A framework to evaluate the impact of uncertainty on design and operation of reactive distillation systems

A. Tsatse[1)], S.R.G. Oudenhoven[2)], A.J.B. ten Kate[2)], E. Sorensen[1)*]

1) Department of Chemical Engineering, University College London, Torrington Place, WC1E 7JE London, UK
2) Nouryon, Zutphenseweg 10, 7418 AJ Deventer, the Netherlands
** Corresponding author*

Abstract

This work is motivated by the current obstacles hindering the implementation of reactive distillation in industry, mainly related to the complexities of its design and control, as well as the impact of uncertainties thereupon. A framework to systematically investigate the impact of uncertainty on reactive distillation processes is presented, considering the relevant control system and potential redesign of the column, possibly including additional ancillary equipment, with the aim to make the process more robust and to mitigate risk. The framework also considers the impact of operational uncertainties, showing that a system which can tolerate design uncertainty may nevertheless still be sensitive to operational uncertainties, in which case the mitigation strategies presented in this work should be applied to enhance system robustness. This framework can be used in an early design stage to quantify the impact of specific input parameters on process performance and costs, and it can therefore be used to steer the experimental work to focus on determining the most critical parameters for a reactive distillation process. Three case studies are considered showing that, for reactive distillation, uncertainty in the rate constant has a more significant impact on the system performance than a similar uncertainty in chemical equilibrium.

Keywords: reactive distillation, design, operation, control, uncertainty

1. Introduction

1.1 Motivation

Reactive distillation is an intensified process where reaction and separation take place simultaneously in a single unit. Due to the integration of the two different phenomena, the impact of model uncertainty at the design stage, or disturbances during operation, can be amplified and must therefore be carefully considered to evaluate their impact on the process performance and to develop mitigation strategies in order to tackle potential production failure issues.

In a previous contribution (Tsatse et al. 2021a), we provided a methodology for how to simultaneously optimise the design (total number of stages, feed stage locations etc.) and operation (reflux ratio, bottoms flow rate etc.) of a reactive distillation process at steady state using MINLP optimisation based on a complex reactive distillation superstructure and a cost-based objective function. In a follow-up investigation (Tsatse et al. 2021b), we evaluated

different control strategies for the optimal steady state designs previously found and investigated how design parameters such as total number of stages and tray liquid holdup can be taken into consideration to enhance process controllability. However, reactive distillation models, as all simulation models, depend heavily on accurate parameter input, and as design and control studies are typically performed considering a single fixed value of each parameter a sufficiently large range of uncertainty in this input may render the design solution suboptimal and/or the process operation infeasible. As a result, the type and the impact of these uncertainties must be carefully investigated during the process design phase in order to ensure process robustness and flexibility. In general, parameters whose values may be uncertain are present at the design stage, during operation and/or in the commercial environment, uncertainty is therefore always present, although the degree of uncertainty typically reduces along a project lifetime. The robustness and flexibility of a process is evaluated by its ability to maintain, under the given uncertainty, the defined key process indicators (KPIs) such as product quality, operability, safety, environmental impact, economic performance etc.

For distillation processes, including reactive distillation, design uncertainty is mainly introduced through the basic process data. For reactive distillation, these are the experimentally determined reaction rates and chemical equilibrium as well as physical property data (volatilities, heat of vaporization, density etc.). The timeframe for which market forecasts are made is in industry typically only a few years (usually 1-3 years), and as a result, there is limited time to collect (during feasibility screening and design study phases) all the basic process data (which will still have some uncertainty due to experiments, analysis etc.) required to very accurately develop a new intensified process. In addition, operational deficiencies may occur during operation due to catalyst deactivation, fouling, feed flow rate and/or composition changes, disturbances in cooling water/heating medium flow rates etc. Finally, uncertainty in the commercial environment may be caused by deviation in the forecasted market demand and corresponding product prices or even related to feedstock availability and pricing.

As a result, given that uncertainty may be introduced during both process development and operation and from various sources, and in some cases appear as combination of these, it is essential for the design engineer to be aware of their impact. If the uncertainties and/or disturbances cannot be tolerated and they result in process failures, mitigation steps have to be taken such as revising design and operation as well as investing time and resources to reduce the parameter uncertainty range, and these potential mitigation alternatives must be considered at the design stage.

This work will therefore develop a framework to consider mitigation strategies for reactive distillation systems in order to tackle issues related to design and operational uncertainties. Using this framework, time to develop either a preliminary design used for cost comparisons or a final process design can be reduced; decisions can be revised at the design stage to improve system robustness; in certain cases pilot scale testing may be skipped (reducing the project time by approximately 1-2 years); and investment decisions can be better supported.

1.2 Literature review

The first reference to the importance of uncertainty in relation to process design within the PSE community was made by the pioneering work of Grossmann and Sargent (Grossmann and Sargent 1978) who proposed a methodology for the rational overdesign of a chemical plant when uncertain parameters, expressed as variables within a specific range, exist. Soon, further progress was made regarding the consideration of input uncertainty to ensure feasible operation (Halemane and Grossmann 1983). Their method included the

optimisation of the design of a process by solving a nonlinear infinite programming problem. In both contributions, a multi-period design optimisation problem was formed to develop plants (e.g. heat exchanger networks) that can operate under a wide range of conditions while still satisfying process specifications.

Soon after the first publications which dealt with uncertainty, the concept of flexibility was introduced. Swaney and Grossmann (Swaney and Grossmann 1985) first introduced a quantitative feasibility index to measure the ability of a plant to operate under a range of parameter uncertainty without violating the imposed constraints and specifications, and this was later used to redesign an existing process to enhance its flexibility (Pistikopoulos and Grossmann 1988). Pistikopoulos and Mazzuchi (Pistikopoulos and Mazzuchi 1990) extended the concept of flexibility to systems under the influence of stochastic disturbances by considering Gaussian distribution of parametric uncertainty, e.g. in inlet temperatures of hot/cold streams in heat exchangers, whilst Ierapetritou and Pistikopoulos (Ierapetritou and Pistikopoulos 1994) incorporated process flexibility and economic loss in operational planning by solving a mixed-integer programming formulation.

Flexibility and controllability of a process were later integrated into a unified framework in the work presented by Mohideen and colleagues (Mohideen et al. 1996), and by Bahri and colleagues (Bahri et al. 1997) where the interaction between control and process design under uncertainty was discussed. In a more recent approach, Sánchez-Sánchez and Ricardez-Sandoval (Sánchez-Sánchez and Ricardez-Sandoval 2013) considered the optimisation of the design and control of a ternary distillation column in order to ensure dynamic feasibility and flexibility under uncertainty in feed composition. Their work was inspired by the work conducted by Mohideen and colleagues (Mohideen et al. 1996), however, in the contribution by Sánchez-Sánchez and Ricardez-Sandoval they perform the dynamic flexibility and feasibility analyses simultaneously, and not sequentially as in Mohideen's work, by having the single MINLP formed complemented with simulations of the closed-loop dynamic model. In the majority of the contributions mentioned so far, the methodology was illustrated using Heat Exchanger Networks (HENs), Continuous Stirred Tank Reactors (CSTRs) or distillation columns as practical examples.

Gani and Constantinou (Gani and Constantinou 1996), in a more theoretical approach, discussed from a process/product design point of view, the need for estimation methods for thermodynamic properties (mainly for pure components) which can give consistent values within a large application range and with reliable extrapolation. At that time, reactive distillation also started attracting attention and as a result, a similar observation to the observation made by Gani and Constantinou (Gani and Constantinou 1996) was made by Pilavachi and collaborators (Pilavachi et al. 1997), who identified the existence of a set of sensitive thermodynamic properties for reactive distillation systems. They also discussed that the prediction of the properties needs to be made using appropriate thermophysical properties models as incorrect choices of the latter may have a significant impact on the performance of the system.

Several authors have considered input uncertainty for the design of reactive distillation systems. Seferlis and Grievink (Seferlis and Grievink 2001) optimised the design of an ethyl acetate reactive distillation column considering perturbations in reaction kinetics, feed composition and column pressure using orthogonal collocation on finite elements to solve the optimisation problem formed. Kaymak and Luyben (Kaymak and Luyben 2004, Kaymak et al. 2004) investigated the impact of uncertainties in relative volatilities and in chemical equilibrium on the design and steady-state performance of reactive distillation systems. They highlighted that when relative volatilities are not constant and decrease significantly for temperatures required for reasonable reaction rates, then reactive distillation may become no longer economically attractive over the conventional process of reactor followed by separation. In terms of chemical equilibrium, it was shown that reducing chemical

equilibrium from the steady state value leads to more expensive reactive distillation processes as the design becomes more demanding, e.g. by requiring an increase in the number of reactive trays.

Most contributions for reactive distillation systems deal with uncertainty by incorporating this into the optimisation algorithm used for the design of the control structure. Tian and colleagues (Tian et al. 2003) developed pattern-based predictive control for a pilot-scale reactive distillation process for the synthesis of ethyl tert-butyl ether (ETBE). The authors used feature pattern-based prediction incorporated with conventional proportional-integral (PI) control in order to eliminate the requirement of good process models, therefore tolerating a large degree of process uncertainties. Olanrewaju and Al-Arfaj (Olanrewaju and Al-Arfaj 2006) considered uncertainty in relative volatilities in order to design and implement a state estimator in a feedback control system of a generic reactive distillation process, highlighting the need for an additional online analyser when a highly erroneous process model is considered. Paramasivan and Kienle (Paramasivan and Kienle 2012) considered disturbances in vapour boil-up rate, reflux ratio and the purity of the two fresh feeds for an ideal reactive distillation column. They used simultaneous optimisation of a decentralised control structure and controller parameters under uncertainty using the sigma point method. The latter was found superior compared to heuristic or deterministic approaches for the given Mixed-Integer Dynamic Optimisation (MIDO) problem under uncertainty, which was successfully solved to design inferential control. Most recently, Haßkerl and collaborators (Haßkerl et al. 2018) discussed optimising control based on economics for a multi-product transesterification reaction. The controller was made robust under uncertainty in reaction equilibrium constants using control optimisation.

Very few contributions have simultaneously considered uncertainty in the optimisation of both the design and the control of a reactive distillation process. Georgiadis and colleagues (Georgiadis et al. 2002) compared simultaneous optimisation to sequential optimisation of the design and control system for an ethyl acetate reactive distillation column, considering uncertainty in the cooling water inlet temperature disturbance, by solving the MIDO problem formed. It was found that the simultaneous approach resulted in a process that was economically more attractive and more efficient in terms of control. Mansouri et al. suggested that designing the multi-element (2016a) and binary (2016b) reactive distillation process at the maximum driving force (i.e. difference in mole fraction of a component i between two coexisting phases) results in an optimal design in terms of controllability and operability when process disturbances are considered. Recently, Tian and collaborators (Tian et al. 2020) considered uncertainty in a unified framework for the design of flexible and operable reactive distillation processes, applying their methodology to the production of methyl tert-butyl ether (MTBE). The authors used a Generalised Modular Representation Framework (GMF) synthesis model to design a structure which guaranteed flexibility performance under feed flow rate uncertainty.

As stated above, a range of methods have been used to consider uncertainty for reactive distillation systems both in terms of design and operation. However, no contributions to date has provided insight into how the characteristics of uncertain parameters (their type, direction, range) impact on both the optimal steady state design of the process as well as on the corresponding dynamic performance during operation. More specifically, to the best of the authors' knowledge, no contributions have considered how, and to what extent, uncertainty impacts on the performance of the overall process and how this uncertainty can be considered in order to mitigate production failure issues. These issues could be the result of design uncertainty (uncertainty in kinetic parameters, tray efficiency uncertainty etc.) and/or operational uncertainties (e.g. feed composition disturbance, catalyst fouling, market demand change etc.).

The objective of this work is therefore to provide a framework for the control, design and process mitigation of production failure issues due to design and/or operational deficiencies, including an evaluation of the impact of different types of design and operational uncertainties on optimal reactive distillation processes. As examples, design uncertainty in reaction kinetic and separation performance parameters will be considered, in addition to operational disturbances in the form of feed flow rate disturbances and purity demand changes. The uncertainty is considered based on simulations within the Global System Analysis tool in gPROMS ProcessBuilder (Process Systems Enterprise 2020) as well as the framework developed and presented below.

2. Global System Analysis in gPROMS

In the previous section, the importance of evaluating the impact of uncertainties during the design phase of a reactive distillation process was highlighted and available methodologies for this in the existing literature were reviewed. This section will describe how uncertainty is implemented in the reactive distillation model framework considered in this work using the Global System Analysis (GSA) tool of gPROMS ProcessBuilder (Process Systems Enterprise 2020) for the performance of the uncertainty simulations. It will be described how, for instance, the impact of slower kinetics or more challenging relative volatilities on process performance can be evaluated when the type of uncertainty (e.g. in reaction kinetics or VLE parameters), and given certain performance criteria and/or specifications (also known as KPIs (e.g. product purity), is known.

The GSA tool within gPROMS ProcessBuilder can be used to perform multiple model evaluations (simulations) with deterministically and/or probabilistically selected model input (i.e. uncertain input). The outcome of these evaluations is then used to determine the uncertainty in the model output and thereby to evaluate model robustness. In more detail, by performing uncertainty simulations, the following investigations can be considered (there are others):

- Prediction of the effect of parameter uncertainty on plant performance and profitability;
- Prediction of the effect of variability in raw material on product quality;
- Quantification of the risk of plant performance problems due to operational deficiencies.

As the input considered in this work is deterministic only (more details included in Section 4.3), its input is sampled along a grid. When probabilistic input is considered, the uncertainty investigation within the GSA tool can be performed through Monte Carlo simulations, but this was considered beyond the scope of this work.

The procedure followed to perform a GSA analysis is presented in Figure 1. The procedure is exactly the same regardless of whether the mathematical model is considered in steady state or dynamic mode and is explained below. The reader is directed to our previous work (Tsatse et al. 2021a, Tsatse et al. 2021b) for a detailed description of the steady-state and dynamic configuration of reactive distillation models considered, along with the relevant equations, related to the design and control of the process, respectively. Assuming an initialised base case, a GSA file is created in gPROMS where the user specifies a number of parameters for the process (i.e. model) considered which determine the type of input considered (deterministic/probabilistic) and the sample generation method; the uncertainty factors (along with their probability distribution); as well as the output considered (Process Systems Enterprise 2020):

- **Sample generation method**: This selection, which is relevant for probabilistic factors only and therefore not for this work, determines how the generated random data set will fill the uncertainty space and what the selected seed is (which determines the starting point of this data set). This was not of relevance in this work as only deterministic input was considered, hence the default values for the sample generation method (pseudo-random sampling) and seed (0) were used. For the deterministic simulations performed in this work, the number of samples equals to the number of uncertainty simulations performed, as one simulation is performed for each value of the uncertain parameter. For instance, when 100 different pre-exponential factors (i.e. the uncertain parameter) are considered, the number of samples equals to 100. For more information, the reader is directed to the GSA user guide (Process Systems Enterprise 2020).
- **Uncertainty factors and model responses**: For the analysis to be performed, input variables under uncertainty consideration (named as *factors*, for instance reaction kinetic parameters in this work), and output variables on which the impact of uncertainty will be investigated (named as *responses*, for instance product purities), must be defined. The selection of ranges (lower/upper bounds), distributions and constraints for the factors must be done carefully as the selection can have a large impact on the estimated ranges and distributions for the responses.
- **Probability distribution**: The user has to select the type of distribution to be applied to the uncertainty factors. For individual factors, normal/uniform/discrete distribution, gridded set etc., are some of the possible variability/probability selections. For grouped factors (i.e. factors which vary similarly), multivariate normal or discrete distribution, as well as multivariate enumerated set, are the possible choices.

When factors (along with their ranges, constraints etc.), responses and the sample generation method have been defined, the user can perform the analysis. The number of total realisations (i.e. simulations) of the model to be performed depends on the type and method of analysis and for uncertainty analysis is equal to $N_d \cdot N$, where N_d is the number of deterministic cases and N is the number of user-defined uncertainty scenarios. Uncertainty simulations are usually fast to perform, although time increases significantly for higher sample numbers and/or complex flowsheets with slow initialisation procedures. More details are included in Section 4.3.

3. Methodology and origins of design uncertainties

This section discusses the potential origins of design uncertainties within the process considered, followed by the presentation of the methodology developed and used in this work.

3.1 Origins of design uncertainties

Before presenting in detail the design uncertainties considered in this work, it is important to explain how uncertainties usually appear in the design of a reactive distillation process. During the initial design stage (screening phase), basic data is typically limited and usually obtained through screening experiments or from industrial experience of the considered process. In this early design phase, the number of possible process alternatives is already reduced to a small number of options, typically only 2 or 3. Knowing which parameters are critical to the overall cost of the project, and properly understanding their impact, can contribute to making a sound final process decision. In the second phase, when the selected alternatives are investigated in more detail, more information/data is typically collected and/or becomes

available which, however, usually still contains a certain level of uncertainty originating from the way the data is obtained (i.e. experimental work, parameter estimation etc.). The goal in this phase is typically to obtain sufficient data to improve the initial design choice, as the time required for implementation (the market opportunity) is very important and usually short, and therefore limited time is available to reduce the uncertainties. Errors or uncertainties in basic data in this phase can be due to:

- **Experimental work and/or equipment errors**: Such errors include impurities or inaccurate concentration of reactants, errors in sensor readings, insufficiently mixed liquid phase, wrong recording of sampling time, continuation of reaction between sampling time and analysis time, analytical errors etc. In VLE measurements for reactive distillation there is also the issue of reaction between components which can lead to VLE measurement errors.

- **Models used to describe the experimental trends**: Mathematical models are always a simplification of real behaviour. For reactions, errors can originate from the selected reaction mechanism and the units used (kg/l, mol/l, activity, mol/mol etc.) for the reaction rate expression basis (i.e. concentration, activity, mole fraction etc.). In addition, decisions need to be made regarding the importance of side-reactions and how VLE will be modelled (typically via binary interaction).

- **Fitting errors**: For an equilibrium reaction (as considered in this work), the forward rate constant is typically fitted based on the initial reaction rate (low conversion) whilst chemical equilibrium is based on the composition at the end of the reaction. Note that in a batch reactor (which is typically used to determine conversion time), different conversions are expressed as functions of time, whilst in a continuous reactive distillation column each stage operates at a specific conversion. It may happen that a significant part of the reactive column operates at conditions (e.g. close to equilibrium) that are rather difficult to fit accurately from batch experiments, thus leading to errors when fitting parameters.

As a result of the above, having a good understanding of the impact of design uncertainty in the early design phase using the framework developed in this work can help to direct the experimental efforts required in obtaining the required model parameters. The latter may be performed in later stages of the design in order to reduce uncertainty in the factors which have most impact on the performance of the process considered.

3.2 Framework

Based on the above, a general framework (Figure 2) has been developed to systematically investigate the impact of uncertainty on the design and operation of reactive distillation processes and to identify suitable mitigation strategies to tackle production failure issues. The framework is demonstrated for reactive distillation in this work, however, can also be extended to different distillation processes such as conventional distillation, dividing-wall columns etc, and can be performed using other approaches than the GSA approach used in this work. Based on the requirements and the desired outcome of the investigation, the framework can be applied to different case studies; different key performance indicators (KPIs) (e.g. product purity, recovery, production rate or total annualised costs); different types of uncertainties (e.g. in reaction kinetics or VLE); and different control schemes (for instance, single- or dual-point control). The framework can consider both uncertainty in design parameters and operational disturbances (Section 5.4) and can be applied for one uncertain parameter at a time or for combinations of uncertain parameters. The framework is illustrated

using three case studies (Section 4.1) and the results are presented in Section 5. The framework starts from an optimal solution, and first considers whether this design can tolerate the uncertainty considered based only on process control and if not, revision of the design (including addition of ancillary units) is considered. A brief introduction to the individual steps of the framework is provided, followed by detailed explanation and discussion on each step.

In brief, the individual steps of the framework are (see Figure 2):

1. Base case system optimisation at steady-state, without considering uncertainty.
2. Transition to the controlled dynamic process and performance of uncertainty simulations using GSA tool.
3. Decision based on whether the design can tolerate (framework termination) or not (see next step) the uncertainty introduced.
4. Control scheme revision, if required.
5. Reduction of uncertainty range, if required.
6. Process re-optimisation based on worst-case uncertainty.
7. Evaluation of whether a feasible solution has been achieved (see next step) or not (consideration of ancillary equipment).
8. Adjustment of process operation found in step 7 using the base-case input of the uncertain factors.
9. Framework termination.
10. Evaluation of mitigation options (not considered in this work).

A more detailed description of the individual steps is provided below:

1. Optimise the base case system at steady state without considering uncertainty. Optimisation can be performed using the superstructure methodology developed and presented in our previous work (Tsatse et al. 2021a). In this step, an optimal steady-state design (total number of stages, feed stage locations, reflux ratio, production rate and variables related to ancillary equipment, if present, e.g. pre-reactor dimensions, side-draw flow rates etc.) is found which meets the problem constraints (such as product quality constraints and other KPIs), and minimises or maximises the given objective function (e.g. the minimum production-based total annualised cost as considered in the case studies). This procedure cannot guarantee that a global optimum has been found, however, strategies to increase the possibility of locating the global optimum (e.g. perform the optimization using various initialization points) are discussed in detail in Tsatse et al. 2021a.
2. For this optimal design, now consider the system as a dynamic, controlled system. When multiple steady-states are present or expected, tighter control is required to ensure that the process remains around the desired operating regime (e.g. Kumar and Kaistha 2008). Based on the chosen control strategy (for instance see our previous work on controllability of reactive distillation systems (Tsatse et al. 2021b)), define the uncertainty range for the chosen variable(s) and the key performance indicators (KPIs), add this uncertainty to the problem description and run uncertainty simulations (see Section 2) to evaluate the impact of the uncertainty on the KPIs using for instance the GSA tool. For example, if the uncertain variable is a reaction kinetic factor and the user would like to investigate the impact of 100 different values of this factor within a specific range, the GSA tool will perform 100 different simulations (one for each kinetic factor value), initializing each simulation at steady state. This step will identify how robust the controlled optimal system is to the uncertainties considered, and will determine if the optimal design can still meet the specifications given this

uncertainty (control mitigation), and if not, how far away from the specifications the system may be.

It might be a temptation to perform this step using the steady-state model, however, this would not provide insight into how tolerant the system is towards operational uncertainty, as in the steady-state model all operational parameters (which in a dynamic model are considered degrees of freedom) are fixed.

3. If the whole uncertainty range considered is tolerated, and all specifications (e.g. purity, recovery, production rate) are still met, then the optimal design is robust (for the points considered within the uncertainty range) and the control strategy is able to mitigate the uncertainty, hence no further action is required (go to Step 9). Increasing the number of sample points (i.e. simulations) can further increase the confidence on process robustness, although will also increase the associated computational cost. If, on the other hand, some or all of the uncertainty range is not tolerated, then proceed to Step 4.
4. In Step 4, consider if the control scheme must, or can be, changed, either by including more control loops or by changing control parameters (this requires having an actual selection of control options and not just one option). If the control scheme can/should be revised, then revise it and repeat from Step 2. If not, then proceed to Step 5. For distillation, if for instance one-point control is initially envisioned and is found insufficient, then dual-point or advanced process control (e.g. Model Predictive Control etc.) should be considered.
5. In Step 5, the opportunity of reducing the uncertainty range considered is given. It may be that the uncertainty range considered can be reduced by investing time/resources in obtaining more accurate data. For example, uncertainty in experimental data can be reduced by increasing the amount of data collected (i.e. performing more experimental work) although this may delay the project and/or increase cost. However, it is expected that the smaller (i.e. more accurate) range will ultimately result in a less expensive design (compared to the design based on a wider uncertainty range), therefore justifying any extra cost or delay that may have occurred.

   If the uncertainty range can be reduced, either as the current range is wider than the typical precision by which these values can be determined in dedicated experiments, or because the current range could not be successfully accommodated by a new optimal design (found in Step 6), then reduce the uncertainty range and return to Step 2. If the range cannot be reduced, then proceed to Step 6.

If the optimised design from Step 1 is not able to meet the specifications for the uncertainty range considered, and the control scheme cannot be revised and the uncertainty range cannot be (further) reduced, then the current process design must be reconsidered. The starting point for this is the initial base-case system from Step 1. We propose that the design is re-optimised by including the worst-case uncertainty that led to the specifications being violated, in other words, using the worst-case input (i.e. the upper or lower bound of the uncertain parameter instead of the base case value). Selecting the worst-case input is a challenging task as this might not be straight-forward in some cases and in addition, it might be state- and input-dependent. In this case, the role of the trained engineer and their critical thinking is essential, as they need to select the values that are likely to have the worst impact on their process based on their experience. In the case when a combination of uncertain parameters is considered, the worst-case uncertainty (upper or lower bound) is introduced for the parameter that has the biggest impact on the system based on the previous investigations or for the combination of uncertain parameters that leads to the worst process performance, based on previous individual or combined (synergistic effects) investigations. Worst-case

scenarios where synergistic effects are present (i.e. several parameter settings are simultaneously beyond their base-case values and not necessarily on their upper or lower bound) can also be assessed using the framework presented but is not illustrated in the case studies in this work.

At this point, it is worth considering why uncertainty simulations were used (Steps 2-5) given that the system is now re-optimised using the worst-case input, which is a single point. By initially performing uncertainty simulations (Steps 2-5), the entire range of scenarios between the worst-case scenario and the best-case scenario can be investigated in order to explore the system behaviour, observe new trends and potentially allow the prediction of system behaviour beyond the current uncertainty bounds considered. The uncertainty simulations will also identify which uncertain parameter set have the most significant impact on the system performance. If simulations were performed just for the end-points of the uncertainty range (base case and worst cases based on lower and upper bounds), then this behaviour across the range would not be evaluated. Nevertheless, as will be explained later in Section 4.3, for uncertainty factors which cannot currently be considered in the GSA tool in gPROMS ProcessBuilder (i.e. VLE which is externally configured in Multiflash (Infochem 2019)), we have considered simulations just for the two end-points (i.e. lower and upper bound of the uncertainty range) due to this limitation in the software.

6. Based on the above, in Step 6, re-optimise the design, now based on the worst-case input of the parameters that led to specification violations for the original base-case optimal design; i.e. mitigate the uncertainty or risk by changing the design (design mitigation). The new design will have more demanding design/operational characteristics such as increased total number of stages, increased reflux ratio etc. for reactive distillation, but will now be able to tolerate even the worst uncertainty. It should be noted that if this optimisation had instead been performed for moderate uncertainty values (i.e. between the base- and worst-case input) in order to potentially reduce the cost of the new flexible design, then the new design might still not meet specifications using control mitigation for the entire uncertainty range. Therefore, the worst-case input is a sensible choice for the re-optimisation as it would always guarantee that all the uncertainty can be mitigated although most likely leading to a more expensive design. This re-optimised design will later be modified (Step 8).
7. If the optimisation is feasible and an acceptable solution that meets all the specifications has been found, then move to Step 8. If a feasible and/or acceptable solution is not achievable, then this is likely to mean that ancillary equipment must be added to the process to mitigate the uncertainty, such as pre-/side-reactors or additional distillation columns for reactive distillation. Ancillary equipment should then be added to the design and the framework restarted from Step 1 (process mitigation). If no ancillary equipment can be added (e.g. because all suitable ancillary units have already been considered but do not improve the performance), then the framework terminates and the uncertainty considered cannot be tolerated by the process using the mitigation strategies considered. When new processes are under development and/or at the design stage, such risks may be present. In situations when the framework presented indicates that the uncertainty considered cannot be tolerated using the mitigation options provided, it is then up to the project or business management team to decide what are the next steps, e.g. whether other solutions to tackle the expected uncertainty exist and should be investigated, whether the risk can be accepted, whether time and costs for further investigations are acceptable etc.

8. With the new optimal design found in Step 6 (new number of stages, feed stage locations, reflux ratio etc), which was obtained considering the worst-case uncertainty, return to the base-case values for the uncertain parameters (e.g. reaction kinetics) and adjust the main operational parameters (e.g. reflux ratio and bottoms flow rate) but keep the design parameters fixed (number of stages, feed stage locations etc) until that the same specifications as in Step 1 are met (e.g. same product purity and recovery). Return to Step 2 with this revised optimal design and operation to investigate the uncertainly for the revised process.
9. At Step 9, a flexible design (including design mitigation, control mitigation and/or process mitigation) that can meet the specifications for the uncertain scenarios considered has been found and no further action is needed. The additional cost associated with the flexible design is also considered at this step to assess the relative benefits of process improvement (i.e. improved certainty of process performance vs cost).
10. Further investigation is still required, for instance to include a safety evaluation, but this is not considered in this work.

The applicability of the framework outlined above was evaluated using three reactive distillation case studies, characterised by different combinations of reaction and separation parameters, and the outcomes of which are presented in the following.

An alternative to the developed methodology would ideally be using robust optimisation to simultaneously optimise the design and control of the process under input uncertainty and/or process disturbances. However, the superstructure to be optimised in this work includes a large range of process alternatives (for more details on the ancillary units included and the overall superstructure optimisation problem formed please see Tsatse et al. 2021a). Given that the steady-state optimisation of a flowsheet of such a high level of complexity (highly non-linear and highly non-convex) is challenging and optimisation may not always lead to a feasible solution, the authors believe that optimising the same superstructure dynamically, considering uncertainty at the same time would be computationally challenging, if not impossible.

4. Case studies

4.1 Systems considered

Tsatse et al. (Tsatse et al. 2021a) presented a methodology for how to determine the optimal design and operation (total number of stages, feed stage locations, reflux ratio etc.) of a reactive distillation process and illustrated this methodology for 15 different case studies based on a quaternary system of components A and B which react towards components C and D. The same optimisation methodology is considered in this work (Step 1) and illustrated using three of the same case studies (see Section 5). The impact of uncertainty is investigated in order to explore how rigorous the earlier identified designs of Tsatse et al. are under both design and operational uncertainties. The case studies consider systems of different separation difficulty as well as different kinetic characteristics to identify how these parameters impact the design of an economically attractive and flexible process, and to identify if the process is able to mitigate production failure issues due to design and/or operational deficiencies.

The separation difficulty is defined based on the relative volatilities between the components and for each, fast and/or slower kinetic expressions were investigated (Table 1). For all three case studies, the components were considered of equal density (900 kg/m^3), equal molecular weight (50 g/mol) and equal boiling point of the heavy reactant, component B (413 K). Equal density and molecular weight was considered for all components so as to reduce the degrees of freedom of the problem and ease the interpretation of the results. This boiling point was assumed to be fixed and all other volatilities were calculated using the heavy reactant as the reference in order to create the desired relative volatilities. It should be noted that these assumptions were made solely to ease the interpretation of the case studies, and the framework can of course be applied to systems without these assumptions/limitations.

A quaternary system is considered, in which the following auto-catalysed reversible reaction occurs in the liquid phase with component D as the desired product:

$$A + B \leftrightarrow C + D$$

The kinetic expressions for the forward (f) and backward (b) reaction rates are the following:

$$r_f = k_{f0} e^{-Ea_f/RT} C_A C_B$$

$$r_b = k_{b0} e^{-Ea_b/RT} C_C C_D$$

where reaction rate, r, is expressed in kmol/(m^3·s), pre-exponential kinetic factors, k_{f0} and k_{b0}, are expressed in m^3/(kmol·s), activation energy, E_a, is expressed in kJ/mol (assumed to be 80 kJ/mol for both directions), and component concentration C_i is expressed in kmol/m^3. Heat of reaction was assumed to be negligible, thus the activation energy is the same for both reaction directions and K_{eq} is independent of temperature, based on the previous assumptions.

Fast and slow kinetic characteristics were considered in combination with the relative volatility systems, resulting in the three case studies given in Table 1. The values of the reaction parameters as well as relative volatilities were selected based on industrial interest.

For the systems considered, the following assumptions are made:

1) Thermodynamic vapour-liquid phase equilibrium is assumed on every stage of the distillation columns.
2) Perfect mixing in the liquid and vapour phases on each tray was assumed.

3) Constant relative volatilities were assumed throughout the columns (reactive and non-reactive stages).
4) Pressure drop was calculated based on column hydraulics.
5) Reaction occurs only in the liquid phase.
6) All column stages (stages 2 to N_T-1) were considered reactive in the reactive column, with the same liquid holdup per reactive tray.
7) There was no heat loss or gain from the environment in any of the equipment used, therefore, all unit models were assumed to operate adiabatically. Heat sink effects (e.g. heating capacity of wall) were also ignored.

The feed streams to the overall system (Table 1) were one stream of reactant B (Feed 1 inFigure 3) of flow rate 12.6 kmol/hr, and one stream of reactant A (Feed 2 inFigure 3) of the same flow rate (1:1 feed molar ratio). This corresponds to 5 ktn/year of product D for full reactant conversion. The feeds were assumed to be at their boiling points at 1 atm. Liquid hold-up of the reactive distillation column was assumed equal for all reactive stages, fixed at 0.1 m^3/reactive tray.

The following three specifications are considered:

- bottom product purity ($x_{B,D} \geq 0.99$ mol/mol);
- product recovery ($x_{REC} \geq 0.90$ mol/mol, i.e. amount of component D in the bottom product divided by the total amount of component D generated from the reaction);
- bottoms flow rate (B ≥ 12.55 kmol/hr)

As KPIs are not necessarily problem constraints/specifications, in addition to these three KPIs, the values of the following KPIs were monitored in order to investigate the behaviour of the systems: top product purity ($x_{D,C}$); distillate flow rate (D); pressure at the top of the column (P_T); condenser and reboiler duties (Q_C and Q_R, respectively); reflux drum and sump liquid level (M_C and M_R, respectively); and molar reflux ratio (RR). With respect to the top product purity, in particular the composition of component C in the distillate ($x_{D,C}$), although this is considered a controlled variable, it is not used as a KPI as the steady-state optimisation is performed using product quality constraints only on the main product, component D, which is the heavy component leaving in the bottom stream. As a result, component C is not considered a product of interest (which is the case for typical esterifications where the top product is water) and the reason that its composition is controlled in the LV control configuration is only such that the system is under tighter control, taking advantage of all degrees of freedom (Tsatse et al. 2021b). (It should be noted, however, although not of interest in this work, the stream nevertheless needs to meet some specification even if it is later discarded). The aim is in this work therefore for the distillate to just remain at the set-point of the control loop. In addition, with regards to the bottom flow rate B, for which the base-case value is 12.6 kmol/hr, values down to 12.55 kmol/hr were considered acceptable, as a production rate of 12.55 kmol/hr still meets the desired production target of 5 ktn/yr of component D.

4.2 Control schemes configuration

This section describes the configuration of the dynamic controlled systems as implemented in this work (Step 2 of the framework), which is based on the work of Tsatse et al. (2021b). For any ancillary units considered (e.g. pre-reactor), perfect liquid level and temperature control is assumed as the main focus of the investigation is on the performance of the reactive distillation columns and additional control loops could introduce inconsistencies (i.e. additional assumptions) between the models.

For the reactive distillation systems, Figure 3 shows the configuration of the two control schemes which is used in this work for the reactive distillation columns. Two conventional

control schemes are considered: V-only (single-point) and LV (dual-point) control. In both control schemes, pressure at the top (stage 2) is controlled by the condenser duty (PI control, PC loop, K_c = 20 and τ = 12 min) and the liquid levels of the reflux drum (P-only, LCT loop, K_c = 2) and the sump (P-only, LCB loop, K_c = 2) are controlled by the distillate flow rate and bottoms flow rate, respectively. Reboiler duty is manipulated in order to control bottom product purity (PI control, CCB loop, K_c = 3 and τ = 25 min) (composition of component D, the main product). For LV control (which it should be noted is not always suitable when stoichiometric feed imbalance is expected as discussed in Tsatse et al. 2021b), additionally the top product purity (composition of component C, side product) is controlled (PI control, CCT loop, K_c = 3 and τ = 25 min) by manipulating the reflux ratio, expending all degrees of freedom of the system in this case. A reasonable alternative to direct composition control would be temperature inferential control, i.e. indirectly controlling composition by manipulating the temperature of a column tray where a sharp change in temperature profile is observed. However, as this tray would generally differ for each reactive distillation column considered, direct composition control was preferred to ensure that all composition control loops are configured in a consistent way. The tuning parameters remained the same for all case studies in order to ensure consistency with previous control investigations for the same case studies (see Tsatse et al. 2021b) and are based on typical values. These tuning parameters work well for the cases considered (see Tsatse et al. 2021b) as feed flow rate was fixed for all case studies and column dimensions were not significantly different leading to well-defined time constants. The extent of the impact of the uncertain parameters on these time constants, and subsequently on process performance, depends on the type of the uncertain parameters considered, as well as their corresponding uncertainty range, as expected.Controller tuning parameters could also be selected based on alternative methods, through optimisation for instance, to improve control performance. It should be noted that the framework presented in this work is not limited to the control configurations describe above and could be applied to other conventional control schemes such as DB, (L/D V/B) as well as advanced control strategies (e.g. model predictive control, adaptive control etc.).

4.3 Types of uncertainties considered

As mentioned above, uncertainty can be introduced in the process design by model uncertainty (model parameters), during dynamic operation through disturbances (process disturbances) and/or by the commercial environment (market changes etc.). All types are considered in this work in order to evaluate the tolerance of the system towards both design (lower frequency) uncertainty and towards operational (higher frequency) uncertainties/disturbances. The design uncertainties considered are in the reaction kinetics (in particular, in the forward pre-exponential kinetic factor, k_{f0} and chemical equilibrium, K_{eq} through varying the backward pre-exponential kinetic factor, k_{b0} and therefore overall varying the rate constant); in the separation performance (via the relative volatility between reactant B and product D, α_{BD}, which are the two components mainly found at the bottom of the column); as well as their combination (k_{f0} and α_{BD}, and K_{eq} and α_{BD}). The operational uncertainties considered are a feed flow rate disturbance, as well as a change in the target bottom product purity due to changing market demand.

4.3.1 Design uncertainty

a) Reaction kinetics

In this work, for the reaction kinetics, uncertainty in k_{f0} and K_{eq} is investigated. These two parameters are considered as they characterise the reaction rate equations of the system, and uncertainty in their values may lead to lower than expected reaction conversion, rendering

the design of the process inefficient. In order to consider faster/slower kinetics, where uncertainty may or may not be introduced in K_{eq}, two cases are investigated (Table 1):

a) k_{f0} is varied along with k_{b0} to keep K_{eq} constant
b) k_{f0} remained at the nominal value, varying K_{eq} and therefore, k_{b0}

In this work, the pre-exponential factors, which work as a measure for the whole reaction rate constant, are considered deterministic input, therefore the range generated for this input is not a result of probabilistic distribution but of sampling along a grid with specified values. The framework presented so far can, however, take probabilistic factors into consideration, in which case they can be investigated using Monte Carlo simulations within the GSA tool, as explained in Section 2, or via another calculation procedure.

The forward and backward pre-exponential factors are grouped and varied as a multivariate enumerated set within the GSA tool. Defining k_{f0} and k_{b0} as a multivariate enumerated set allows their varied values (i.e. grid) to be specified (so that their ratio always yields the desired K_{eq}) and associated with a scenario to facilitate the analysis of the responses. This is necessary as the ratio of k_{f0} and k_{b0} needs to be kept to the desired K_{eq} value and this cannot be guaranteed if uniform or normal distribution is applied to k_{f0} and k_{b0} individually. The number of combinations of k_{f0} and k_{b0} considered is 100 in a single scenario, therefore the number of model realisations (i.e. simulations or samples) performed once the GSA is completed is 100. The range of uncertainty was selected based on industrial experience whilst the number of samples was chosen based on the physical meaning of the parameters considered (i.e. reaction kinetics) as for the range considered, a much larger number of samples would indicate a very small step which would not be evident to the reaction/separation system itself and would also increase computational cost.

b) Separation performance

For uncertainty in separation performance (VLE), uncertainty in relative volatilities is considered. The relative volatility between the heavy reactant, component B, and the desired product, component D, (α_{BD}) was selected as the source of uncertainty, as this parameter impacts directly on the product purity and recovery which are the specifications for the steady-state optimisation.

For this type of uncertainty, GSA cannot be used due to the way VLE is imported into gPROMS ProcessBuilder, which is the software tool used in this work. As an alternative, the bounds of the uncertainty range are therefore instead investigated for two scenarios through simulations, worst-case and best-case, with the worst-case input being the lower bound, and the best-case input being the upper bound, of a_{BD}. If relative volatilities between the other components were to be considered (α_{CD}, α_{CA} etc.), the worst-case input would generally again be the lower bound, but would be the upper bound of a_{AB} as in that case it is harder to keep the reactants in the reactive zone.

4.3.2 Operational uncertainty

In addition to the design uncertainties mentioned above, operational uncertainties are considered as: a) a disturbance in the molar flow rate of the heavy feed (Feed B), and b) change of the bottom product purity specification ($x_{B,D}$) due to market demand. These two disturbances were considered as they are both considered industrially relevant scenarios for a reactive distillation process. In this work, the disturbances were introduced as sharp ramps over 500s as this is both numerically less challenging and industrially more relevant compared to a direct step change which is not the way a disturbance is usually introduced in a real system. The disturbances were introduced at time t=0.5 hr, whilst each simulation lasted t=15

hrs to ensure that the system had definitely reached the new steady state. It has to be noted that operational uncertainty was considered in parallel with design uncertainty, therefore for every pair of the uncertain parameters k_{f0} and k_{b0}, the disturbance was introduced, and the output of the uncertainty simulation was taken at the final time i.e. after the end of the 15 hrs.

5. Results & Discussion

The framework developed in this work is illustrated by considering three case studies (Table 1). The case studies were selected so that they explore all three types of mitigation strategies included in the framework (control, design and process revision) and are characterised by different combinations of reaction and separation parameters in order to investigate their impact on process flexibility. Case study 1 was selected as it is characterised by both favourable kinetics and relative volatilities. Case study 2 was selected as it is characterised by the same relative volatilities as Case study 1 although the kinetics are less favourable. As a result, the impact of slower kinetics on the performance of the system under uncertainty could be investigated. Finally, Case study 3 is characterised by favourable kinetics (as in Case study 1) but challenging relative volatilities so that the impact of less favourable volatilities on the performance of the system under uncertainty could be investigated. The optimal designs (Table 1) for the three case studies are found using the superstructure methodology described by Tsatse et al. (Tsatse et al. 2021a).

In this work, the uncertainty simulations using GSA in gPROMS ProcessBuilder v1.3.1 (Process Systems Enterprise 2020) needed approximately 0.2-5 min CPU time. The short times are due to the fact that the number of samples (100) and the number of factors (k_{f0} and k_{b0}) and responses (controlled and manipulated variables, objective function value) was moderate, as was the complexity of the flowsheet.

In the following, the impact of the uncertainties (design uncertainties in Sections 5.1 to 5.3 and operational uncertainties in Section 5.4) on the KPIs (presented in Section 4.1) is considered and appropriate mitigation strategies are applied. A production-based Total Annualised Cost (TAC) of the final process (see Tsatse et al. 2021a for more details) obtained using the framework in this work is compared to the corresponding production-based TAC of the initial optimal process (initial Stage 1) to evaluate the cost penalty required to design the process such that it can implicitly mitigate uncertainty.

5.1 Case study 1

In this section, the framework presented in Section 3 will be applied to Case study 1 considering uncertainty in reaction kinetics, (k_{f0} and K_{eq}, independently) first (Section 5.1.1) whilst combined uncertainty (in reaction kinetics and separation performance) will be considered next (Section 5.1.2), in order to evaluate the relative importance of the two uncertainty factors. Case study 1 is characterised by relative fast kinetics, large chemical equilibrium constant and favourable relative volatilities, i.e. all main process parameters are relatively favourable based on the operating window considered.

5.1.1 Uncertainty in reaction kinetics

As mentioned in Section 4.3, two cases (case a: uncertainty in k_{f0} so varying k_{b0} in order to keep K_{eq} in the base case value, case b: uncertainty in K_{eq} so fixing k_{f0} and varying k_{b0} to form the desired K_{eq} uncertainty values) are considered for uncertainty in kinetics. For both cases, the uncertainty range considered was ±50% based on industrial experience and the two pre-

exponential factors were grouped and varied as a multivariate enumerated set (i.e. 100 pairs or samples of the predefined values of the two pre-exponential factors to uniformly cover the uncertainty range). Such a high uncertainty will also allow the illustration of the framework properly. Based on the base-case values presented in Table 1, the value ranges considered are therefore:

a) $15.138 < k_{f0} = 30.276 < 45.414$ (10^9 m^3/(kmol·hr)) so
$0.187 < k_{b0} = 0.374 < 0.561$ (10^9 m^3/(kmol·hr)) to keep K_{eq} constant (here at 81)

b) $40.5 < K_{eq} = 81 < 121.5$, and since $k_{f0} = 30.276 \cdot 10^9$ m^3/(kmol·hr)
$0.249 < k_{b0} = 0.374 < 0.748$ (10^9 m^3/(kmol·hr))

In the following, the framework in Figure 2 will be applied with these uncertainties. The results will present KPIs as a function of the uncertain reaction kinetic parameters.

Step 1: Case study 1 is optimised (see Tsatse et al. 2021a) using base-case input and the optimal parameters are obtained (Table 1).

Step 2: In Step 2, uncertainty in kinetics is introduced in the dynamic, controlled, system initially using V-only control. The values of the KPIs, i.e. product purity ($x_{B,D}$), product recovery (x_{REC}), and bottoms production rate (B) are monitored in order to investigate whether the uncertainty is tolerated and if not, how far away from the specifications the system is. In addition, the values of condenser and reboiler duties (Q_R and Q_C) are presented in order to show the corresponding control actions along with the values of the top product purity ($x_{D,C}$) to also show the impact on top purity (although not controlled under V-only control).

Figure 4 (left: case a, right: case b) shows that the product purity ($x_{B,D}$) is maintained (top of Figure 4) by the V-only controlled system (consider the *V-only* lines), but this is only possible by reducing the bottom production rate (i.e. B < 12.55 kmol/hr, see Section 4.1) when k_{f0} drops below $18.2 \cdot 10^9$ m^3/(kmol·hr)) (top left of Figure 4). (Note that the red line ($x_{B,D}$-V only) overlaps with the blue line ($x_{B,D}$-LV)) This means that with the current optimal design and control configuration, slower kinetics (case a) down to $18.2 \cdot 10^9$ m^3/(kmol·hr)) can be mitigated by control action alone for the V-only control scheme. Uncertainty in K_{eq} does not impact on the performance of the system as for all the K_{eq} considered, the system met the specifications (right in Figure 4). This therefore shows that for this design and parameter set and the uncertainties considered, slower kinetics (k_{f0}) have a more significant impact on the performance than lower K_{eq}. It should be noted that the 50% uncertainty range considered for K_{eq} corresponds to a range of 86.4% to 91% conversion (the base case conversion, i.e. for K_{eq}=81, is 90%) which is not a broad range. Changes in the condenser and reboiler duties, Q_C and Q_R, as well as in the distillate composition, $x_{D,C}$, due to the uncertainty in the pre-exponential factors (k_{f0} and k_{b0}) (case a) are more significant compared to changes due to uncertainty in K_{eq} (case b), as expected. The recovery, x_{REC}, is well above (in fact equal to 1) its specification (0.90) for both uncertainty cases and for all the ranges considered (not shown).

Step 3: This step decides whether the current design can tolerate the uncertainty range. For both slower kinetics (case a) and lower equilibrium (case b), the purity is maintained, however, this is only possible with an undesired reduction in production rate (B) for slower kinetics (case a), which cannot be tolerated. Hence, we proceed to Step 4.

Step 4: Single-point (V-only) control is initially considered for the dynamic system, however, dual-point control can also be considered. We therefore return to Step 2 where we repeat the uncertainty simulations for the same range of uncertainty, now considering LV control for the dynamic system. In the LV control scheme, the pairings are exactly the same as in the V-only

control scheme but in addition, the top product purity ($x_{D,C}$) is controlled using molar reflux ratio (RR).

In the following, repeating steps will be indicated for all case studies using the symbol R (for *round Ri*) next to the associated framework step, to demonstrate the fact that this is the i^{th} time the framework starts from Step 2.

Step 2 (R2): The uncertainty range considered is introduced in the dynamic controlled system now using LV control scheme (consider the *LV* lines in Figure 4). As can be seen, the system is now able to tolerate the entire range of uncertainty in kinetics considered, not only in terms of product purity and recovery (not shown) but also in maintaining the production rate, B, at the desired level also for slower kinetics (case a). Changes in chemical equilibrium (case b) as expected do not have an impact on performance, similarly to the behaviour observed using V-only control. Changes in condenser and reboiler duties are slightly more significant for slower kinetics (case a) than for lower chemical equilibrium (case b), as observed previously for V-only control. The bottom plots of Figure 4 show the top product purity ($x_{D,C}$) and the corresponding changes of molar reflux ratio to maintain this, when LV control is applied and shows that the top purity is maintained at the set point.

Step 3 (R2): Since the uncertainty considered is now tolerated when LV control is implemented, no further design/control/process changes are required and we go directly to **Step 9**, and at this step, the procedure terminates. The user can now have confidence that the optimal design with the corresponding LV control can mitigate the uncertainties considered, here up to ±50% uncertainty in kinetics. As no revision of the design was required, the production-TAC remained at its initial optimal value of 2.073 €/kg.

5.1.2 Combined uncertainty in kinetics and separation performance

In the previous section, the only uncertainty considered was in the reaction kinetics. This section considers the effect of combined uncertainty in both reaction kinetics and in the separation performance and considers the optimal controlled system under LV control. In addition to the uncertainty in kinetics considered in the previous section, uncertainty in the relative volatility between the heaviest reactant B and the product D (α_{BD}) was considered in a reasonable range (±40%). A wider range would lead to reverse boiling point rankings, for which the current design would clearly be inefficient as shown by Tsatse et al. (2021a). Therefore, the lower bound for the uncertainty (i.e. worst-case input) was α_{BD}=1.2 and the upper bound (i.e. best-case input) was α_{BD}=2.8 as the base case value was α_{BD}=2. All the other relative volatilities remained the same, except for the volatility between components C and D, $\alpha_{CD,}$ which was changed accordingly. This was due to the fact that the boiling points of components A, B (the reference component for vapour pressure calculation), and C remained unchanged, therefore the relative volatilities between those components ($\alpha_{CA,}$ α_{AB}) remained the same as well. When the boiling point of component D changed in order to agree with the new value for α_{BD}, then α_{CD} had to be changed accordingly.
As mentioned in Section 4.3, uncertainty simulations as those presented above when considering uncertainty in kinetics cannot be performed for uncertainty in VLE using gPROMS ProcessBuilder, therefore worst- and best-case input must be introduced as input in the system separately in order to study the impact of those two bounds, in addition to the uncertainty in kinetics.
In the following, the framework described previously and presented in Figure 2 will be applied for the worst-case VLE uncertainty as this is a more challenging situation in terms of system

performance compared to the best-case VLE input for which the system will easily meet the specifications (not shown).

Step 1: Case study 1 is optimised using base-case input and the optimal parameters are obtained (Table 1) as before.

Step 2: In Step 2, uncertainty in kinetics is introduced in the dynamic, (LV) controlled system using the worst-case relative volatilities (α_{BD}=1.2). The results are presented in Figure 4 (lines indicated as *combined*), and it can be seen that even the combined VLE and kinetics uncertainty can be mitigated by LV control action alone. The bottom product purity ($x_{B,D}$) and recovery (x_{REC}, not shown), as well the bottoms product rate (B), meet the specifications for the entire range of uncertainty. However, it is shown that the changes that the system has to undertake, in terms of condenser and reboiler duties as well as reflux ratio, in order to meet the specifications under the combined uncertainty considered are much more significant compared to uncertainty in kinetics only (Figure 4), showing the significant impact of the combined uncertainty on the system. (Note that the set-point of the top product purity ($x_{D,C}$) is different between the initial design and the combined uncertainty design as only $x_{B,D}$ needs to meet a specification (of 0.99) and the value of $x_{D,C}$ is simply an output of the model based on its design and operational parameters, without any (optimisation) specification.)

Step 3: As the system is able to mitigate the combined uncertainty introduced, no further steps need to be considered and we can proceed to **Step 9**. At this point, the engineer can have confidence that with ±50% uncertainty in reaction kinetics and 40% reduction in relative volatility, the initial design, when controlled, will still be able to meet the product specifications under LV control. As no revision of the design was required, the production-TAC at the design phase remained in its initial value of 2.073 €/kg. However, when worst-case VLE and uncertain kinetics are encountered, the operational parameters (i.e. heating and cooling duties, reflux ratio, bottom flow rate etc.) must adjust to meet the specifications, leading to increased production-based TACs ranging from 2.240 €/kg (worst VLE and best-case kinetics) up to 2.480 €/kg (worst VLE and worst-case kinetics).

5.2 Case study 2

In this section, the framework presented in Section 3 is applied to Case study 2, considering uncertainty in reaction kinetics. Case study 2 is characterised by slower kinetics and lower chemical equilibrium compared to Case study 1, whilst the relative volatilities are the same as in Case study 1. The range of uncertainty in kinetics is again ±50%. The value ranges considered are therefore:

a) $3.78 < k_{f0} = 7.56 < 11.34$ (10^9 m^3/(kmol·hr)) so
   $1.68 < k_{b0} = 3.36 < 5.04$ (10^9 m^3/(kmol·hr)) to keep K_{eq} constant (here at 2.25)
b) $1.125 < K_{eq} = 2.25 < 3.375$, and since $k_{f0}= 7.56 \cdot 10^9$ m^3/(kmol·hr)
   $2.24 < k_{b0} = 3.36 < 6.72$ (10^9 m^3/(kmol·hr))

Step 1: The optimal parameters for Case study 2 are presented in Table 1. The optimal steady state design for Case study 2 is more demanding compared to the design of Case study 1, showing that slower kinetics do impact on the optimal steady state design and operation as additional reactive/separation stages as well as higher reflux ratio are required in the reactive distillation column to meet the specifications.

Step 2: In Step 2, uncertainty in kinetics is introduced in the dynamic, controlled system (LV control). LV control was selected as the starting point as it was previously shown for Case study 1 that a single point scheme cannot successfully control the process under uncertainty. The results from the uncertainty simulations are shown in Figure 6 (left: case a, right: case b).

First consider the lines labelled *initial*. Figure 6 shows that the bottom product purity are maintained (top of Figure 6) by the controlled system. Bottom product recovery (not shown) is also maintained at 1. Note that for faster kinetics (i.e. k_{f0} above $9.51 \cdot 10^9$ $m^3/(kmol \cdot hr)$), the simulations are infeasible (i.e. simulations cannot converge) and no results are shown. This is because for faster kinetics, the system can easily meet the top and bottom specifications and, unless the condenser and reboiler duties as well as reflux ratio are lowered compared to the base case, the system will exceed the specifications. For instance, for the fastest kinetics considered the system is able to reach top product purities up to 0.997 with the base-case reflux ratio (4.65), while maintaining the bottom specification of $x_{B,D}$=0.990. As a result, to maintain the top product purity set-point of 0.990, the reflux ratio needs to be lowered significantly, leading to unacceptably reduced column liquid flowrates given the specified column diameter and as a result, an infeasible simulation. This case study demonstrates one of the limitations of the computational tools and reminds the importance of the trained engineer to be critical. Although in practice a higher purity product is not an issue, the software solves the model in order to meet the given specification of 0.990 for the entire uncertainty range. As a result, it is not able to accept the solutions resulting in higher purity for some of the uncertainty values and therefore fails those simulations which in reality would be less challenging as the kinetics are faster. Consequently, although in reality the initial design would be able to tolerate the entire uncertainty range considered, this cannot be confirmed by the simulations. Although the design engineer would in practice be able to verify this, we will nevertheless proceed with the next step of the framework to illustrate the procedure to follow when the whole uncertainty range is not tolerated.

With the current optimal design and control configuration, and the given control set points, kinetics up to $9.51 \cdot 10^9$ $m^3/(kmol \cdot hr)$) can be mitigated by control action alone. Uncertainty in K_{eq} did not impact on the performance of the system as for all the K_{eq} considered, operation was feasible as the simulations converged and the system met the specifications (Figure 6, right). It has to be noted that, for Case study 2 and for a K_{eq}=2.25 (60% conversion) the 50% uncertainty range corresponds to 51.5% to 64.8% reaction conversion which is a larger range compared to Case study 1. However, for both cases the same observation is made, that k_{f0} and k_{b0} have a more significant impact than K_{eq} on the performance of the system under the uncertainty considered. This validates one of the most important benefits of reactive distillation as a process. The fact that the top and bottom products are continuously removed shifts the chemical equilibrium towards the products, therefore any potential reduction in chemical equilibrium is less evident in the system. Product recovery (not shown) under both forms of kinetic uncertainty (cases a and b) was well above specification (1.0 vs 0.90). Changes in condenser and reboiler duties as well as reflux ratio due to slower kinetics (case a) are more significant compared to changes in chemical equilibrium (case b), as expected.

Step 3: For Case study 2 and for both slower kinetics (case a) and lower equilibrium (case b), the purity is maintained, however, for faster kinetics (i.e. higher k_{f0}) the performance of the system cannot be evaluated as simulations/operations are infeasible, hence we proceed to Step 4. Note that even though Case study 1 had faster kinetics than case study 2, and increasing the speed of the reaction for Case study 2 towards that of Case study 1, the optimal design is different in the two cases and the performance can therefore not be directly compared.

Step 4: Dual-point control is already considered in this system and in order to illustrate the framework, the control scheme in this case study is considered suitable and will therefore not be revised. Thus, we proceed to Step 5.

Step 5: This step considers whether the uncertainty range can be reduced. In this case study, the uncertainty range is assumed to be the narrowest possible and should therefore not be reduced. As a result, we proceed to Step 6.

Step 6: As mentioned previously, the infeasible simulations are in this particular case study not of significance as the operation will clearly be practically feasible across the uncertainty range considered. Nevertheless, in order to demonstrate the framework we now re-optimise the design but now based on the worst-case uncertainty. Here, the worst-case input for reaction kinetics is the lowest kinetics values considered. Although faster kinetics lead to infeasible operation in this case, re-designing the system to be flexible based on the most challenging kinetics is expected to be more beneficial from a design and operation perspective (i.e. potential increase in number of stages will lead to smaller column diameter which will allow lower liquid flowrates for faster kinetics), compared to optimising the system using the best-case values which may result in a design unable to tolerate slower kinetics. Given that uncertainty in kinetics (case a) has a more significant impact than uncertainty in K_{eq}, the optimisation is performed for the uncertainty in kinetics (case a), i.e. $k_{f0}=3.78\cdot10^{9}$ ($m^3/(kmol\cdot hr)$) (minimum value) and $K_{eq}=2.25$ (base case value), and the results are given in the middle column of

Table 2. The results show that nine additional reactive/separation stages are required to meet the specifications using the worst-case input and the new column also has smaller diameter, as expected, and the reflux ratio has also increased.

Step 7: Since a feasible and acceptable solution was achievable, i.e. the specifications are met and the new design parameters are acceptable, we proceed to Step 8.

Step 8: The re-optimisation in Step 6 was performed assuming the worst-case situation in terms of uncertainty. The current design therefore represents the most stringent situation. In this step, we return to the base-case kinetics whilst maintaining these new design parameters for design, i.e. the number of stages and feed stage locations found in Step 6, but not necessarily the new operating parameters, to explore if the new design can now tolerate the entire uncertainty range based on only control mitigation. The operating parameters, here the reflux ratio, is now likely to be too high for normal conditions without disturbances, as the base case kinetics are faster than those considered for the re-optimisation. The product purity is therefore higher than the specification, hence the reflux ratio can be reduced until the purity is returned to the specification, which will also reduce the operating costs. The new reflux ratio required for the base-case kinetics is shown in the final column in

Table 2 and has been reduced from 5.75 to 3.48. (Note that this revision of the process is done in gPROMS ProcessBuilder by using the *Adjust specification* model, which offers the possibility of meeting a specification, in this case product purity, by varying (in a single simulation) a specified model variable, in this case reflux ratio).

Next, we return to Step 2, where uncertainty simulations are performed for the same range of uncertainty on the new flexible design found in Step 8.

Step 2 (R2): The uncertainty range considered is introduced in the new flexible, dynamic controlled system (LV control) and the results are shown in Figure 6 (lines indicated as *flexible*). The system is now able to tolerate the entire range of uncertainty in kinetics, not only in terms of product purity and product recovery (not shown) but also maintaining production rate at the desired level for slower kinetics (case a). Model evaluations (simulations) are now feasible for the entire range of uncertainty considered. Changes in condenser and reboiler duties as well as in reflux ratio, in other words the control actions for the system to maintain the controlled variables at the set-points, are more significant for slower kinetics (case a) than for lower chemical equilibrium (case b).

Step 3 (R2): As shown above, since the entire range of uncertainty is now tolerated and operation in the entire range is feasible, we go directly to **Step 9**. In this step, the procedure terminates. The user can now have confidence that the new flexible LV controlled design can mitigate the uncertainty considered, here up to ±50% uncertainty in kinetics. The case of combined uncertainty in both kinetics and VLE is not considered as Case study 2 has the same VLE as Case study 1 where uncertainty in VLE did not deteriorate process performance. It was therefore decided to focus on the impact of only the slower reaction kinetics for Case study 2. The framework could of course be used to consider combined uncertainty (not considered in this work).

Compared to the initial design, the new flexible design (including nine additional reactive-separation stages) can tolerate the uncertainty in kinetics considered, with an approximately 3% increase in the objective function as shown in

Table 2 (TAC=2.140 €/kg vs 2.195 €/kg) indicating an effective, and cost-attractive, mitigation option which is now able to meet the control specifications for both the top and bottom composition control loops (although for this particular case Component C in the top stream is considered waste).

5.3 Case study 3

In this section, the framework presented in Section 3 is applied to Case study 3, considering uncertainty in separation performance. Case study 3 is characterised by the same fast kinetics and large chemical equilibrium constant as for Case study 1 but with more challenging relative volatilities. This will allow the investigation of the impact of uncertainty in a system where VLE is more challenging whilst kinetics are favourable. The framework could of course be used to consider combined uncertainty (not considered in this work).

Uncertainty in relative volatility between the heaviest reactant B and the product D, $\alpha_{BD,}$ was initially considered to be in the same range as before (±40%). This range is considered as it allows, for this particular system, the investigation of the case where the impact of uncertainty leads to a change in boiling point ranking, which will clearly impact on the performance of the system. Therefore, the worst-case scenario was α_{BD}=0.72 (reverse boiling points as α_{BD} <1) and the best-case scenario was α_{BD}=1.68 (base case α_{BD}=1.2) and those two scenarios could be the result of wrong assumptions of the engineer with regards to system's VLE. All the other relative volatilities remained the same, except for α_{CD} which changed accordingly, as explained for Case study 1. As mentioned previously, only the end points of the uncertainty range are considered due to limitations in the software.

Step 1: The optimal parameters for Case study 3 are presented in Table 1. It can be seen that Case study 3 has a more demanding design and operation compared to Case study 1 showing that challenging relative volatilities lead to a requirement of additional reactive/separation stages as well as a higher reflux ratio in the reactive distillation column.

Step 2: In Step 2, uncertainty in VLE is introduced in the dynamic, controlled system based on LV control.

Table 3 shows that the best-case relative volatility is successfully accommodated by the system, as expected. This means that with the current optimal design and control configuration, larger relative volatilities can be mitigated by control action alone, which is obvious as the separation is now easier than expected.

Table 3 shows that for α_{BD}=1.68, it is easier for the system to meet the specifications, leading to lower condenser and reboiler duties as well as lower reflux ratio compared to the values obtained for α_{BD}=1.20. However, it can also be seen that the worst-case scenario (α_{BD}=0.72) cannot be successfully simulated. This is clearly because with the current design, the system cannot meet the product specifications given the worst-case VLE as for α_{BD}=0.72, the heaviest component is reactant B, therefore, given the incomplete conversion, the target top and bottom product purities cannot be achieved.

At this point, it is useful to compare the behaviour of Case study 1 and Case study 3. As Case study 3 has the same favourable reaction kinetics but more challenging separation characteristics compared to Case study 1, and Case study 1 could tolerate the same uncertainty in separation performance considered, it can be seen that when one of the two phenomena of the process is more challenging, mitigation strategies are likely to be required to tackle the impact of design uncertainty. This observation was also made in Case study 2 showing that, when uncertainty is considered, either in reaction kinetics or separation performance (i.e. even in one of the two key system characteristics)it is possible that the system cannot tolerate potential design uncertainty, requiring the application of mitigation strategies.

Step 3: For the worst-case VLE, uncertainty cannot be tolerated and the simulation is infeasible, hence we proceed to Step 4.

Step 4: Dual-point control is already considered in this system and is considered suitable and will therefore not be revised. Thus, we proceed to Step 5.

Step 5: To illustrate the use of the framework, it will be assumed that the uncertainty range can be reduced. This is not unusual for the later stages of a design as more information may have become available (e.g. more experimental work). In the following, the uncertainty range is thus reduced to ±20%. Thus, the worst-case scenario now is α_{BD}=0.96 and the best-case scenario is α_{BD}=1.44. Using the new uncertainty range, we return to Step 2.

Step 2 (R2): Table 3 shows that the best-case relative volatility (α_{BD}=1.44) is successfully accommodated by the system. This means that with the current optimal design and control configuration, larger α_{BD} up to 1.44 can easily be mitigated by control action alone as expected from previous results. However, it can also be seen that the worst-case scenario (α_{BD}=0.96) cannot be, again, successfully simulated as for α_{BD}=0.96 the boiling point range is still reversed.

Step 3 (R2): For the worst-case, the VLE uncertainty cannot be tolerated, hence we proceed to Step 4.

Step 4 (R2): Dual-point control is already considered in this system, and it is assumed that more advanced control is not to be considered, thus we proceed to Step 5.

Step 5 (R2): It is now assumed that the uncertainty range considered cannot be further reduced, therefore we proceed to Step 6.

Step 6 (R2): Here, the worst-case input for VLE is α_{BD}=0.96 hence re-optimisation of the system is performed.

Step 7 (R2): The optimisation of a single reactive distillation column was infeasible given the worst case volatility as even for a very large number of stages (N_T=100) the system could still not meet the specifications and provide an optimal solution for the worst-case VLE. The existence of ancillary equipment must therefore be considered as this may increase the reaction and/or separation efficiency of the overall process and as a result may lead to a feasible solution. Thus, we add the option of using ancillary equipment and return to Step 1. As a first attempt, we add a pre-reactor (CSTR) as in previous work (Tsatse et al. 2021a) it was

found that a pre-reactor is included in the optimal solution for systems with this type of reverse boiling point rankings.

Step 1 (R3): Case study 3, now including the pre-reactor, was re-optimised using the base-case input (Table 1) and the optimal parameters are presented in the final column of

Table 4 showing that the cost of the optimal process, including the pre-reactor, is TAC = 2.441 €/kg, i.e. a 10% increase from the initial design.

Next, we proceed to Step 2, where simulations are performed for the same VLE uncertainty on the new optimal design found in Step 1 using the base-case VLE and the process including the ancillary equipment.

Step 2 (R3): The two VLE scenarios considered (worst case and best case) are introduced in the new flexible, LV controlled system.

Table 5 shows that the best-case relative volatility is successfully accommodated by the system, and shows that for α_{BD}=1.44, it is easier for the system to meet the specifications, leading to lower condenser and reboiler duty as well as lower reflux ratio compared to the values obtained for α_{BD}=1.2. More significantly, it can be seen that the worst-case scenario (α_{BD}=0.96) again cannot be successfully simulated. This is because with the current design, the economically optimal system (optimised with the base-case input) cannot meet the product specifications given the worst-case VLE, even with the existence of the pre-reactor. This indicates that re-designing the existing process including the pre-reactor is required so that the system can tolerate the uncertainty in VLE considered.

Step 3 (R3): For the worst-case VLE, operation is not feasible and simulation fails, hence we proceed to Step 4.

Step 4 (R3): Dual-point control is already considered thus we proceed to Step 5.

Step 5 (R3): The uncertainty range is assumed to be the narrowest possible and should therefore not be reduced and we proceed to Step 6.

Step 6 (R3): The worst-case input for VLE is α_{BD}=0.96 and the results of the re-optimisation are presented in

Table 6. The results show that a larger pre-reactor and 13 additional reactive/separation stages are needed to meet the specifications when considering the worst-case input.

Step 7 (R3): Since a feasible and acceptable solution was achievable, i.e. the specifications are met and the new design parameters are acceptable (middle column of Table 6), we proceed to Step 8.

Step 8 (R3): The re-optimisation in Step 6 was performed assuming the worst-case situation in terms of uncertainty. In this step we fix the design and consider the operation of the process. The new reflux ratio is shown in the final column in

Table 6 and has been reduced from 16.6 to 10.96. Next, we return to Step 2.

Step 2 (R4): The uncertain VLE scenarios considered are introduced in the new flexible, dynamic (LV) controlled system and the results are shown in

Table 7. The system is now finally able to tolerate both worst- and best-case uncertainty in relative volatility, and product purity, product recovery (not shown) and bottoms rate are maintained at their target values. Changes in condenser and reboiler duties as well as in reflux ratio, are more significant for worst- rather than best-case uncertainty, as expected.

Step 3 (R4): Since the entire range of uncertainty is now tolerated and operation in the entire range is feasible, we go directly to **Step 9**. In this step, the procedure terminates. The user can now have confidence that the new flexible LV controlled design, including a pre-reactor, can mitigate the uncertainty considered, here up to ±20% uncertainty in α_{BD}.

Comparing the very initial design (see Table 6, first column), the new flexible design (see Table 6, final column) including a pre-reactor and 23 additional reactive-separation stages can tolerate the ±20% uncertainty in VLE considered with a 16% increase in the objective function as shown in

Table 6 (TAC=2.210 €/kg vs 2.572 €/kg) indicating a cost effective mitigation option.

5.4 Impact of operational disturbances

Having considered design uncertainties in the previous sections, this section considers the impact of operational disturbances on process performance, in addition to the design uncertainties investigated so far. The goal is to evaluate the tolerance of the system towards the combined effect of design and operational uncertainty, and to investigate how far the system is from the specifications, in case it is unable of meeting those. Two different disturbances were considered and applied to Case study 1:

a) a molar flow rate disturbance in the heavy feed (2% increase) (Section 5.4.1)
b) a change in target purity ($x_{B,D}$) from 0.990 to 0.995 required due to market demand (Section 5.4.2)

5.4.1 Operational disturbance 1: Feed flow disturbance

In this section, the performance of the system under a load disturbance in addition to design uncertainties is investigated. A 2% increase in Feed B (heavy feed) flow rate is considered in addition to both kinetics uncertainty and VLE uncertainty. Case study 1 is considered and suitable mitigation strategies are proposed.

Step 1: As before and given in Table 1.

Step 2: In Step 2, a 2% increase in Feed B (heavy feed) flow rate was introduced in the LV controlled system, and considered in conjunction with combined uncertainty in both separation (VLE) efficiency and kinetics. The investigated disturbance level of 2% was chosen for computational reasons as a larger feed flow rate increase would require very wide bounds for the operational parameters, thereby increasing the computational cost and complexity for initialisation and convergence purposes. The worst-case VLE design uncertainty (α_{BD}=1.2) was considered as this scenario was expected to have the worst impact on the performance of the system, as was the design uncertainty in kinetics (the design uncertainties as presented in Section 5.1), combining both types of uncertainty, design and operation. Uncertainty

simulations were performed to evaluate how the system responds to the feed flow rate disturbance, in addition to uncertain kinetics and the worst-case VLE, and the results are shown in Figure 7. As mentioned in section 4.3.2, the disturbances were introduced at time t=0.5 hr, whilst each simulation lasted t=15 hrs to ensure that the system had definitely reached the new steady state and the output of the uncertainty simulation was taken at the final time i.e. after the end of the 15 hrs (the same also applies in section 5.4.2).

First consider the lines labelled *initial*. It can be seen that for the worst-case VLE uncertainty and uncertain kinetics (for the latter both in cases a) and b)) in addition to the feed flow rate disturbance, the system cannot meet the desired production rate (12.6 kmol/hr), reducing the production rates down to 10.7 kmol/hr due to the reduced production of component D. For all cases, bottom product purity and recovery (not shown) remain at their target values, however, not the top product purity, as expected, due to the additional amount of component B needed to now be removed over the top. Figure 7 also shows the changes in condenser and reboiler duties as well as in reflux ratio. For the latter, reflux ratio reaches the upper bound without being able to meet the target top product purity. The maximum reflux ratio was set to 150, although practically any number above 10 will result in a very low distillate flow rate and to very high internal flow rates. From Figure 7 it appears that the effect of low chemical equilibrium (case b) seems more significant than slow kinetics (case a), which is not what was observed so far. This is because in both cases, the reflux ratio reaches a very high value in which almost all of the overhead stream (which mainly consists of component C) returns to the column, shifting the chemical equilibrium to the left towards the reactants, therefore making it harder for the system to reach the specifications. As the reflux ratio is at the upper bound, however, this result is not conclusive and results presented later will confirm that when no variable hits their bounds, the slower kinetics (case a) are indeed more impactful than lower chemical equilibrium (case b), showing that this reverse trend was only due to the variable hitting the bound.

Step 3: For both slower kinetics (case a) and lower equilibrium (case b), the purity is maintained, however, this is only possible with reduced production rate hence we proceed to Step 4.

Step 4: Dual-point control is already considered and we proceed to Step 5.

Step 5: The uncertainty range of kinetics and VLE remains constant to be consistent with Section 5.1 and for the feed flow disturbance the value is considered reasonable (both from an academic and industrial perspective) and should therefore not be reduced. As a result, we proceed to Step 6.

Step 6: Here, the worst-case input for reaction kinetics is the lowest kinetics values considered and the worst-case VLE. Feed flow rate disturbance is not considered for the re-optimisation, as in previous work (Tsatse et al. 2021b) we have shown that this type of operational disturbances (when only these are present) are easily rejected by the system. Although the disturbance in the feed stoichiometric ratio can lead to purity violations when strict purity control is considered for both product streams, in this case we have a 97% purity specification at the top (and not 99% or above) so a larger column which can undertake larger changes in operational variables exhibits a larger tolerance to the disturbance under two-point control. As a result, for Step 6, only worst-case kinetics and worst-case VLE are considered. The re-optimisation is therefore performed for uncertainty in kinetics (as this is usually more impactful as shown so far), i.e. $k_{f0}=15.138\cdot10^9$ ($m^3/(kmol\cdot hr)$) and $K_{eq}=81$, as well as for $\alpha_{BD}=1.2$. The results are given in Table 8 and show that seven additional reactive/separation stages are needed to meet the specifications using the worst-case combined input.

Step 7: Since a feasible and acceptable solution was achievable, i.e. the specifications are met and the new design parameters are acceptable, we proceed to Step 8.

Step 8: The re-optimisation in Step 6 was performed assuming the worst-case situation in terms of uncertainty. Next the new optimal design is relaxed by allowing a change in the operational parameters. The new reflux ratio required for the base-case kinetics is shown in Table 8 and has been reduced from 4.54 to 2.72. Next, we return to Step 2, where uncertainty simulations are performed for the same range of uncertainty on the new optimal design found in Step 8 with the base-case kinetics.

Step 2 (R2): The uncertainty range considered is introduced in the new flexible LV controlled system and the results are shown in Figure 7 (lines indicated as *flexible*). The system is now able to tolerate the entire range of uncertainty in kinetics, VLE and in the feed flow rate increase considered, not only in terms of product purity and product recovery (not shown) but also maintaining production rate at the desired level for case a. Changes in condenser and reboiler duties as well as in reflux ratio, are more significant for slow kinetics than for lower chemical equilibrium, which is the observed behaviour so far given that the reflux ratio now has lower and more reasonable values. In this way, the choice of re-optimisation using the worst-case input of slow kinetics (case a) rather than low chemical equilibrium (case b) is validated. In addition, changes in the manipulated variables are less significant for the flexible design compared to the initial design, as expected, which is also desired from a safety perspective.

Step 3 (R2): Since the entire range of combined uncertainty is now tolerated, we go directly to **Step 9**, and in this step, the procedure terminates. The user can now have confidence that the new flexible controlled design can mitigate the uncertainty considered, here up to ±50% uncertainty in kinetics, -40% in relative volatility and a 2% feed flow rate increase, under LV control.

Comparing the initial design to the new flexible design (including seven additional reactive-separation stages), the new design can tolerate the uncertainty in kinetics and VLE, as well as the operational uncertainty considered, with a 2% increase in the objective function as shown in Table 8 (TAC=2.114 €/kg vs 2.073 €/kg) indicating a cost effective mitigation option.

5.4.2 Operational disturbance 2: Set-point product purity increase

So far, the impact of design uncertainty (Sections 5.1-5.3), as well as the impact of undesired operational disturbance (Section 5.4.1) on the performance of a reactive distillation process have been investigated. It is also important to investigate how the system responds to a desired change in product criteria (or customer demand). Therefore, the second operational disturbance investigated is the increase of the target bottom product purity, $x_{B,D}$, from 0.990 to 0.995 due to market demand. This investigation aims to evaluate the flexibility of the system to adjust to a product purity specification increase under combined design uncertainty, considering both kinetics uncertainty and VLE uncertainty. Case study 1 is again considered.

Step 1: Case study 1 was presented in Table 1.

Step 2: VLE uncertainty and kinetics uncertainty was considered as presented in Section 5.1 and uncertainty simulations were performed as shown in Figure 8Figure 7. The system is able to tolerate the entire range of uncertainty in kinetics considered for all three VLE scenarios (worst, base, best) as well as maintain the increased product purity specification (0.995 mole ratio of component D) in the bottom stream whilst also maintaining the production rate at the desired level. (Note that the lines for product purity are overlapping in the figure). It is

therefore shown that in this case, the impact of a load disturbance (feed flow rate disturbance shown in Section 5.4.1) is more significant than the impact of a tighter product purity specifications.

For condenser and reboiler duties and reflux ratio, slower kinetics are more significant than lower chemical equilibrium, showing that similarly to design uncertainties, for operational disturbances, uncertain equilibrium has less impact than uncertain rate constants (i.e. pre-exponential factors). The most significant changes are observed for the worst-case VLE as expected, however, unlike the feed flow disturbance, the initial design is able to meet specifications. Also, it is noticed that the base- and best-case VLE systems undertake similar and smaller changes to meet specifications comparing to the worst-case VLE system.

Step 3: For all cases, the purity is maintained along with the desired production rate for the product purity set-point change. As a result, we directly go to **Step 9**. In this step, the procedure terminates. The user can now have confidence that the initial controlled design can mitigate the uncertainty considered, here up to ±50% uncertainty in kinetics, ±40% in relative volatility and a 0.5% product purity specification increase, under LV control. As no revision of the design was required, the initial production-TAC remained at its initial value of 2.073 €/kg. However, for the worst-case VLE and uncertainties in reaction kinetics, in addition to the target product purity change, the production-based TACs ranged from 2.609 €/kg (worst-case VLE, best-case kinetics) up to 3.080 €/kg (worst-case VLE, worst-case kinetics). This change in cost stems from the changes in operational variables (e.g. reboiler duty etc.) due to process control and reflects nearly a 50% increase in costs which is a considerable difference compared to the initial estimated cost.

6. Conclusions

In this work, a framework for how to consider the impact of uncertainty on reactive distillation systems is presented. Both design and operational uncertainties were considered and the framework was demonstrated using three case studies with different reaction and separation characteristics. Mitigation strategies for reactive distillation systems were considered, however, the framework can be extended also to other distillation-based processes and for different control schemes and can also be used for different uncertainties and KPIs to reflect different process requirements.

The case studies illustrated that an economically optimal process may nevertheless be inefficient when design uncertainty (for instance in reaction kinetics and separation performance) and/or operational uncertainty (for instance in feed flow rate and target product purity changes) is considered, and that different mitigation strategies may be required to make the process more robust depending on the reaction and separation characteristics of the system, including the addition of ancillary equipment (e.g. a pre-reactor) to meet specifications under the uncertainty considered. For the case studies considered, it was found that uncertainty in rate constant (slower/faster kinetics) affected the performance to a larger extent than uncertainty in reaction equilibrium (equilibrium conversion).

The findings indicate that when uncertainty is expected in a reactive distillation process, a careful consideration of its impact is essential as an economically optimal steady state design solution may be very sensitive to uncertainties and therefore revision of its design and control strategy may be required to improve its robustness. As this revision is associated with increased cost, the framework thus provides a basis to make an assessment of the relative benefits (process robustness vs cost) helping to make a more profound business decision.

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Figures and Tables

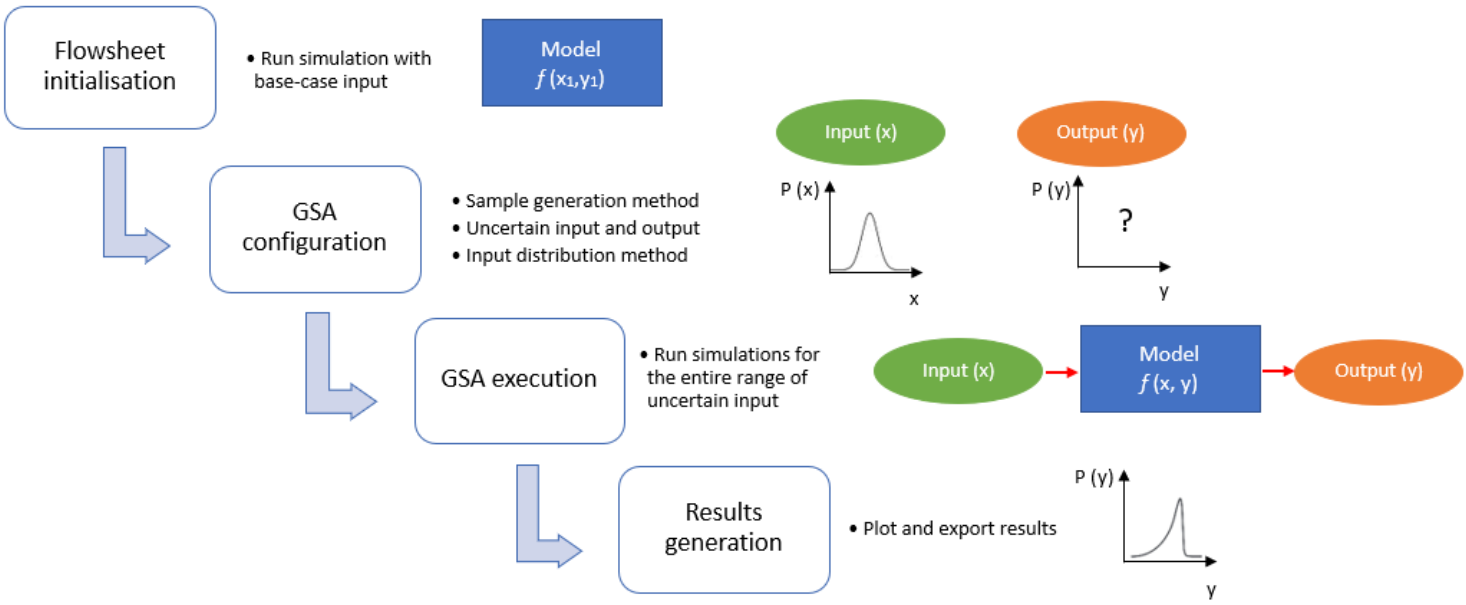


Figure 1: Procedure for investigating uncertainty using GSA in gPROMS. *x* corresponds to uncertain input whilst *y* corresponds to the output (KPI). *P* corresponds to probability.

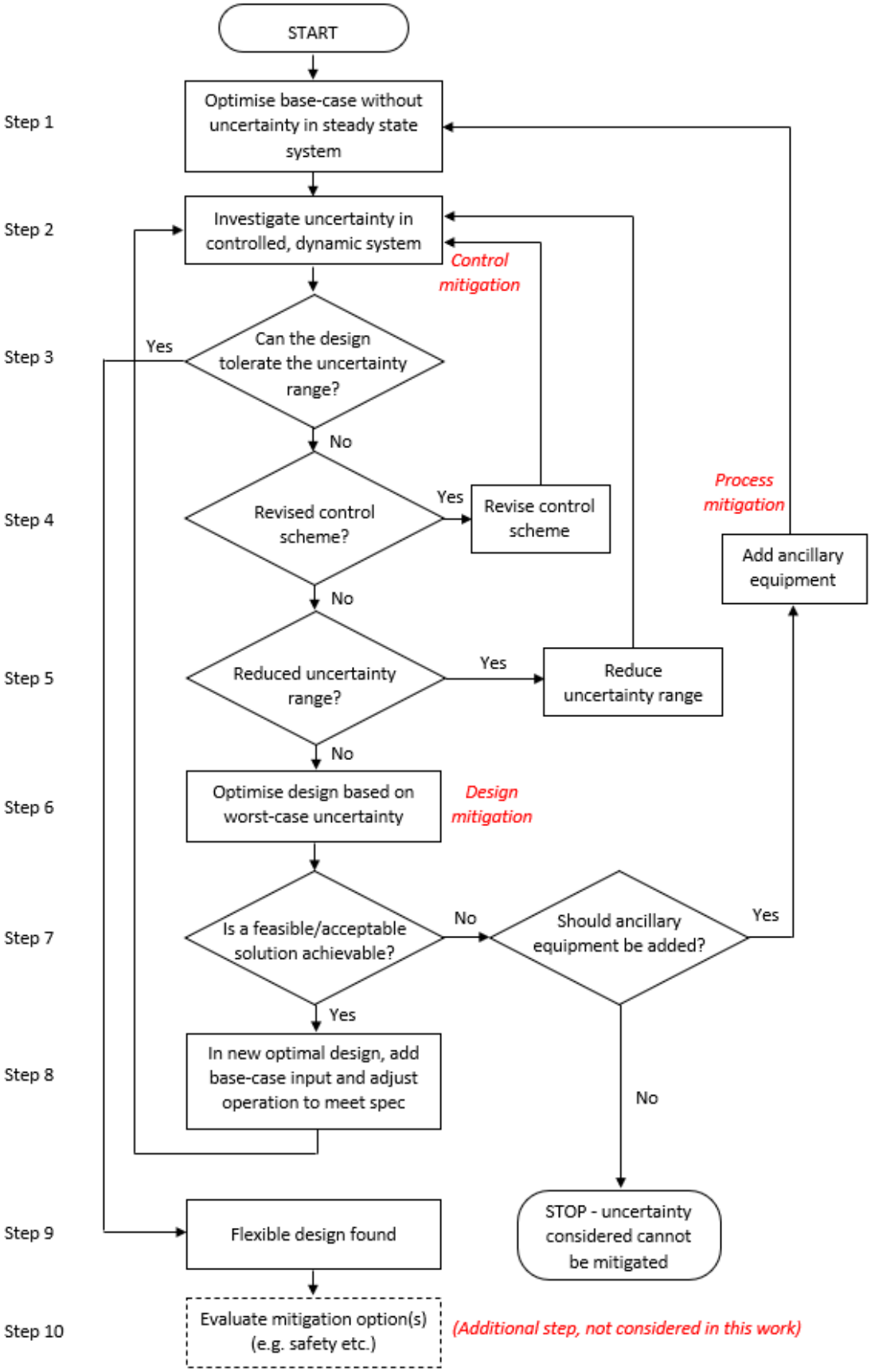


Figure 2: Methodology for mitigation of uncertainty in reactive distillation systems.

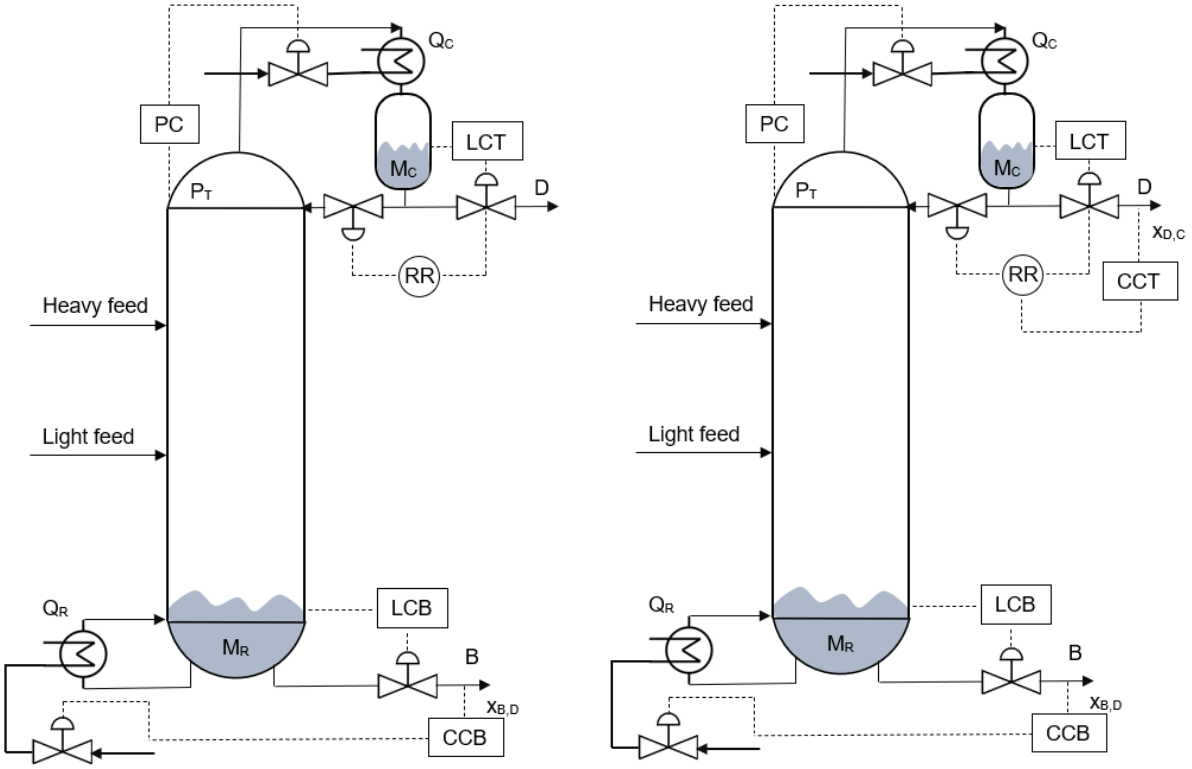
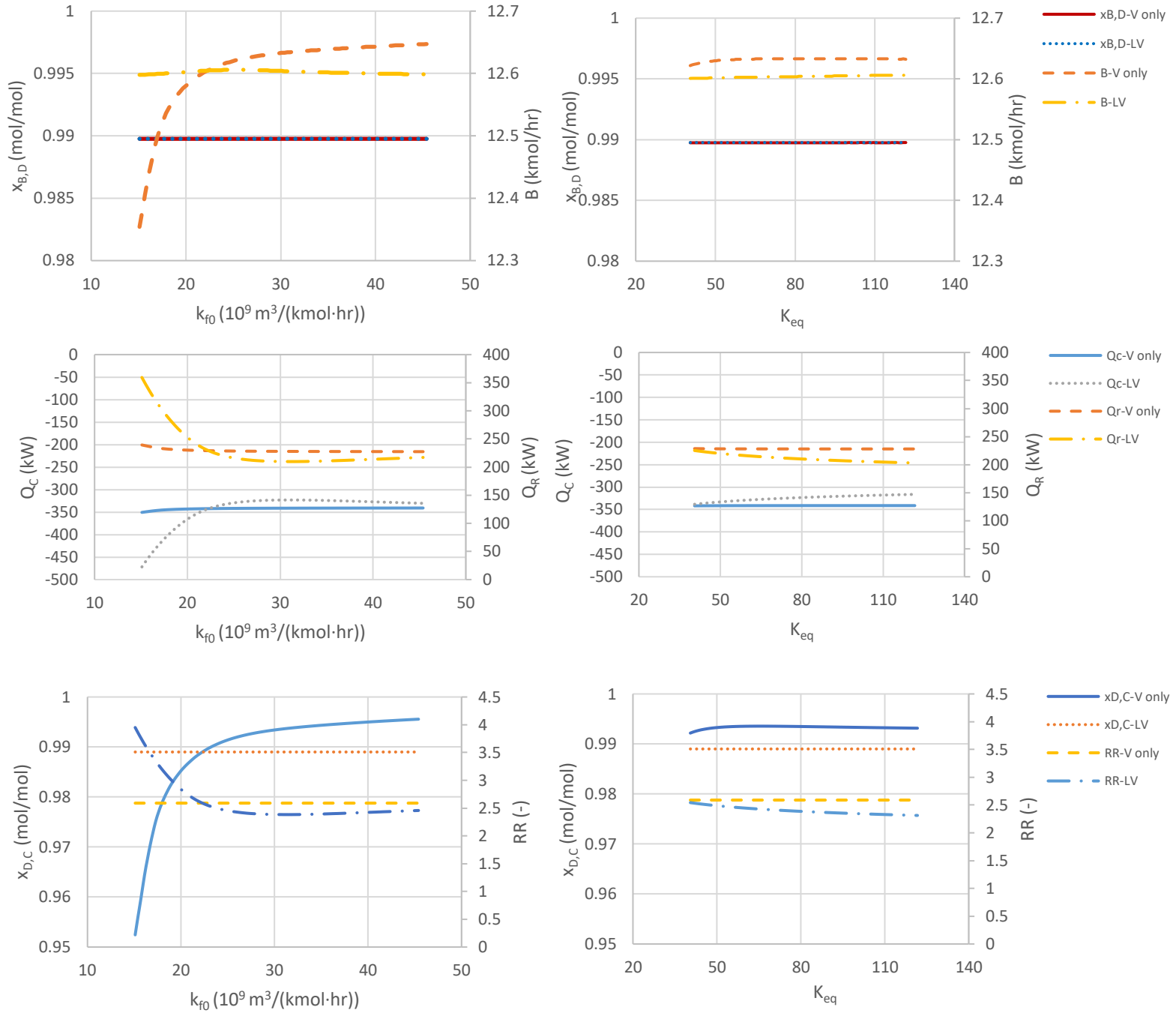
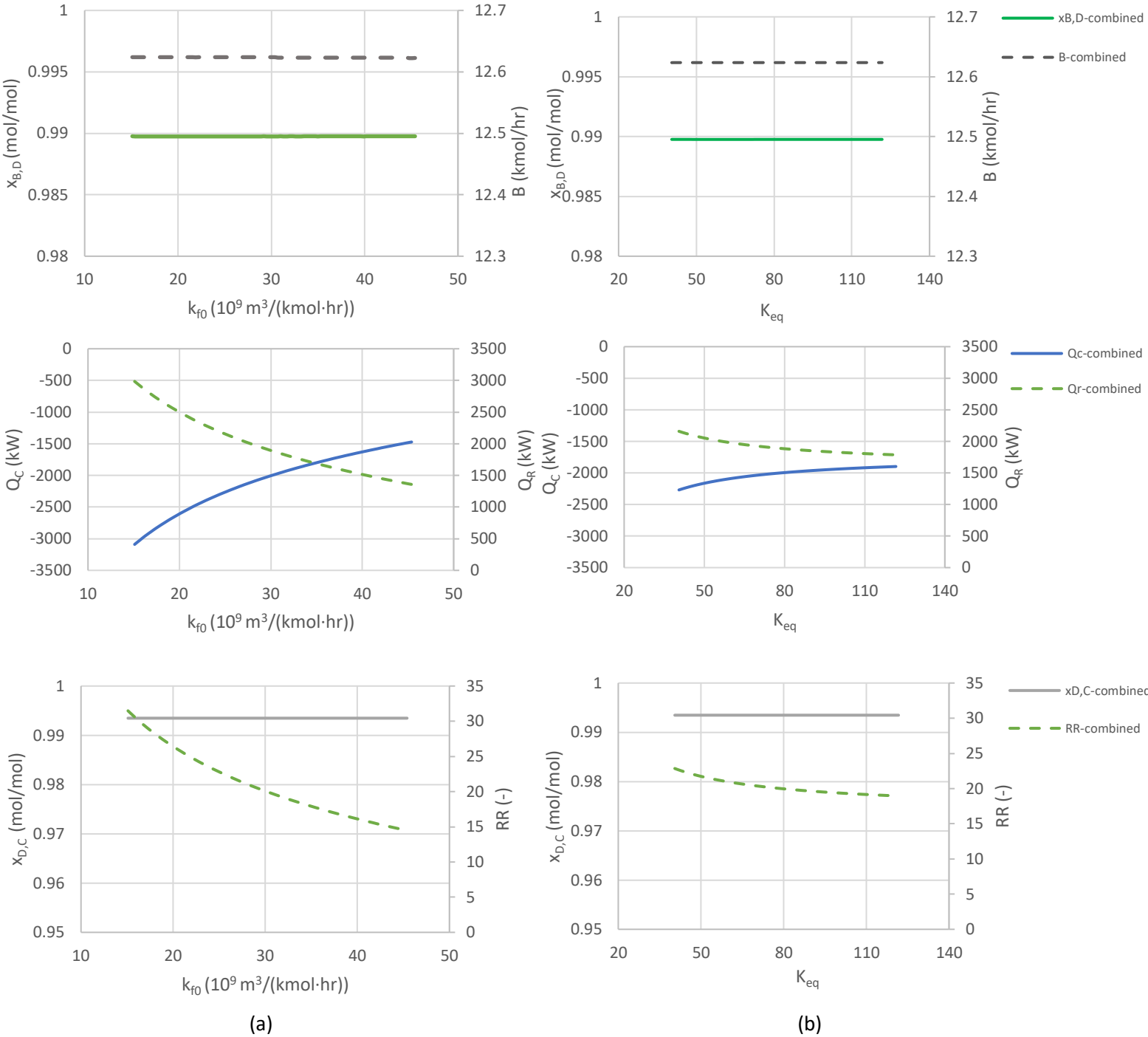


Figure 3: V-only (left) and LV (right) control configurations.



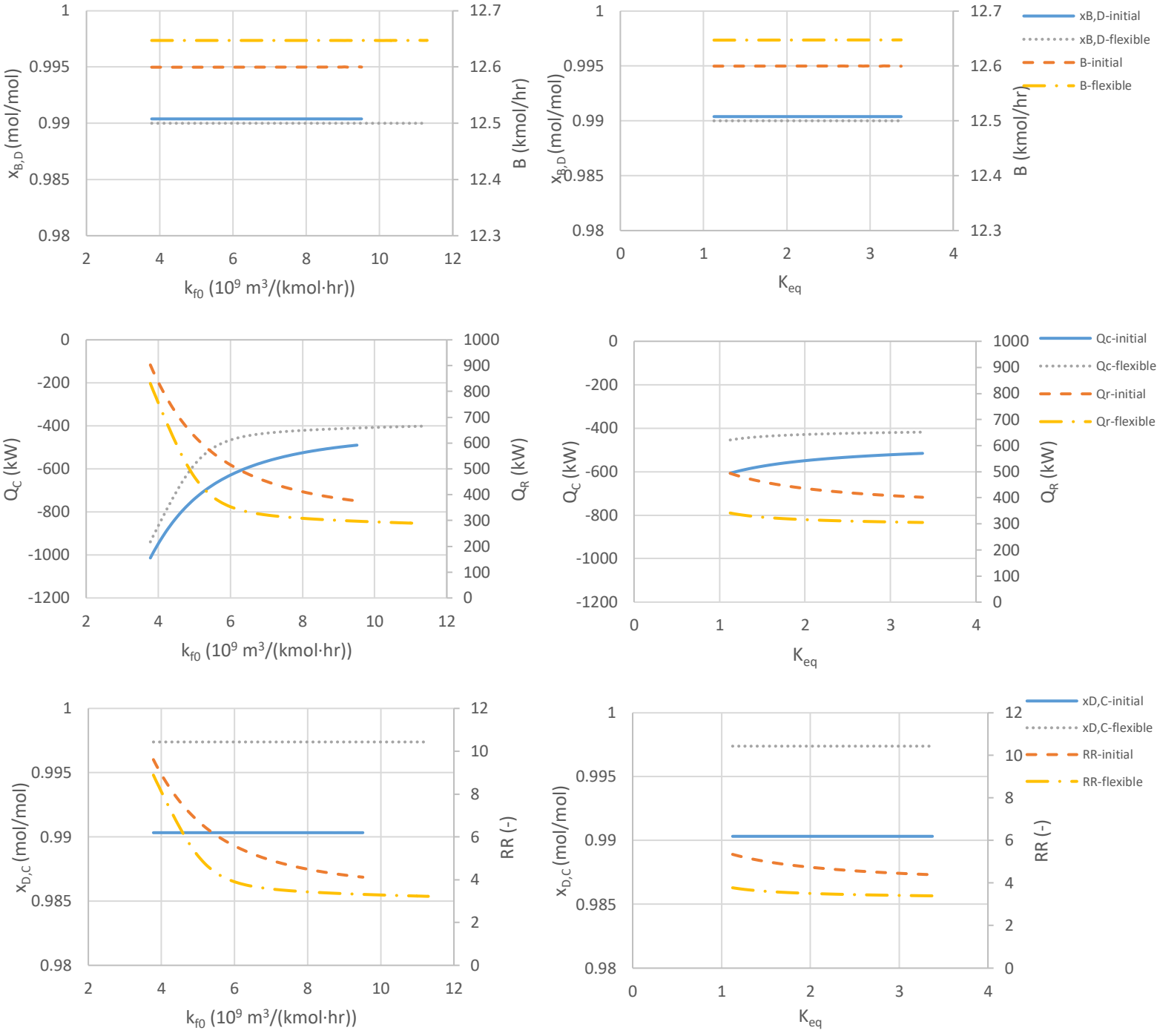
(a) (b)

Figure 4: Case study 1 uncertainty simulations. Product purity ($x_{B,D}$) together with bottom production rate (B), condenser (Q_C) and reboiler (Q_R) duties and top product purity ($x_{D,C}$) together with molar reflux ratio (RR) for initial optimal dynamic controlled V-only (lines indicated as *V-only*) and LV (lines indicated as *LV*) design. Uncertainty in kinetics (case a-left, case b-right) is considered.



(a) (b)

Figure 5: Case study 1 uncertainty simulations. Product purity ($x_{B,D}$) together with bottom production rate (B), condenser (Q_C) and reboiler (Q_R) duties and top product purity ($x_{D,C}$) together with molar reflux ratio (RR) for initial optimal dynamic controlled LV design. Combined uncertainty in kinetics(case a-left, case b-right) and VLE.



(a) (b)

Figure 6: Case study 2 uncertainty simulations. Product purity ($x_{B,D}$) together with bottom production rate (B), condenser (Q_C) and reboiler (Q_R) duties and top product purity ($x_{D,C}$) together with molar reflux ratio (RR) for initial optimal (lines indicated as *initial*) and flexible (lines indicated as *flexible*) dynamic controlled LV design. Uncertainty in kinetics (case a-left, case b-right).

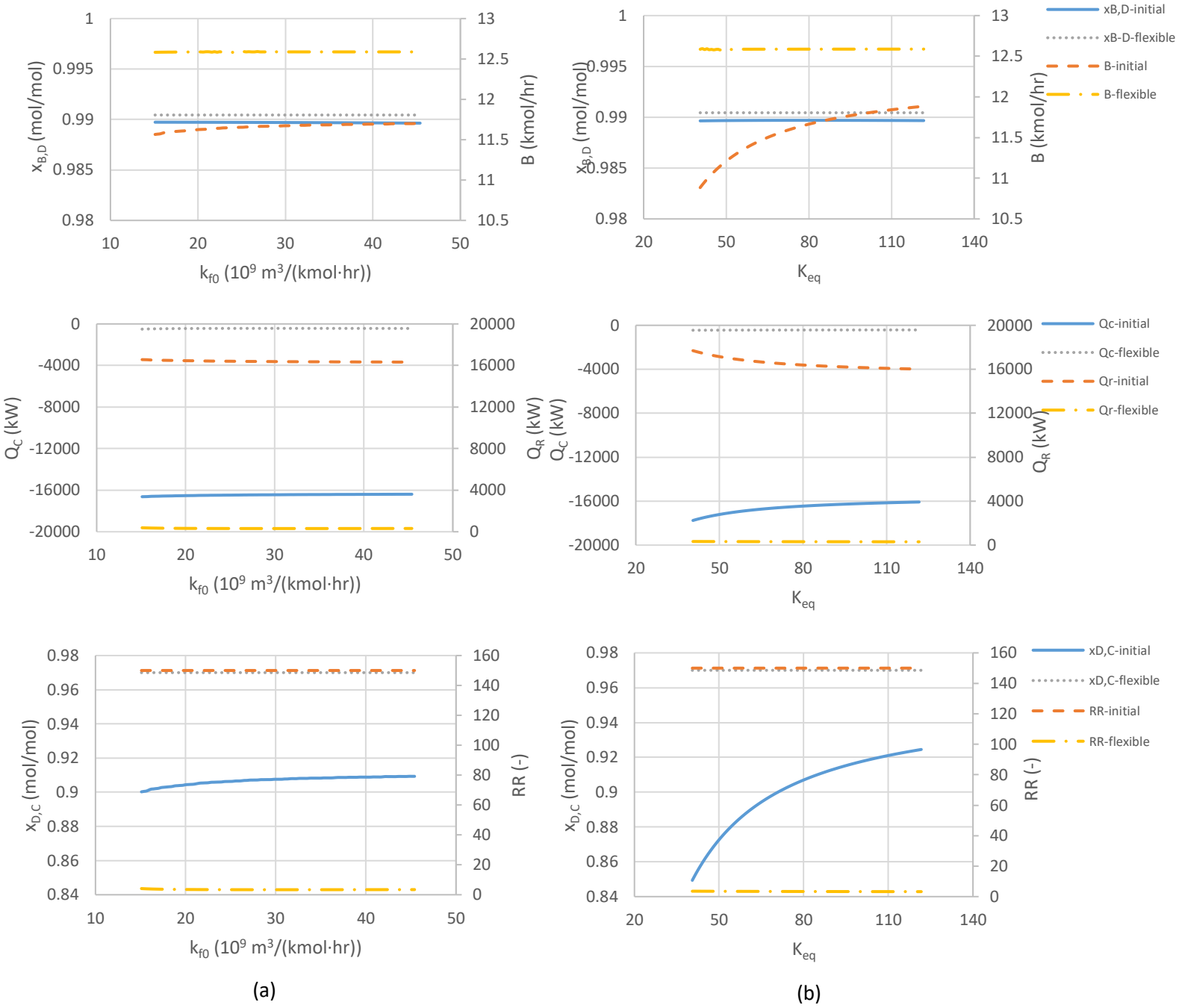


Figure 7: Case study 1 uncertainty simulations for operation disturbance in feed flow rate. Product purity ($x_{B,D}$) together with bottom production rate (B), condenser (Q_C) and reboiler (Q_R) duties and top product purity ($x_{D,C}$) together with molar reflux ratio (RR) for initial optimal (lines indicated as *initial*) and flexible (lines indicated as *flexible*) dynamic controlled LV design. Uncertainty in kinetics (case a-left, case b-right) and VLE, as well as operational (feed flow rate increase) uncertainty.

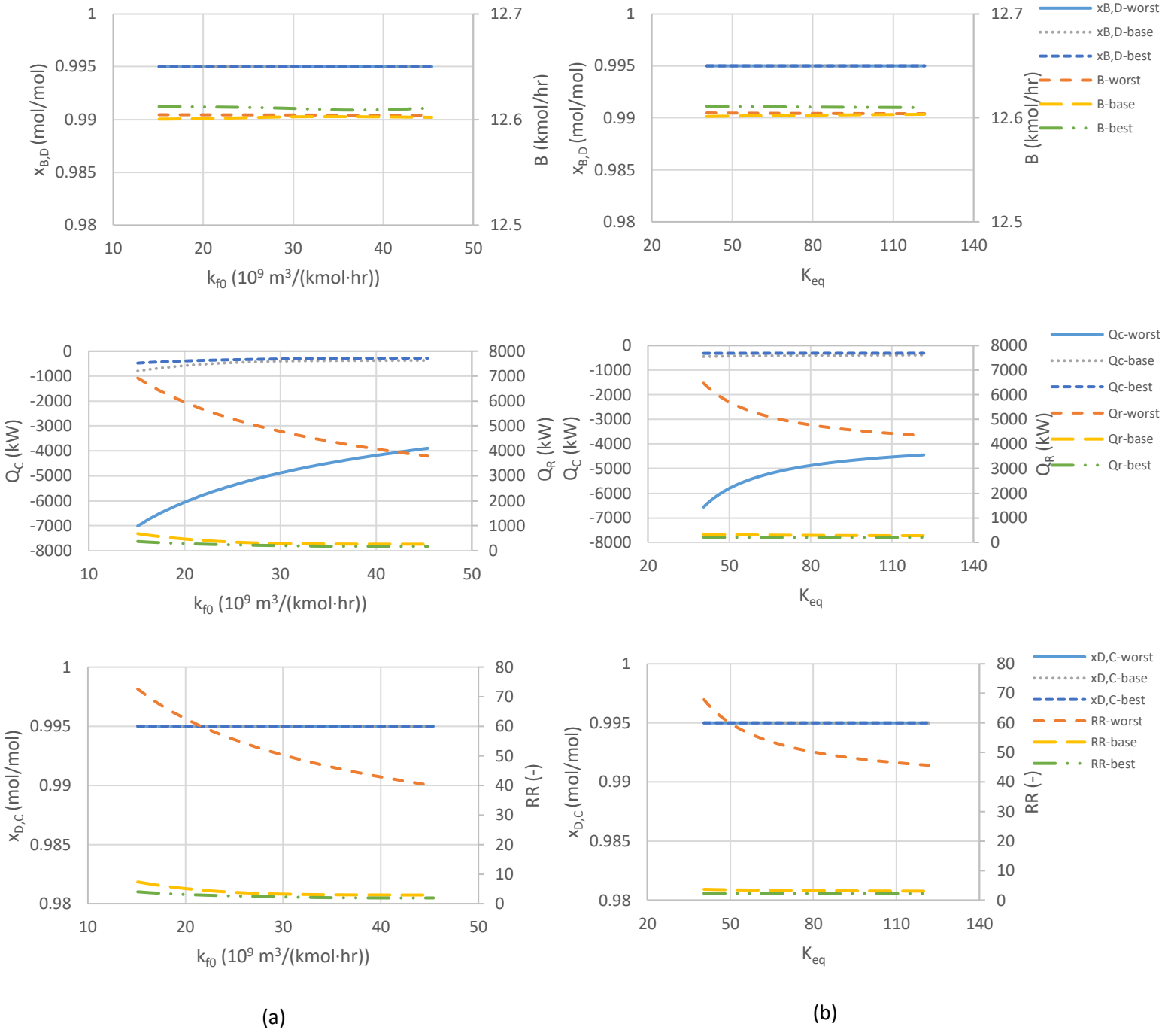


Figure 8: Case study 1 uncertainty simulations for product purity increase. Product purity ($x_{B,D}$) together with bottom production rate (B), condenser (Q_C) and reboiler (Q_R) duties and top product purity ($x_{D,C}$) together with molar reflux ratio (RR) for initial optimal dynamic controlled LV design. Uncertainty in kinetics (case a-left, case b-right), VLE (lines indicated as *worst-base-best* for each VLE scenario) and operational (target product purity change) uncertainty.

Table 1: Case studies considered. Reaction and separation characteristics, feed conditions and optimal results according to superstructure base case optimisation (Tsatse et al. 2021a).

		Case study 1	Case study 2	Case study 3
Input				
α_{CA}		2	2	1.2
α_{AB}		1.5	1.5	1.5
α_{BD}		2	2	1.2
k_{f0} (m^3/(kmol·hr))		$30.276 \cdot 10^9$	$7.56 \cdot 10^9$	$30.276 \cdot 10^9$
K_{eq}		81	2.25	81
Feed 1 (component B)	F (kmol/hr)	12.6		
	T (K)	413		
	P (atm)	1		
Feed 2 (component A)	F (kmol/hr)	12.6		
	T (K)	398.5		
	P (atm)	1		
Optimal results				
Heavy feed (B) stage (N_{T1})		12	11	15
Light feed (A) stage (N_{T2})		13	19	20
Number of stages (N_T)		18	25	31
Reflux ratio (RR,-)		2.59	4.65	6.2
Bottoms flow rate (B, kmol/hr)		12.6	12.6	12.5
Reactive stages		2-17	2-24	2-30
Column diameter (D_C, m)		0.62	0.78	0.91
Bottom purity ($x_{B,D}$, mol/mol)		0.99	0.99	0.99
Product recovery (x_{REC}, mol/mol)		1.00	1.00	1.00
Top purity ($x_{D,C}$, mol/mol)		0.99	0.99	0.98
Production - TAC (€/kg)		2.073	2.140	2.210
OPEX (M€/yr)		10.32	10.52	10.68
CAPEX (M€/yr)		0.15	0.27	0.40

Table 2: Optimal results for Case study 2, considering uncertainty in kinetics.

	Initial optimal design (Step 1)	**Optimal design (Step 6)**	**Flexible design (Step 8)**
k_{f0} (m^3/(kmol·hr))	$7.56 \cdot 10^9$	**$3.78 \cdot 10^9$**	$7.56 \cdot 10^9$
K_{eq}	2.25	2.25	2.25
α_{BD}	2	2	2
Values in optimal design			
Heavy feed (B) stage (N_{T1})	11	11	11
Light feed (A) stage (N_{T2})	19	23	23
Number of stages (N_T)	25	34	34
Reflux ratio (RR,-)	4.65	5.75	**3.48**
Bottoms flow rate (B, kmol/hr)	12.6	12.6	12.6
Reactive stages	2-24	2-33	2-33
Column diameter (D_C, m)	0.78	0.70	0.70
Bottom purity ($x_{B,D}$, mol/mol)	0.99	0.99	0.99
Product recovery (x_{REC}, mol/mol)	1.00	1.00	1.00
Top purity ($x_{D,C}$, mol/mol)	0.99	0.99	0.99
Production TAC (€/kg)	2.140	2.219	2.195
OPEX (M€/yr)	10.52	10.70	10.56
CAPEX (M€/yr)	0.27	0.49	0.50

Table 3: Results for Case study 3, considering ±40% (Step 2) and ±20% (Step 2-R2) VLE uncertainty range in initial optimal design.

±40% VLE uncertainty			
	α_{BD}=0.72	**α_{BD}=1.20**	**α_{BD}=1.68**
Manipulated variables			
Q_C(kW)	Infeasible	-660.850	-477.011
Q_R(kW)		551.544	371.558
RR		6.20	4.20
D (kmol/hr)		12.7	12.7
B (kmol/hr)		12.5	12.5
Controlled variables			
P_T (bar)	0.966	0.966	0.966
$x_{B,D}$ (-)	0.99	0.99	0.99
$x_{D,C}$ (-)	0.98	0.98	0.98
M_C (-)	0.50	0.50	0.50
M_R (-)	0.50	0.50	0.50
±20% VLE uncertainty			
	α_{BD}=0.96	**α_{BD}=1.20**	**α_{BD}=1.44**
Manipulated variables			
Q_C(kW)	Infeasible	-660.850	-507.091
Q_R(kW)		551.544	399.738
RR		6.20	4.56
D (kmol/hr)		12.7	12.7
B (kmol/hr)		12.5	12.5
Controlled variables			
P_T (bar)	0.966	0.966	0.966
$x_{B,D}$ (-)	0.99	0.99	0.99
$x_{D,C}$ (-)	0.98	0.98	0.98
M_C (-)	0.50	0.50	0.50
M_R (-)	0.50	0.50	0.50

Table 4: Optimal results for Case study 3, considering base-case values of VLE (Step 1) with and without additional ancillary equipment.

	Initial optimal design (Step 1)	**Optimal design incl. ancillary equipment (Step 1-R3)**
k_{f0} (m^3/(kmol·hr))	$30.276 \cdot 10^9$	$30.276 \cdot 10^9$
K_{eq}	81	81
α_{BD}	1.2	1.2
Values in optimal design		
Heavy feed (B) stage (N_{T1})	15	20
Light feed (A) stage (N_{T2})	20	20
Number of stages (N_T)	31	41
Reflux ratio (RR,-)	6.2	14.05
Bottoms flow rate (B, kmol/hr)	12.5	12.5
Reactive stages	2-30	2-40
Column diameter (D_C, m)	0.91	1.33
Reactor diameter (D_R, m)	-	1.3
Reactor length (L_R ,m)	-	1.3
Bottom purity ($x_{B,D}$)	0.99	0.99
Product recovery (x_{REC})	1.00	1.00
Top purity ($x_{D,C}$)	0.98	0.98
Production TAC (€/kg)	2.210	2.441
OPEX (M€/yr)	10.68	11.39
CAPEX (M€/yr)	0.40	0.80

Table 5: Results for Case study 3, considering ±20% VLE uncertainty range in initial optimal design including pre-reactor (Step 2-R3)

	α_{BD}=0.96	α_{BD}=1.20	α_{BD}=1.44
Manipulated variables			
Q_C(kW)	Infeasible	-1385.05	-491.604
Q_R(kW)		1261.04	369.209
RR		14.05	4.36
D (kmol/hr)		12.7	12.7
B (kmol/hr)		12.5	12.5
Controlled variables			
P_T (bar)	0.972	0.972	0.972
$x_{B,D}$ (-)	0.99	0.99	0.99
$x_{D,C}$ (-)	0.98	0.98	0.98
M_C (-)	0.50	0.50	0.50
M_R (-)	0.50	0.50	0.50

Table 6: Optimal results for Case study 3, considering ±20% uncertainty in VLE (Steps 6 and 8)

	Initial optimal design (Step 1)	**Optimal design (Step 6-R3)**	**Flexible design (Step 8-R3)**
k_{f0} (m^3/(kmol·hr))	$30.276 \cdot 10^9$	$30.276 \cdot 10^9$	$30.276 \cdot 10^9$
K_{eq}	81	81	81
α_{BD}	1.2	**0.96**	1.2
Values in optimal design			
Heavy feed (B) stage (N_{T1})	15	23	23
Light feed (A) stage (N_{T2})	20	23	23
Number of stages (N_T)	31	54	54
Reflux ratio (RR,-)	6.2	16.6	**10.96**
Bottoms flow rate (B, kmol/hr)	12.5	12.6	12.6
Reactive stages	2-30	2-53	2-53
Column diameter (D_C, m)	0.91	1.18	1.18
Reactor diameter (D_R, m)	-	1.30	1.30
Reactor length (L_R ,m)	-	2.17	2.17
Bottom purity ($x_{B,D}$)	0.99	0.99	0.99
Product recovery (x_{REC})	1.00	1.00	1.00
Top purity ($x_{D,C}$)	0.98	0.98	0.98
Production TAC (€/kg)	2.210	2.632	2.572
OPEX (M€/yr)	10.68	11.84	11.49
CAPEX (M€/yr)	0.40	1.45	1.45

Table 7: Results for Case study 3, considering ±20% VLE uncertainty range in new, flexible design (Step 2-R4)

	α_{BD}=0.96	α_{BD}=1.20	α_{BD}=1.44
Manipulated variables			
Q_C(kW)	-1604.09	-1129.51	-1059.86
Q_R(kW)	1477.00	1004.37	936.87
RR	16.6	11.38	10.64
D (kmol/hr)	12.6	12.6	12.6
B (kmol/hr)	12.6	12.6	12.6
Controlled variables			
P_T (bar)	0.947	0.947	0.947
$x_{B,D}$ (-)	0.99	0.99	0.99
$x_{D,C}$ (-)	0.98	0.98	0.98
M_C (-)	0.50	0.50	0.50
M_R (-)	0.50	0.50	0.50

Table 8: Optimal results for Case study 1, considering uncertainty in VLE, kinetics and operational disturbances (2% feed flow rate increase)

	Initial optimal design (Step 1)	**Optimal design (Step 6)**	**Flexible design (Step 8)**
k_{f0} (m^3/(kmol·hr))	$30.276 \cdot 10^9$	$30.276 \cdot 10^9$	$30.276 \cdot 10^9$
K_{eq}	81	81	81
α_{BD}	2.0	**1.2**	2.0
Values in optimal design			
Heavy feed (B) stage (N_{T1})	12	8	8
Light feed (A) stage (N_{T2})	13	14	14
Number of stages (N_T)	18	25	25
Reflux ratio (RR,-)	2.59	4.54	**2.72**
Bottoms flow rate (B, kmol/hr)	12.6	12.6	12.6
Reactive stages	2-17	2-24	2-24
Column diameter (D_C, m)	0.62	0.63	0.63
Bottom purity ($x_{B,D}$)	0.99	0.99	0.99
Product recovery (x_{REC})	1.00	1.00	1.00
Top purity ($x_{D,C}$)	0.99	0.99	0.99
Production TAC (€/kg)	2.073	2.139	2.114
OPEX (M€/yr)	10.32	10.50	10.39
CAPEX (M€/yr)	0.15	0.26	0.26