the simulation result suggested that heterogeneous RD applies to this system. The applicability graph for this setup is presented in Fig. 8(a). This finding highlights a mismatch between the prediction based on the generic cases and the results obtained from the rigorous simulation of the case study. The result indicates that the method is unsuitable for the systems with more than one azeotrope between two compounds that represent 99 mole% pure products and 50 mole% pure reactants because multiple characteristic relative volatilities set as 1, concerning the presence of azeotropes, might underestimate the applicability of reactive distillation.
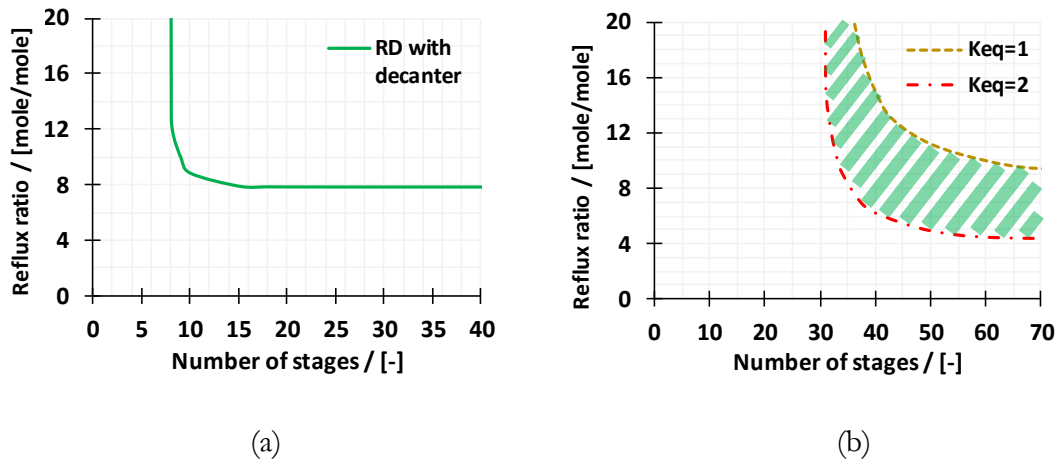
Fig. 8. (a) The actual boundary line of the applicability area of case 4—butyl acetate synthesis via esterification—for a heterogeneous reactive distillation setup and (b) the predicted boundary line of the applicability area of case 5—transesterification of methyl acetate and butanol—within the shaded area.

3.1.5. Case 5: Transesterification of methyl acetate and n-butanol

Methyl acetate is a cheap by-product in the production of polyvinyl alcohol (PVA). It can be converted by transesterification to methanol (a feedstock of the same synthesis route to PVA) and n-butyl acetate (which is widely used as an important extractive agent, a synthetic fruit flavouring and a solvent in plastics, resins, and gums industries). The transesterification reaction between methyl acetate and butanol is given in Eq. (13):

$$\text{Methyl acetate } \textbf{(A)} + \text{n-butanol } \textbf{(B)} \rightleftharpoons \text{methanol } \textbf{(C)} + \text{n-butyl acetate } \textbf{(D)}$$

T_b (°C)   56.9   118.8   64.7   126.0. (13)
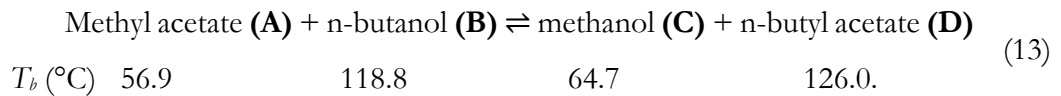
This reaction was selected as case study because it represents another classification of boiling point rankings in quaternary reactions, namely group III$_r$ ($T_{b,A} < T_{b,C} < T_{b,B} < T_{b,D}$). This group may pose a critical challenge for purifying product C at the top stream, especially when the chemical equilibrium constant is considerably low. The UNIQUAC property model represents the non-ideality of the case study (Bożek-Winkler and

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Gmehling, 2006). There are two homogeneous azeotropes identified between two compounds that represent 99 mole% pure products, which are methyl acetate/methanol (reactant A / product C) and n-butanol/n-butyl acetate (reactant B / product D), as shown in Table 6. According to the systematic framework, the mapping method should be not suitable for the assessed case study.

Table 6. Molar composition of the azeotropes and corresponding in the system containing methyl acetate, n-butanol, methanol and n-butyl acetate at 1 atm

No.	Type	Boiling point (°C)	Methyl acetate (A)	n-butanol (B)	Methanol (C)	n-butyl acetate (D)
1	Homogeneous	53.7	0.659	-	0.341	-
2	Homogeneous	116.9	-	0.780	-	0.220

For further validation, rigorous simulations were performed for both generic cases and the case study. The representative relative volatilities of this case study for 99 mole% pure products and 50 mole% pure reactants are $\alpha_{AC} = 3.4$, $\alpha_{AB} = 12$ and $\alpha_{BD} = 1.9$—see Table S6 in the Supporting Information for details. Bożek-Winkler and Gmehling (2006) provide the chemical equilibrium constant expression, as given in Eq. (14); The representative chemical equilibrium constant is 1.08 at the average boiling points of two reactants (87.9 °C):

$$\ln(K_{eq}) = 0.8158 - \frac{267.9}{T} \qquad (14)$$
.

The applicability graphs of generic cases were prepared for values of K_{eq} of 1 and 2 with $\alpha_{AC} = 3.4$, $\alpha_{AB} = 12$ and $\alpha_{BD} = 1.9$, and the actual boundary line for the case study is expected to be within the shaded area in Fig. 8(b). Rigorous simulation of the case study, however, suggested that there is no applicability graph found for a single RD column or any standalone RD setup without additional process equipment, for the targeted purity ≥

99 mole%. Published literature confirmed that the reactive distillation operation to achieve a high product purity for this reaction is only feasible if it is assisted with membrane technology (Steinigeweg and Gmehling, 2004). The mismatch between the expectation from pre-prepared generic graphs and the simulation results of the case study is caused by an overestimation of the representative relative volatilities of the case study.

3.2. Analysis of the applicability prediction by the mapping method

The validation carried out in the previous section highlighted the suitability of the mapping method for non-ideal quaternary systems. Three case studies showed that the method is capable of providing the first screening of reactive distillation designs for high product purity, i.e. $\geq$ 99 mole%. Two case studies showed that the method is unsuitable for the systems with more than one azeotrope that represents 99 mole% pure products and 50 mole% pure reactants. In that instance, the use of the mapping method over-/under-estimates the RD designs.

An additional assessment was performed to quantify the deviations between the prediction and the actual numbers of theoretical stages based on the generic cases, for the configurations with NTS = 2·NTS$_{min}$. The selection of these configurations was only based on our previous knowledge in the classic distillation process. Indeed, other configurations with RR = 1.2·RR$_{min}$, or with any other considerations, can be evaluated. Using the interpolation technique, the predicted numbers of theoretical stages and reflux ratios of the case studies, at NTS = 2·NTS$_{min}$, are given in Fig. 5(b) for case 1, Fig. 6(b) for case 2, Fig. 7(b) for case 3. All triangle markers in these figures show the numbers of theoretical stages and all square markers provide the corresponding reflux ratios. Filled triangle and square markers give the actual values obtained from rigorous simulations of the case studies.

The results obtained from the interpolation were compared to the actual numbers of theoretical stages and reflux ratios of the case studies. All deviations were quantified based on the absolute differences between numbers of theoretical stages or reflux ratios over the actual value obtained from the rigorous simulation of the case study, as listed in Table 7. The deviations are reasonably acceptable for case studies 1 and 3, for the assessment at the very early stage of conceptual design level. Large deviations (> 50%) were obtained

for case 2, because of small numbers of theoretical stages and low reflux ratios. Although percentage-wise there are some differences, in terms of absolute numbers the values are very useful for an early industrial assessment of RD applicability.

Table 7. Comparison of predicted and actual numbers of theoretical stages and reflux ratios

No.	Case studies	Number of theoretical stages / [-]			Reflux ratio / [mole/mole]		
		Predicted	Actual	Deviation	Predicted	Actual	Deviation
1	Case 1	40	60	33%	1.94	1.63	19%
2	Case 2	15	8	88%	0.80	0.39	105%
3	Case 3	29	20	45%	1.90	1.54	23%

Overall, the method gives satisfying results regarding the applicability prediction of reactive distillation. The method is useful for engineers in the chemical industries to obtain a go-/no decision prior to performing rigorous simulations of real systems.

4. Conclusions

This novel systematic framework proposed here is valuable in assessing the applicability of reactive distillation for non-ideal quaternary systems, using as basis a mapping method that was introduced and developed in our prior work for near-ideal systems (Muthia et al., 2018a, 2019a, 2019b). When reactive distillation is applicable, multiple column configurations and a preliminary economic evaluation are obtained for an assessed chemical system. The sequential steps in the workflow consist of the recognition of the group of boiling point rankings, the calculation of the key relative volatilities and chemical equilibrium constant of the real system to select the most relevant pre-prepared applicability graphs of generic cases and the preliminary economic evaluation. For kinetically controlled reactions, the determination of catalyst loading, liquid residence time or liquid hold-up is based on an initial criterion of $Da/K_{eq} \geq 5$, so that one can estimate the values of those design parameters to obtain the optimum RD design.

The use of the systematic framework has been successfully validated using five case studies that represent different groups of boiling point ranking in quaternary systems, and have distinctive separation complexities due to azeotropes. The boiling point rankings give a significant effect on the RD performance. As shown in case studies 1-4, having a product as the lightest compound is favoured, so the product can be easily collected at the top stream with high purity. The given case studies proved that the applicability of reactive distillation is significantly affected by the non-ideality of the systems which is indicated by the number and the types of azeotropes present. Reactive distillation with a decanter might be considered if heterogeneous azeotropes exist between the lightest product and the other compounds.

The validation of the approach using case studies 1-3 showed that the framework is suitable also for complex systems with only one azeotrope between two compounds that represent 99 mole% pure products and 50 mole% pure reactants. Representative relative volatilities calculated for 99 mole% pure products and 50 mole% pure reactants correspond to the desired product compositions and the equimolar feed of reactants. The proposed approach is capable of predicting the applicability of reactive distillation by disregarding the types of column setup, for instance, if a decanter is needed to overcome heterogeneous azeotropes. By only referring to some basic parameters, the systematic framework allows engineers in the chemical industries to reduce the number of rigorous simulations required in the early conceptual design stage.

The validation of the approach using case studies 4 and 5 showed that the framework is unsuitable for strongly non-ideal systems with multiple azeotropes present between two components affecting representative relative volatilities. The limitation of the proposed method is analogous to that of shortcut methods for conventional distillation (such as Fenske-Underwood-Gilliland), where assumed constant relative volatilities are unable to provide accurate initial column designs for the separation of strongly non-ideal systems.

Acknowledgement

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5.1.1. Appendix to Publication 4: Supporting Information

1. Multiple configurations in an applicability graph of reactive distillation

Fig. S1 (a) shows the applicability graph of reactive distillation for an equilibrium-limited reaction in group I_p ($T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$), considering $\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$ and $\alpha_{BD} = 2$ at $K_{eq} = 0.1$. The applicability graph is relevant for the product purity of ≥ 99 mole%. For this case, $2 \cdot NTS_{min} = 36$. Close to the boundary line at NTS = 36, there are multiple configurations available with various combinations of rectifying, reactive and stripping stages – their numbers of reactive stages are highlighted in Fig. S1 (b). Some multiple configurations are given in details in Table S1, in which within only 3% of RR change, at least there are 17 possible RD configurations.

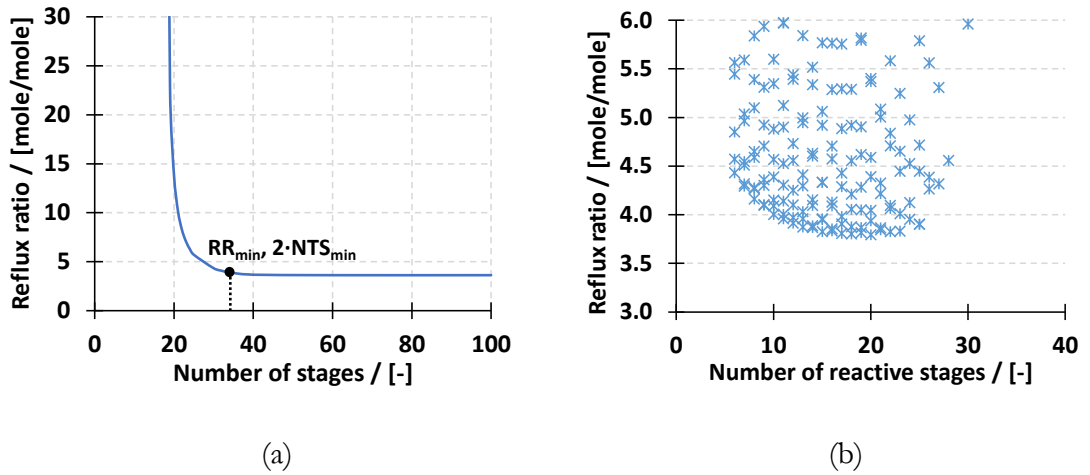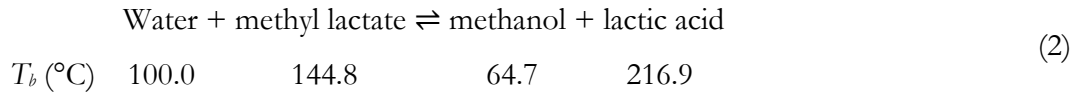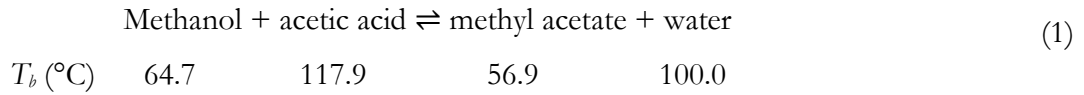(a)   (b)

Fig. S1. (a) Applicability graph of equilibrium-limited reaction ($\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$, $K_{eq} = 0.1$); (b) Number of reactive stages required for different column configurations (NTS = $2 \cdot NTS_{min}$ = 36), according to the Supporting Information provided in (Muthia et al., 2018).

Table S1. Multiple column configurations for an equilibrium-limited reaction, considering ($\alpha_{AB} = 1.5$, $\alpha_{CA} = 2$, $\alpha_{BD} = 2$, $K_{eq} = 0.1$), according to the Supporting Information provided in (Muthia et al., 2018).

Number of theoretical stages	Reflux ratio	Number of rectifying stages	Number of reactive stages	Number of stripping stages
36	3.795	7	20	9
36	3.802	8	18	10
36	3.807	8	17	11
36	3.816	7	19	10
36	3.826	6	22	8
36	3.827	9	15	12
36	3.831	6	23	7
36	3.834	9	16	11
36	3.843	7	21	8
36	3.855	8	16	12
36	3.866	6	21	9
36	3.867	9	14	13
36	3.868	8	19	9
36	3.875	10	13	13
36	3.875	7	18	11
36	3.888	10	14	12
36	3.902	5	25	6

2. Ratio of the Damköhler number to the chemical equilibrium constant

The ratio between the Damköhler number and the chemical equilibrium constant is assessed using two case studies that represent non-ideal reaction systems—synthesis of methyl acetate and hydrolysis of methyl lactate.

$$\text{Methanol + acetic acid} \rightleftharpoons \text{methyl acetate + water} \tag{1}$$

| T_b (°C) | 64.7 | 117.9 | 56.9 | 100.0 |

$$\text{Water + methyl lactate} \rightleftharpoons \text{methanol + lactic acid} \tag{2}$$

| T_b (°C) | 100.0 | 144.8 | 64.7 | 216.9 |

The chemical equilibrium constant and the forward reaction rate constant (mole g_{cat}^{-1} min^{-1}) relationships for the synthesis of methyl acetate are presented by Pöpken et al. (2000) as:

$$\ln(K_{eq}) = -3.82 + 2408.65/T \tag{3}$$

$$k_f = 4.94 \cdot 10^2 \cdot \exp(-49{,}190/R \cdot T) \tag{4}$$

The chemical equilibrium constant and the forward reaction rate constant (mole g_{cat}^{-1} min^{-1}) relationships for the hydrolysis of methyl lactate are provided by Sanz et al. (2004),

$$\tag{5}$$

$$\ln(K_{eq}) = 2.6 - 1954.2/T$$

$$k_f = 1.65 \cdot 10^5 \cdot \exp\left(-50{,}910/R \cdot T\right) \tag{6}$$

In the first case, two homogeneous azeotropes exist between methyl acetate (65.9 mole%)–methanol (34.1 mole%) at 53.7 °C and methyl acetate (89 mole%)–water (11 mole%) at 56.4 °C. In the second case, there is an azeotrope identified between water (97 mole%) and methyl lactate (3 mole%) at 99.8 °C.

Fig. S2 shows applicability graphs for both case studies generated using rigorous simulations in Aspen Plus. It is observed that the applicability areas of both kinetically controlled and equilibrium-limited reactions are similar for $\text{Da}/K_{eq} \geq 5$.
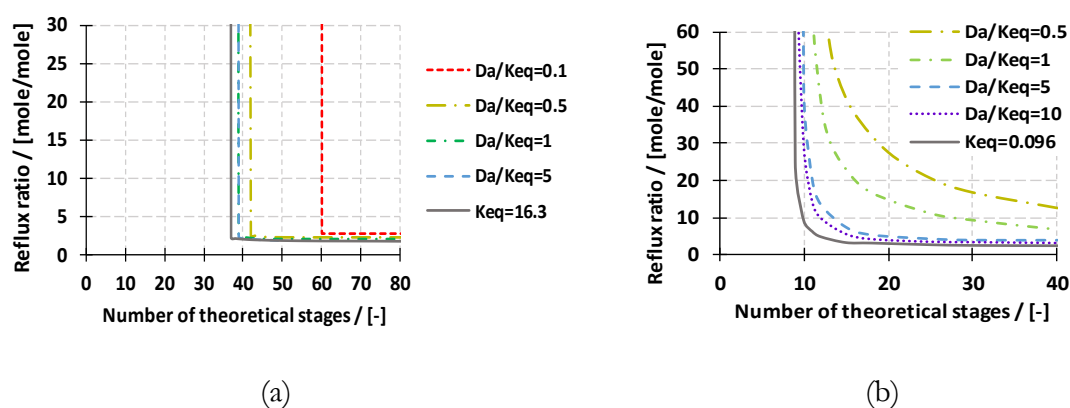
Fig. S2. Applicability graphs of reactive distillation for (a) synthesis of methyl acetate; (b) hydrolysis of methyl lactate.

3. Preliminary economic evaluation of reactive distillation

The systematic workflow presented in this work allows engineers in the chemical industries to assess the applicability of reactive distillation, based on a mapping method that we have developed (Muthia et al., 2018, 2019a, 2019b). When reactive distillation is applicable, preliminary economic evaluation is conducted for the chosen reactive distillation configuration, by using adapted steps of cost estimation for conventional distillation. Complete procedures of economic evaluation for conventional distillation are explained elsewhere (Douglas, 1998; Seider et al., 2010; Towler and Sinnott, 2012).

Total annualised cost (TAC) is a key variable to compare the reactive distillation process with other conventional or hybrid systems. It comprises two elements: annualised investment cost (AIC) defined as the total investment cost (TIC) relative to pay-back period (PBP), and total operating cost (TOC). The components of AIC include the costs of column shell and internals, condenser, reboiler, reflux drum and any additional equipment (e.g. pumps). TOC includes the costs of cooling water, steam and catalyst. Eqs. (1)–(5) present some important cost correlations for TAC, TIC and TOC (Douglas, 1998), where costs are updated from 1998 (Marshall and Swift index, M&S = 280) to the current year using the current value of the M&S index (M&S = 1638.2 at the end of 2018).

$$TAC = \frac{TIC}{PBP} + TOC \tag{7}$$

$$TIC_{RD,Shell} = \left(\frac{M \& S}{280}\right) \cdot 101.9 \cdot D^{1.066} \cdot H^{0.802} \cdot (2.18 + F_C) \cdot F_{lang} \tag{8}$$

$$TIC_{RD,Internal} = \left(\frac{M \& S}{280}\right) \cdot 4.7 \cdot D^{1.55} \cdot H \cdot F_C \cdot F_{lang} \tag{9}$$

$$TIC_c = \left(\frac{M \& S}{280}\right) \cdot 101.3 \cdot A_c^{0.65} \cdot (2.29 + F_c) \cdot F_{lang} \tag{10}$$

$$TIC_r = \left(\frac{M \& S}{280}\right) \cdot 101.3 \cdot A_r^{0.65} \cdot (2.29 + F_c) \cdot F_{lang} \tag{11}$$

A_c	:	Heat-transfer area for condenser
A_r	:	Heat-transfer area for reboiler
D	:	Diameter of reactive distillation column (m)
F_C	:	Correction factor of total of investment cost
F_{Lang}	:	Lang factor
H	:	Height of reactive distillation column (m)
M&S	:	Marshall & Swift equipment cost indexes
PBP	:	Pay-back period (years)
TAC	:	Total annual cost ($/y)
TIC	:	Total investment cost ($)
$TIC_{RD,Internal}$	:	Total investment cost for internals of reactive distillation column ($)
$TIC_{RD,Shell}$	:	Total investment cost for shell of reactive distillation column ($)
TOC	:	Total operating cost ($/y)

4. Calculations of representative relative volatilities of compounds

Eq. (6) defines the relative volatility of i and j in terms of the liquid and vapour mole fractions (x and y) at phase equilibrium:

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{\left(\dfrac{y_i}{x_i}\right)}{\left(\dfrac{y_j}{x_j}\right)} \tag{6}$$

Tables S2–S6 provide the compositions of mixtures in vapour and liquid phases for 99 mole% pure products and 50 mole% pure reactants. The data given is applied at atmospheric pressure and it is assumed that the stream is at saturated conditions (i.e. liquid at boiling point).

Table S2. Case 1: Vapour and liquid compositions of mixtures (methyl acetate production via esterification).

Feed composition	y_i	x_i	y_j	x_j	K_i	K_j	α_{ij}
99 mole% of methyl acetate (i) 1 mole% of methanol (j)	0.98	0.99	0.02	0.01	0.99	1.92	0.52
50 mole% of methanol (i) 50 mole% of acetic acid (j)	0.86	0.50	0.14	0.50	1.73	0.27	6.28
1 mole% of acetic acid (i) 99 mole% of water (j)	0.006	0.01	0.99	0.99	0.60	1.00	1.66

Table S3. Case 2: Vapour and liquid compositions of mixtures (2-ethylhexyl acrylate synthesis via esterification).

Feed composition	y_i	x_i	y_j	x_j	K_i	K_j	α_{ij}
99 mole% of water (i) 1 mole% of acrylic acid (j)	0.99	0.99	0.006	0.01	1.00	0.62	1.63
50 mole% of acrylic acid (i) 50 mole% of 2-ethylhexanol (j)	0.80	0.50	0.20	0.50	1.60	0.40	3.96
1 mole% of 2-ethylhexanol (i) 99 mole% of 2-ethylhexyl acrylate (j)	0.05	0.01	0.95	0.99	5.04	0.96	5.25

Table S4. Case 3: Vapour and liquid compositions of mixtures (amyl acetate production via esterification).

Feed composition	y_i	x_i	y_j	x_j	K_i	K_j	α_{ij}
99 mole% of water (i) 1 mole% of acetic acid (j)	1.00	0.99	0.005	0.01	1.00	0.52	1.95
50 mole% of acetic acid (i) 50 mole% of amyl alcohol (j)	0.63	0.50	0.37	0.50	1.27	0.73	1.73
1 mole% of amyl alcohol (i) 99 mole% of amyl acetate (j)	0.018	0.01	0.98	0.99	1.80	0.99	1.82

Table S5. Case 4: Vapour and liquid compositions of mixtures (n-butyl acetate synthesis via esterification).

Feed composition	y_i	x_i	y_j	x_j	K_i	K_j	α_{ij}
99 mole% of water (i) 1 mole% of acetic acid (j)	0.99	0.99	0.007	0.01	1.00	0.70	1.42
50 mole% of acetic acid (i) 50 mole% of n-butanol (j)	0.49	0.50	0.51	0.50	0.98	1.02	0.95
1 mole% of n-butanol (i) 99 mole% of n-butyl acetate (j)	0.98	0.99	0.02	0.01	0.99	1.75	0.57

Table S6. Case 5: Vapour and liquid compositions of mixtures (transesterification of methyl acetate and n-butanol).

Feed composition	y_i	x_i	y_j	x_j	K_i	K_j	α_{ij}
1 mole% of methyl acetate (i) 99 mole% of methanol (j)	0.03	0.01	0.97	0.99	3.29	0.98	3.37
50 mole% of methyl acetate (i) 50 mole% of n-butanol (j)	0.92	0.50	0.08	0.50	1.85	0.15	12.0
1 mole% of n-butanol (i) 99 mole% of n-butyl acetate (j)	0.02	0.01	0.98	0.99	1.84	0.99	1.85

5. Applicability assessment of Case 1 (methyl acetate production via esterification)

The position of feed stages within the reactive zone notably affects the size of the applicability graph of case study 1, as an immediate contact between reactants contributes to minimize the formation of azeotrope between reactant and product. Fig. S3 presents the applicability graphs of reactive distillation for fixed feed stages at the top and the bottom stages of the reactive zone and varied feed stages within the reactive zone.
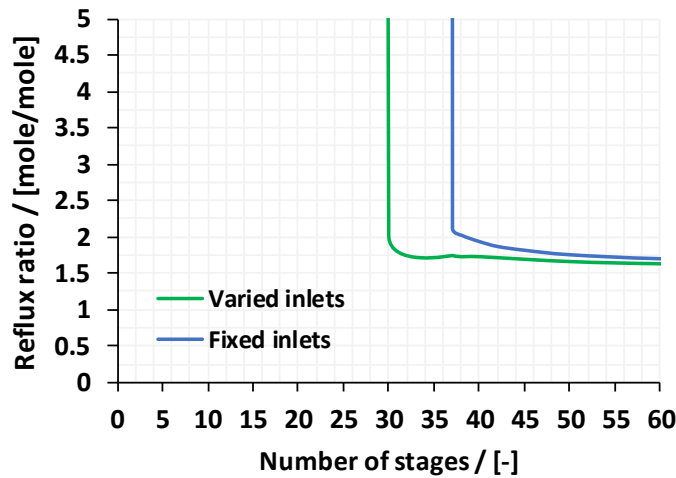
Fig. S3. Applicability graphs of Case 1 obtained from rigorous simulations.

Fig. S4 shows the composition profile of a column configuration (2 rectifying, 51 reactive and 7 stripping stages, and reflux ratio of 1.8) that exists close to the boundary line of the applicability graph for Case 1. The high chemical equilibrium constant of this system (K_{eq} = 16.3 at 91.4°C) allows a high conversion of reactants in the reactive section of the column. In this system classified into group III_p ($T_{b,C} < T_{b,A} < T_{b,D} < T_{b,B}$), it is crucial to prevent reactant B from reaching the stripping section, as it is the heaviest component that could interfere the high purity of product D.
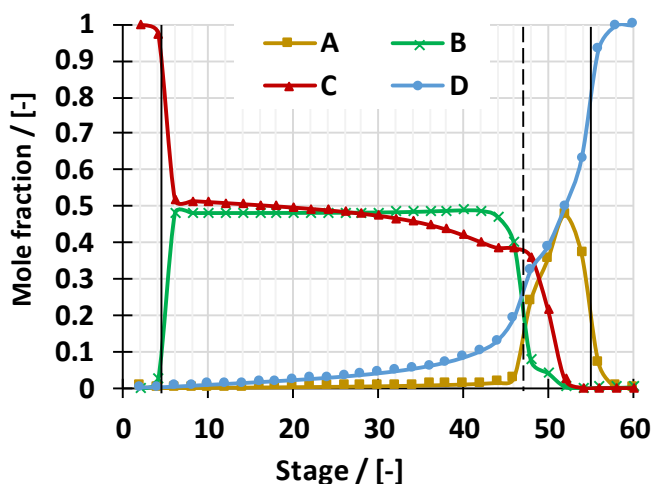
Fig. S4. The composition profile of a column configuration for Case 1. The solid vertical lines depict the start and end of reactive section. The dashed line is the feed stage of reactant A, while the feed stage of reactant B overlaps with the start of reactive section.

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5.2. Publication 5

This section is based on the following publication:

Muthia, R., Jobson, M. and Kiss, A. A. (2020). 'Determining the design parameters of reactive distillation processes by a quick mapping method', accepted for publication in *Computer Aided Chemical Engineering*.

The US English spelling in the original publication has been changed here to the UK English spelling to fulfil the requirements of the PhD theses policy regulated by the University of Manchester.

Determining the design parameters of reactive distillation processes by a quick mapping method

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Abstract

The application of reactive distillation in the chemical process industry promises significant benefits, such as boosting energy efficiency and reducing the overall cost. However, assessing and designing a reactive distillation process is still challenging as these tasks usually demand time-consuming procedures. To overcome this problem, the present work proposes a quick approach to determine the design parameters for a kinetically-controlled reactive distillation process according to the ratio between the Damköhler (Da) number and the chemical equilibrium constant (K_{eq})—thus relating reaction kinetics and chemical equilibrium. This study employs a mapping method featuring an applicability graph that conveniently plots the reflux ratio vs the number of theoretical stages and extends it to account for kinetically controlled reactions. The method is demonstrated using the map for a generic quaternary reaction system, described as $A + B \rightleftharpoons C + D$, considering constant relative volatilities ($\alpha_{AB} = 2$ and $\alpha_{CD} = 6$) and various reaction equilibrium constants (K_{eq} = 0.01, 0.1, 1). For validation purposes, the applicability of reactive distillation is examined in two case studies – hydrolysis of methyl lactate and synthesis of methyl acetate. Modelling of both the generic and real systems suggests that, with a ratio Da/K_{eq} of 5 or more, the generic map can provide initial values for the design parameters of a reactive distillation column. Ultimately, the insights gained save time in effectively assessing the feasibility of reactive distillation at the conceptual design stage.

Keywords:

Reactive distillation, mapping method, Damköhler number, equilibrium constant, conceptual process design

1. Introduction

Reactive distillation is an attractive and efficient process intensification method in the chemical industries. This technology combines reaction and separation functions in a single distillation column; the reaction converts feeds to products, while simultaneous separation enables removal of products. Reactive distillation has many advantages, such as reducing cost and energy consumption, enhancing conversion and selectivity, and overcoming unwanted azeotropes. To gain these benefits, appropriate parameters for column design (e.g. number of stages, reflux ratio, liquid residence time and catalyst loading) must be determined. Over-design might result in an expensive and ineffective unit, while a poor selection of the design parameters can lead to weak separation and reaction performance, or even an infeasible design. Therefore, a good understanding of the interplay between the design parameters of reactive distillation is crucial in the early phase of conceptual design.

The present work proposes a quick approach to determine the design parameters of reactive distillation using the simple ratio of the Damköhler (Da) number over the chemical equilibrium constant (K_{eq}), along with a mapping method. The work aims to find whether the generic maps can be applied for kinetically-controlled reactions, characterised in terms of the Da/K_{eq} ratio, to narrow the range of possible reactive distillation design parameters, namely liquid residence time, catalyst selection and catalyst loading. In this case, these inputs for reactive column design could expedite the development of feasible designs.

2. Problem statement

For almost a century, reactive distillation columns have been designed and optimised, but reactive distillation design, simulation and evaluation remains time consuming (Li et al., 2016): obtaining a feasible reactive distillation column is not an easy or quick task, while column optimisation is even more demanding. To overcome this problem, this work employs a mapping method to provide a rule of thumb for the ratio Da/K_{eq} that guides engineers to quickly determine the liquid residence time, catalyst selection (affecting kinetics) and catalyst loading for designing a reactive distillation column.

3. Overall approach to determine reactive distillation design parameters

3.1. Overview of the mapping method

The mapping method was originally introduced to visualise the applicability of equilibrium-controlled reactive distillation, using pre-defined applicability graphs of generic cases (Muthia et al., 2018a; 2018b). The method was then employed for preliminary economic ranking of reactive distillation designs and to investigate the feed locations of reactive distillation columns (Muthia et al., 2019). The mapping method utilises a so-called applicability graph for reactive distillation, i.e. a plot of reflux ratio (RR) the number of theoretical stages (NTS), depicted in Fig. 7(a). A boundary line limits the applicability area of reactive distillation for products of specified purity (99 mole% in this study). The applicability graph, generated using Aspen Plus process simulator and displayed in Fig. 7(a) for a quaternary system, $A + B \rightleftharpoons C + D$, approximates the region of feasible operation for a single reactive distillation column.

(a) (b)
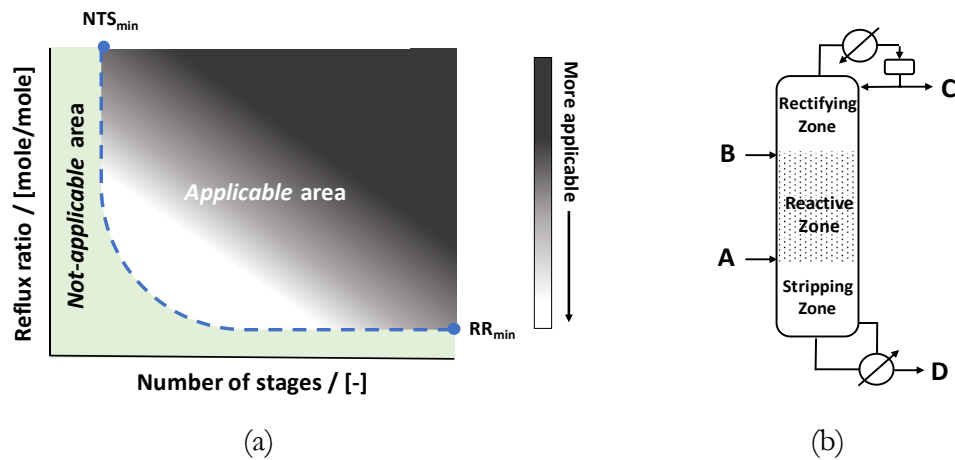
Fig. 7. (a) An illustrative applicability graph of reactive distillation used in the mapping method, and (b) a schematic reactive distillation column.

3.2. Use of mapping method to select the Da/K_{eq} ratio

The mapping method graphically correlates the performance of equilibrium-controlled reactive distillation processes, where each stage achieves the maximum possible conversion. This work extends the approach to consider kinetically controlled reactions, where a smaller applicability area is observed (Muthia et al., 2018a). Finite reaction rates

limit conversion on each stage, for example, due to poor catalyst selection, poor catalyst performance, insufficient quantity of catalyst, or insufficient liquid residence time. The dimensionless Damköhler number, Da, captures these issues quantitatively:

$$Da = k_f \cdot M_r \cdot \beta \cdot \tau \qquad , \qquad\qquad (15)$$

where k_f is the forward reaction rate constant (mole g_{cat}^{-1} min^{-1}), M_r the average molar mass of components ($g_{mixture}$ $mole^{-1}$), β the catalyst loading (g_{cat} $g_{mixture}^{-1}$) and τ the liquid residence time per stage (min). The Da number is defined in terms of average conditions in the column. A large Da value improves the performance of reactive distillation, increasing the applicability area, and *vice versa*. More importantly, when Da is large enough, the applicability area is similar to that of an equilibrium-controlled operation. Therefore, it is crucial to find a quick approach to estimate what Da number is 'large enough'. To do so, the sensitivity of the applicability area to the ratio Da/K_{eq} is explored.

In this work, two groups of generic quaternary systems with different volatility orders are chosen: group I_p ($T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$) and group III_p ($T_{b,C} < T_{b,A} < T_{b,D} < T_{b,B}$). The classification follows the convention proposed by Luyben and Yu (2008). The two selected groups are beneficial in chemical industries because products can be easily collected at the top and bottom streams of a reactive distillation column. Here, constant relative volatilities ($\alpha_{AB} = 2$ and $\alpha_{CD} = 6$) and a range of fixed equilibrium constants ($K_{eq} = 0.01, 0.1, 1$) are assumed.

To validate the approach, two case studies are investigated – hydrolysis of methyl lactate and synthesis of methyl acetate by esterification; these represent typical non-ideal systems relevant to the chemical industries. As in (Muthia et al., 2018a), the representative Damköhler number and chemical equilibrium constant in the case studies are calculated at the average boiling point of the reactants.

4. Results and discussion

4.1. Assessment of generic cases

Group I_p ($T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$) is the predominant class of quaternary systems for the application of reactive distillation, as the products are the lightest and the heaviest

compounds; hence, high purity products can be anticipated in the top and bottom outlets. In this assessment, relative volatilities α_{CA} and α_{BD} are set to 2.0 and 1.5, respectively, to be consistent with the specified volatilities ($\alpha_{AB} = 2$, $\alpha_{CD} = 6$).

Fig. 8 depicts the applicability graphs of group I_p in equilibrium- and kinetically-controlled conditions, for chemical equilibrium constants of 0.01, 0.1 and 1. For each graph, the equilibrium-limited case gives the largest applicability area (bounded by the solid line), as expected. Other lines indicate the applicability boundaries for kinetically controlled reactive distillation; clearly, the applicability area decreases as Da/K_{eq}, i.e. the Damköhler number, is reduced.
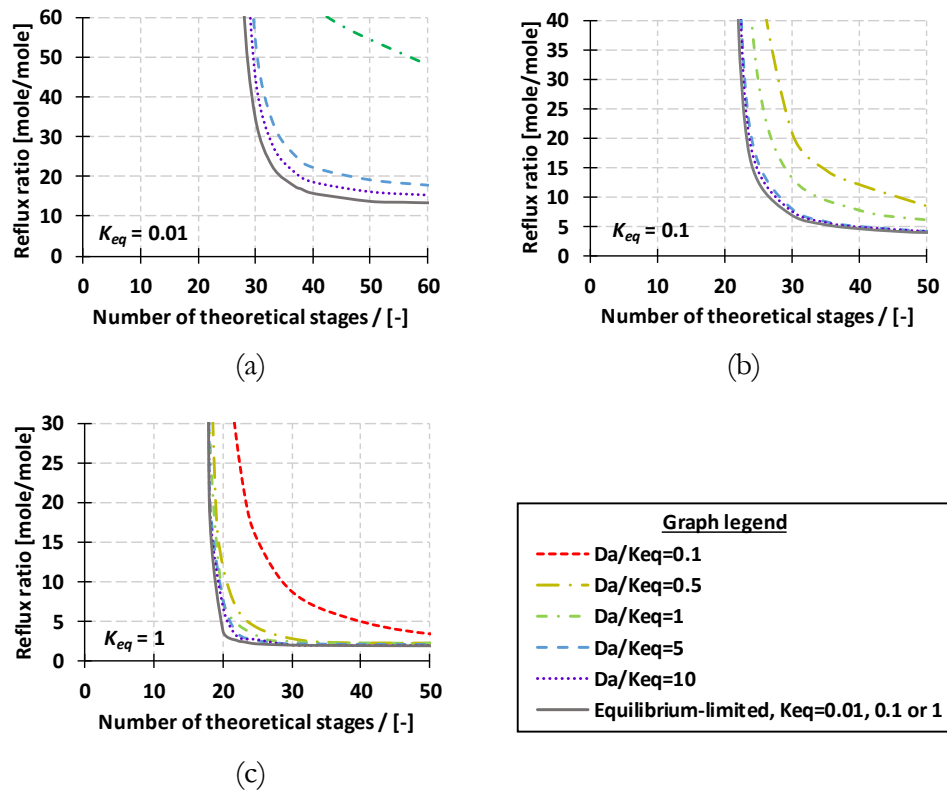
Fig. 8. Applicability graphs for group I_p: (a) $K_{eq} = 0.01$, (b) $K_{eq} = 0.1$ and (c) $K_{eq} = 1$.

The applicability area is determined as the ratio Da/K_{eq} is varied from 0.1 to 10; Fig. 8 shows that the high Da/K_{eq} ratios have a similar applicability area to that of equilibrium-controlled columns. The applicability bounds are almost equivalent when Da/K_{eq} is at least 5, except where the equilibrium constant is relatively low (e.g. $K_{eq} = 0.01$). In general, as K_{eq} increases, the kinetically controlled and equilibrium-controlled boundaries become

more similar. It is concluded that, in this case, $Da/K_{eq} = 5$ can be used as an initial criterion for determining reactive distillation design parameters.

Next, the assessment is performed for another group of quaternary systems—group III_p ($T_{b,C} < T_{b,A} < T_{b,D} < T_{b,B}$), with relative volatilities $\alpha_{CA} = 4$, $\alpha_{AD} = 1.5$ and $\alpha_{DB} = 1.4$. That product D is an intermediate-boiling compound in the reactive distillation column potentially causes more reaction and separation challenges, relative to group I_p. Hence, the number of theoretical stages and reflux ratio of a reactive distillation column for this group are usually larger than those for group I_p (Muthia et al., 2019; 2018b).

Fig. 9 depicts the applicability graphs of group III_p for chemical equilibrium constants of 0.01, 0.1 and 1. The application of reactive distillation is not beneficial for $K_{eq} = 0.01$ as the minimum reflux ratio is too high to be practical ($RR_{min} > 50$); therefore, this assessment only concerns chemical equilibrium constants of 0.1 and 1. As observed for group I_p, Da/K_{eq} values of 5 or greater have applicability areas that are only slightly smaller than those for equilibrium-limited reactive distillation. Again, for lower values of the equilibrium constant, the kinetically controlled column under-performs more. An initial criterion for selecting reactive distillation design parameters is to design for $Da/K_{eq} \geq 5$; this finding is consistent with that for group I_p.
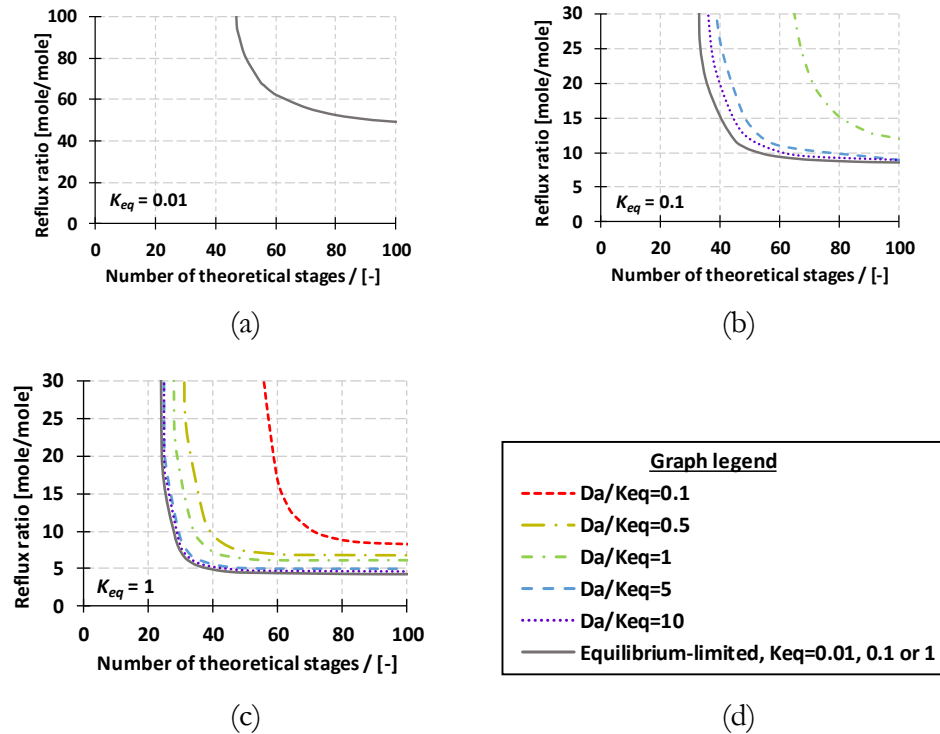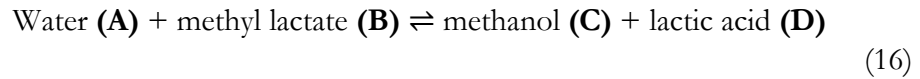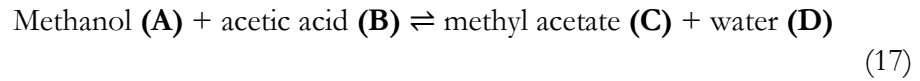

Fig. 9. Applicability graphs in group III_p: (a) $K_{eq} = 0.01$, (b) $K_{eq} = 0.1$ and (c) $K_{eq} = 1$.

4.2. Case studies

Fig. 8 and Fig. 9 demonstrate the approach for generic cases, where relative volatilities and the equilibrium constant are assumed constant in the column. Two case studies aim to validate the findings for the generic cases: hydrolysis of methyl lactate (Eq. 2) and synthesis of methyl acetate by esterification (Eq. 3), representing groups I_p and III_p, respectively. Unlike ideal generic systems, the azeotropes present in these cases are expected to hinder the reactive distillation.

$$\text{Water } \textbf{(A)} + \text{methyl lactate } \textbf{(B)} \rightleftharpoons \text{methanol } \textbf{(C)} + \text{lactic acid } \textbf{(D)}$$

(16)

T_b (°C)	100.0	144.8	64.7	216.9

$$\text{Methanol } \textbf{(A)} + \text{acetic acid } \textbf{(B)} \rightleftharpoons \text{methyl acetate } \textbf{(C)} + \text{water } \textbf{(D)}$$

(17)

T_b (°C)	64.7	117.9	56.9	100.0

Sanz et al. (2004) present temperature-dependent K_{eq} and k_f (mole g_{cat}^{-1} min^{-1}) relationships for the hydrolysis of methyl lactate, where an azeotrope forms between water (97 mole%) and methyl lactate (3 mole%) at 99.8 °C.

$$\ln(K_{eq}) = 2.6 - 1954.2 / T$$

(18)

$$k_f = 1.65 \cdot 10^5 \cdot \exp\left(-50,910 / R \cdot T\right)$$

(19)

In the second case, two homogeneous azeotropes exist (methyl acetate (65.9 mole%)–methanol (34.1 mole%) at 53.7°C and methyl acetate (89 mole%)–water (11 mole%) at 56.4 °C. Pöpken et al. (2000) present correlations for K_{eq} and k_f (mole g_{cat}^{-1} min^{-1}) as:

$$\ln(K_{eq}) = -3.82 + 2408.65 / T$$

(20)

$$k_f = 4.94 \cdot 10^2 \cdot \exp(-49,190 / R \cdot T)$$

(21)

Fig. 10 presents reactive distillation applicability graphs for both case studies generated via extensive simulation studies using Aspen Plus. It may be observed that the proposal to use $Da/K_{eq} \geq 5$ as an initial criterion for designing a reactive distillation column applies very well: in both cases, the boundary line of the applicability region is very close to that in equilibrium-controlled conditions.
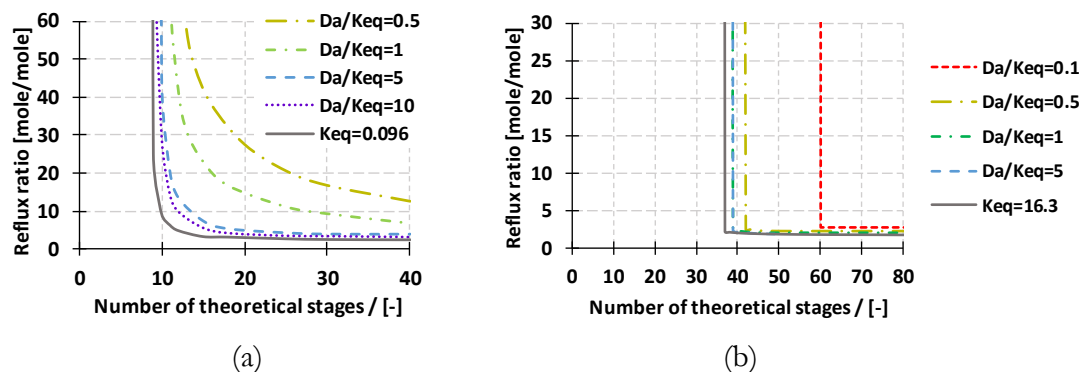
Fig. 10. Applicability graphs for validation studies: (a) Hydrolysis of methyl lactate; (b) Synthesis of methyl acetate

5. Conclusions

The mapping method has been successfully employed to visualise the performance of reactive distillation in equilibrium-limited and kinetically controlled reactions. This work proposes $Da/K_{eq} \geq 5$ as a criterion to initialise reactive distillation design parameters, namely liquid residence time, catalyst selection and catalyst loading, for groups I_p and III_p. This approach should enable the range of design parameters selection to be narrowed, to avoid time-consuming exploration of options at the conceptual design stage. This heuristic may also be useful for other groups of quaternary systems.

Acknowledgements

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Chapter 6

Conclusions and Recommendations

- General conclusions
- Recommendations for future work

This chapter concludes key findings of this work and critically evaluates the development of a new conceptual tool proposed in this thesis. Furthermore, this chapter discusses some recommendations for future work.

6.1. General Conclusions

Reactive distillation (RD) processes potentially provide significant advantages over conventional reaction-separation processes, such as increased conversion and selectivity, lower energy requirement and reduced costs. The application of reactive distillation in the chemical industry is, unfortunately, hindered by difficulties in understanding and designing reactive distillation columns (Harmsen, 2007; Li et al., 2016; Taylor and Krishna, 2000). Despite many design methods reported in literature, the assessment of the performance of reactive distillation remains difficult and time consuming (Almeida-Rivera et al., 2004; Segovia-Hernández et al., 2015). Driven by these problems, this research has generated and developed a novel method to assess the applicability of reactive distillation. This new approach is called the mapping method, which is featured by applicability graphs of reactive distillation processes, i.e. plots of reflux ratio vs the number of theoretical stages, to indicate the performance of reactive distillation.

The development of the mapping method fulfils the gaps in approaches to screen and design reactive distillation processes. Available methods, which are classified into graphical, optimisation-based and heuristic approaches, are capable of initialising the design of reactive distillation columns. However, the application of those methodologies is restrained by their weaknesses: (1) huge computational effort is needed when multiple RD configurations are taken into consideration, and (2) the application of existing methods requires an in-depth knowledge of reactive distillation processes. This study invents the mapping method that uses pre-calculated performance information for hypothetical and idealised generic cases, i.e. pre-generated applicability graphs of generic cases, to reflect the applicability of reactive distillation to industrially relevant chemical reactions; therefore, less computational effort is required. The assessment of the applicability of reactive distillation using this method is carried out by correlating only two or three process characteristics—relative volatilities of compounds (α_{ij}), chemical equilibrium constants (K_{eq}) and, in kinetically controlled reactions, Damköhler numbers

(Da) —with the column performance, thus giving an ease for process engineers in the chemical industry to employ the method.

This work has developed the mapping method for quaternary reaction systems (A + B $\rightleftharpoons$ C + D) as this class of reaction systems is frequently encountered in the chemical industry for the application of reactive distillation (Hiwale et al., 2004; Luyben and Yu, 2008; Sharma and Mahajani, 2002). The development of the mapping method has been carried out systematically, in which the complexities of the assessed chemical reactions are increased gradually in different chapters. At the beginning, **Chapter 3** focuses on (near-) ideal quaternary reaction systems, which are not hindered by the formation of azeotropes, with both reactants as mid-boiling compounds, $T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$. With this order of boiling points, an ease of products separation is expected as the most volatile product is largely present at the top and the least volatile product is predominantly available at the bottom part of RD columns. Then, **Chapter 4** presents the development of the mapping method for (near-) ideal quaternary reaction systems considering various orders of boiling points of compounds: group I_p ($T_{b,C} < T_{b,A} < T_{b,B} < T_{b,D}$), group I_r ($T_{b,A} < T_{b,C} < T_{b,D} < T_{b,B}$), group III_p ($T_{b,C} < T_{b,A} < T_{b,D} < T_{b,B}$) and group III_r ($T_{b,A} < T_{b,C} < T_{b,B} < T_{b,D}$); the naming convention of these groups follow rules set by Luyben and Yu (2008). Finally, **Chapter 5** extends the development of the mapping method for non-ideal quaternary reaction systems with various orders of boiling point orders, which contain homogeneous and/or heterogeneous azeotropes.

This work has demonstrated the usefulness of the mapping method, as follows.

1. The mapping method is applied to investigate the effects of key process characteristics considered in the proposed method—relative volatilities of compounds, chemical equilibrium constants and Damköhler numbers—on the performance of reactive distillation, as demonstrated in **Chapter 3**. While relative volatilities are used as a process characteristic for the design of conventional distillation columns with shortcut methods, the interplay of these three process characteristics is newly introduced in the mapping method to assess the design and performance of reactive distillation. This study shows that relative volatilities influence not only separation but also reaction performance, as indicated by the increase of both numbers of reactive and separation stages when relative volatilities of compounds are lowered. In a very slow reaction, the

design parameters of reaction distillation including liquid residence time, catalyst loading and catalyst type—characterised by the Damköhler number—are the controlling parameters regardless of the chemical equilibrium constant. In particular, this work shows that for the cases with both high and low chemical equilibrium constants, i.e. K_{eq} values are 0.1 and 10, the column configurations for both cases are identical for a low Damköhler number—Da ≤ 0.01.

2. The mapping method is used to generate heuristics for the initialisation of reactive distillation designs, as demonstrated in **Chapters 4 and 5**.

- The findings in this study suggest that the boiling point orders of compounds strongly affect the applicability and the optimal feed stage locations of reactive distillation columns. When relative volatilities of different groups of quaternary reaction systems are similar, the preliminary economic ranking of quaternary reaction systems (A + B $\rightleftharpoons$ C + D) for the operation of conventional reactive distillation is group I_p, group III_p and group III_r, respectively from the lowest to the highest cost. The preliminary economic ranking is obtained by taking into account both reflux ratio and the number of theoretical stages as key parameters affecting cost of reactive distillation columns. This finding is in agreement with the results obtained by Luyben and Yu (2008) who performed detailed economic calculations. Furthermore, this study has evaluated the optimal feed stage locations for generic cases by considering all possible combinations of feed stages of both reactants and accounting for reflux ratio as the key parameter of an optimal design. The results of this assessment is in agreement with the finding reported by Tang et al. (2005) who performed rigorous simulations and detailed economic calculations to find the optimal feed stage locations for the production of methyl acetate. This agreement suggests that, for group III_p ($T_{b,C} < T_{b,A} < T_{b,D} < T_{b,B}$), the lowest reflux ratio is attained when the inlet of the least volatile reactant is placed at the top of the reactive zone, while the inlet of the most volatile reactant is located within the reactive zone of a RD column.

- The performance of reactive distillation in both equilibrium-limited and kinetically controlled reactions has been visualised and compared by using applicability graphs. When the Damköhler number is high enough, the applicability area of a kinetically controlled reaction is similar to that of its equilibrium-limited reaction. This work suggests that a ratio of Da/K_{eq} of 5 or more can be used to initialise the design of

reactive distillation columns for groups I_p and III_p of quaternary reaction systems, as validated by two case studies: hydrolysis of methyl lactate and synthesis of methyl acetate via esterification. This heuristic is expected to be applicable for other groups in quaternary reaction systems. The application of this rule of thumb narrows the range of possible RD design parameters; therefore, it saves time when assessing the applicability of reactive distillation at the conceptual level.

3. The mapping method is employed to assess the applicability of reactive distillation to both near-ideal and non-ideal reaction systems, as demonstrated in **Chapters 3 and 5**. The applicability of reactive distillation to real reaction systems is reflected only from pre-generated applicability graphs of generic cases; therefore, rigorous simulations are not required for real systems in the early phase of the conceptual level.

The development of the mapping method suggests that the applicability of reactive distillation to a real system can be predicted by overlaying the representative key process characteristics considered in the mapping method onto the applicability graphs of generic cases. This research has set approaches to quantify representative process characteristics of real reaction systems requiring huge simulations effort that is only needed to be performed during the method development. Representative chemical equilibrium constant and the Damköhler number are calculated at the average boiling temperatures of both reactants, as the temperature profile in the reactive zone of a reactive distillation column is usually within the range of the reactant boiling temperatures. Representative relative volatilities of compounds, α_{CA}, α_{AB} and α_{BD}, are calculated using the compositions of the mixed reactants, top and bottom streams. In this study, with an equimolar ratio of reactants and a targeted product purity of ≥ 99 mole%, the representative relative volatilities are calculated for 50 mole% of pure reactants and 99 mole% of pure products. The relative volatility of compounds forming a binary azeotrope is set at 1 to represent the difficult separation caused by the azeotrope.

The validation of the mapping method using two case studies representing near-ideal reactions—transesterification of methyl benzoate with benzyl alcohol and hydrolysis of methyl lactate—shows the promising application of the mapping method, as the prediction of the applicability of reactive distillation based on generic applicability graphs is in agreement with the results of rigorous simulations for the case studies. Furthermore, the suitability of the mapping method to predict the applicability of

reactive distillation to non-ideal reaction systems is validated using five case studies that represent unique separation challenges due to the presence of homogeneous and/or heterogeneous azeotropes. The mapping method is shown by three case studies to be suitable for non-ideal systems containing only an azeotrope formed by binary mixtures affecting the value of any representative relative volatilities. While, other two case studies confirm that the method is unsuitable for strongly non-ideal mixtures. This limitation is analogous with that of shortcut methods for conventional distillation, such as the Fenske-Underwood-Gilliland method, where assumed constant relative volatilities are unable to provide accurate column designs for the separation of strongly non-ideal mixtures.

Ultimately, the development of the mapping method gives rise to the synthesis of a new framework for assessing the applicability of reactive distillation that includes heuristics and knowledge developed in **Chapters 3, 4 and 5**. The sequential steps in the framework comprise the recognition of the group of boiling point orders to quickly identify the opportunity of a RD process being not/more/less applicable, the calculation of the representative relative volatilities, chemical equilibrium constant and the Damköhler number of the assessed real system to select the most relevant pre-prepared applicability graphs of generic cases, the assessment of the RD applicability by using generic applicability graphs, and finally, the preliminary economic evaluation to compare reactive distillation with conventional processes. The proposed framework enables help for process engineers in the chemical industry who wish to explore potential benefits offered by reactive distillation, while minimising the engineering time required to identify potentially attractive design solutions.

Finally, the methodology for the validation of the method, the generation of generic applicability graphs and the use of the mapping method by end-users has been clarified extensively in **Chapter 5**. Before end-users, i.e. process engineers in the chemical industry, apply the mapping method, a team of researchers or engineers acting as map generators, produce a bundle of many generic applicability maps with different sets of fixed relative volatilities, chemical equilibrium constants and reaction rates. Once those graphs have been generated through multiple simulations, further rigorous simulations are not required and the graphs can be used multiple times for process screening. End-users

employ the mapping method in a similar way to a global positioning system (GPS), where determined representative relative volatilities of compounds and calculated equilibrium constant (and the Damköhler number for a kinetically controlled reaction) are overlaid onto generic applicability graphs that are pre-generated by map generators. The invention of this new approach has successfully addressed research questions that arise in Section 1.2 of Chapter 1 in this thesis: one can perform the assessment of the RD applicability with less computational effort by applying the mapping method.

6.2. Recommendations for Future Work

This work has developed, demonstrated and validated the usefulness of the mapping method for assessing the applicability reactive distillation. Some limitations in the present work are:

- the assessed reactions are limited to quaternary reaction systems ($A + B \rightleftharpoons C + D$),
- conventional reactive distillation is the only type of RD configurations considered,
- a single reaction is assumed to take place in reactive distillation columns, i.e. there are no side reactions neither consecutive reactions, and
- there is no inert taken into consideration in the feed inlets.

The following studies are recommended to be performed in the future to extend the development of the mapping method.

1. The suitability of the mapping method should be checked and validated for binary ($A \rightleftharpoons B$) and ternary ($A + B \rightleftharpoons C$ or $A \rightleftharpoons B + C$) reaction systems as they are also commonly encountered in the industrial application of reactive distillation. For those reaction systems, approaches to determine representative process characteristics in the mapping method, i.e. relative volatilities of compounds, chemical equilibrium constants and Damköhler numbers, should be further developed.

2. Further work should further develop a systematic framework to select the most beneficial reactive distillation setup, such as conventional reactive distillation, heterogeneous azeotropic reactive distillation, reactive dividing wall column, reactive distillation with pre- and side reactors, for a given reaction system. Depending on the

complexities of reactions, such as a complex process with side and/or consecutive reactions, other RD configurations than conventional reactive distillation might offer more beneficial RD processes.

3. Further work needs to be performed to develop the mapping method for chemical systems with the presence of an inert. In some industrial cases, an inert is inseparable from a reactant and it is fed simultaneously with the desired reactant to a reactive distillation column. The presence of an inert affects the approach in the mapping method to determine representative relative volatilities of compounds for the assessed reaction systems.

4. Further work should be performed to extend the use of the mapping method to assess the applicability, feasibility, sustainability and controllability of reactive distillation. To bring a reactive distillation process to the commercial level, different aspects including technical, economic, environmental and safety need to be considered. Besides the RD applicability, the consideration of other aspects would strengthen the capability of the mapping method in evaluating promising RD designs.

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