An investigation of the interactions between system characteristics and controllability for reactive distillation systems

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Abstract

Reactive distillation is an emerging process intensification technology, although its operation and control are complex due to the interactions between reaction and separation within the column. In this work, the impact of reaction and separation, as well as design parameters, on the controllability of reactive distillation processes is investigated, using a systematic methodology developed. Case studies of industrial interest are considered, varying in the key (reaction, separation and design) parameters, in order to investigate the relative impact of the latter on the controllability of the reactive distillation systems. It is shown that the system with slower kinetics demonstrates an increased difficulty in rejecting feed disturbances for both one point (V-only) and two-point (LV) control configurations. Even when linear model predictive control (MPC) is considered based on a state-space representation of the model, the system with slower reaction kinetics is still more difficult to control, for both set point change and load disturbance. It is also shown that revision of the optimal steady state design variables, such as the total number of stages, may be beneficial for the controllability of the process. The importance of maintaining feed ratio in stoichiometric processes is identified and discussed, as failure to do so may result in failure to maintain both product purities when two point control is considered.

Keywords: reactive distillation, controllability, process control, model predictive control

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1. Introduction

Reactive distillation integrates reaction and separation into one single unit, offering significant energy and potentially capital savings as well as improvements in reaction selectivity and yield (Luyben and Yu 2008). After the introduction of the methyl acetate process by Eastman Kodak (Agreda et al. 1990), which clearly demonstrated the potential of reactive distillation, the latter has gained significant interest from both the scientific and industrial communities, and understanding of the process has thus significantly improved. Currently, more than 150 columns are operated industrially (Harmsen 2007). Although this intensified process is attractive, there are factors which limit its industrial application. For instance, the operating windows of reaction and separation do not always overlap (Harmsen 2007), and therefore the application of reactive distillation is, in some cases, economically unfavourable or even technically infeasible. Furthermore, due to the large amount of design parameters and alternative flowsheet configurations, optimising the process design is challenging and no generalised heuristic rules are available. Overall, the integration of the two phenomena makes the extension of conventional distillation design and control strategies to reactive distillation systems a challenge, and renders reactive distillation difficult to design and operate under process disturbances and design uncertainties, thus limiting its wider industrial implementation.

In a previous contribution, we discussed how the steady state design and operation of a complex reactive distillation superstructure, which also included additional pre-/side-equipment, can be simultaneously optimised to meet the given product quality constraints (Tsatse et al. 2021). In this paper, the dynamic performance and controllability of a reactive distillation process is evaluated using a proposed methodology, in order to obtain insight into the impact of various system characteristics on the controllability of the process. This work focusses on several cases for which the optimal steady state configuration was determined in our previous work (Tsatse et al. 2021). Authors who have discussed the controllability of reactive distillation systems have generally only considered the dynamic behaviour and control of specific chemical systems and reactive distillation designs by implementing various control strategies, conventional or advanced, to indicate which technique is the most effective in their specific case. Few authors (Mansouri et al. 2015, Contreras-Zarazúa et al. 2017, Al-Arfaj and Luyben 2000b, Cheng and Yu 2005, Cho and Han 2018 and Georgiadis et al. 2002) have addressed the interaction between the design of the system and the associated control of the process. To the best of the authors' knowledge, no contribution to date has considered how reaction and separation phenomena interact within the column, and the corresponding impact on process controllability. One of the objectives of this work is therefore to systematically evaluate the controllability of reactive distillation systems as well as the suitability of the proposed control strategies based on time domain analysis, following a developed methodology. Using the latter for a number of reactive distillation systems varying in the key system characteristics (reaction and separation parameters), it is therefore possible to evaluate how reaction and separation phenomena, as well as their combination, impact on the controllability of reactive distillation. The work will also consider how design variables such as the total number of stages of the reactive column and its liquid holdup can be taken into consideration in order to improve the controllability of the process.

Several authors have confirmed that the control of reactive distillation processes is more challenging than the conventional distillation counterpart. In one of the early contributions, Sneesby et al. (Sneesby et al. 1997) mentioned that the combination of reaction and separation causes controllability problems, and commented that when additional aims are imposed (e.g. catalyst deactivation monitoring etc.), control becomes even more complex. Later, Kaymak and Luyben (2008) studied the controllability of a generic reactive distillation system as well as the conventional multi-unit process of reactor followed by two columns, highlighting that the integrated process is more difficult to control and that the operability region is smaller due to the existence of fewer degrees of freedom. Kumar and Kaistha (2008b) also recognised that there is a need for deeper understanding of the interactions between the reaction and separation as input (e.g. reboiler duty, reflux rate etc.) multiplicities might

cause state transition and incorrect control action, as also confirmed by Luyben (2006), who additionally found the control of the reactive distillation process more challenging due to the interaction between phase equilibrium and chemical reaction.

Regardless of the difficulties identified, there are a number of contributions in the open literature which have successfully investigated the controllability of reactive distillation processes and proposed suitable control strategies, and current literature focuses on both open- and closed-loop dynamics. Up to 2000, most of the publications studied the open-loop dynamics of the process (e.g. Al-Arfaj and Luyben 2000b), mainly focusing on the existence of multiple steady states and input/output multiplicities. However, during the last two decades, closed-loop dynamics have also drawn attention since more information on the behaviour of reactive distillation has been brought into light and its industrial applicability and operability more widespread (e.g. Al-Arfaj and Luyben 2002a, Kaymak and Luyben 2006 etc.). Investigation of closed-loop dynamics mainly includes implementing either decentralised (i.e. conventional proportional (P), proportional-integral (PI) and proportional-integral-derivative (PID) controllers) or more advanced, centralised, control strategies (e.g. model predictive control, state observers etc.), and evaluating the efficiency of each strategy towards set point or load changes using a number of different criteria (e.g. settling time, offset, oscillatory behaviour etc.).

1.1 Decentralised control

Decentralised control is the strategy most commonly applied in the literature when considering reactive distillation, mainly due to the similarities to conventional distillation control. Whether the column operates in stoichiometric reactant balance or in reactant excess appears not to have a significant impact on control and both operations have been found to be controllable. Luyben (2000) was the first to make this statement, suggesting, however, that operation in excess is slower dynamically due to the recycle of excess reactant and the added complexity of the two-column process that is then required. Literature includes a number of reactive distillation cases where conventional feedback (P, PI and PID) control loops have been found effective in controlling mainly product purity and reaction conversion, and the most comprehensive of these studies are included below to illustrate the application of this type of control scheme. For instance, Hung and their colleagues (Hung et al. 2006), studied a set of systems with acetic acid and different alcohols (C1 to C5) and showed that temperature control and feed ratio control was successful in all cases considered. Wang and their co-workers (Wang et al. 2003a), who investigated the control of a kinetically controlled n-butyl acetate reactive distillation process, successfully applied feed ratio (i.e. ratio between the two feed flow rates) and temperature control (cascade) using stages insensitive to throughput or catalyst changes. Moraru and Bildea (2017) showed that direct composition control is sometimes required, using the n-butyl acrylate case study as an example. Medina-Herrera et al. (Medina-Herrera et al. 2020) demonstrated that even dynamic transitions towards different products are possible in a silane multi-product reactive distillation column using switchability analysis, as long as the location of the PI temperature control loop has been well investigated to avoid catalyst deactivation. Feedforward control has not often been considered, however, in a relevant contribution by Mahindrakar and Hahn (2016), feedforward control of a benzene hydrogenation system was found to be effective as long as time delay in composition measurement was small. In a different contribution, feedforward control schemes were applied for the control of a pressure-swing heat integrated reactive distillation process for methanol production under feed flow rate and composition disturbances (Zhang et al. 2020).

In addition to simple reactive distillation columns, the controllability of more complex reactive distillation processes, still using conventional control schemes, has also been studied. For instance, heat integrated reactive distillation processes have been studied in a number of contributions (Kiss 2011, Chen et al. 2016, Alcántara-Avila et al. 2017, Zhang et al. 2017) and have been found to have good controllability characteristics. The authors of these contributions agreed that heat integration

could improve controllability compared to the conventional reactive distillation process and that the application of conventional PI control loops (e.g. temperature inferential control by manipulating feed ratio) is successful. Internal heat integration by feed re-arrangement or catalyst re-distribution was studied by Kumar and Kaistha (2008a, 2008b) who found that internal heat integration may or may not be beneficial in terms of controllability, depending on the system considered.

Although conventional distillation control schemes have been successfully applied to reactive distillation systems as presented by several authors, the combination of reaction and separation in a single unit has been found to have, in some cases, a negative impact on the controllability of the process. The non-linear nature of the process and process gain bi-directionality, for example, have often been discussed in literature. For instance, Sneesby et al. (Sneesby et al. 2000) advised that process directionality must be carefully considered since unsuitable organisation of control loops could easily result in an unstable controller. Later, Kumar and Kaistha (2007) suggested that temperature difference should be controlled instead of using simpler temperature control loops when process gain sign reversal is observed due to non-linearities.

1.2 Advanced control

Since conventional P, PI and PID control loops have been found to be insufficient for the effective control of the process in some cases due to the non-linear nature of the problem, several authors have discussed advanced, centralised, model-based control. A number of contributions have compared the performance of model predictive control (MPC) strategies over the conventional PI/PID control loops. In the majority of cases, nonlinear MPC was found to be superior for set point tracking when experiencing feed flow rate and composition disturbances (Agachi 2006, Athimathi and Radhakrishnan 2006, Chandra and Venkateswarlu 2007, Pham and Engell 2011, Sharma and Singh 2012, Purohit et al. 2013, Seban et al. 2015, Mahindrakar and Hahn 2016) although in some cases, the difference in control performance was not significant (Kawathekar and Riggs 2007). In those cases, the performance of the control strategies under model/plant mismatch was additionally considered and MPC was found insensitive and more effective. Nonlinear MPC often provides more satisfactory performance for highly nonlinear processes (such as reactive distillation) and/or processes where a wide operating regime is considered (Nagy et al. 2007), however, linear MPC is far less computationally demanding and has therefore been applied in this work to show one example of the impact of slightly more advanced control on control performance. The methodology followed in this work can of course also be applied to nonlinear MPC control.

In some contributions, other advanced control strategies such as pattern-based predictive control (Tian et al. 2003) or constrained dynamic matrix control (Dwivedi and Kaistha 2009) were successfully applied and were found to be efficient when a good process model is difficult to obtain or implement in real-time control. Sharma and Singh (2012) showed that neural network predictive control and MPC give smoother and better control performance for the production of TAME compared to its PID equivalent. In another contribution, Bisowarno and their co-workers (Bisowarno et al. 2003) applied model gain scheduling to one-point control for the ethyl tert-butyl ether (ETBE) system, showing that the system could cope with nonlinear characteristics and overcome gain directionality issues, which cannot be handled by PI controllers. However, the authors recognised that such a strategy required pre-programming or online gain identification, and that large noise values could destabilise the strategy and therefore suggested that in the case of feed composition changes a state estimator is needed.

State estimators, linear or nonlinear, have been used in a number of contributions. A linear state estimator was implemented by Olanrewaju and Al-Arfaj (2005, 2006), and was found to be effective under measurement errors, model uncertainties and erroneous initial conditions. However, the authors recognised that when model-plant mismatch is expected, limiting the state estimator to the

inaccessible states only, then using additional composition analysers, is recommended. Furthermore, Grüner et al. (Grüner et al. 2003) developed a state observer for a real reactive column. The specific chemical system considered was not revealed (i.e. components were named A, B etc.) assuming due to confidentiality considerations related to the full-scale production plant of Bayer AG considered. The observer was based on temperature measurements and was found to be superior compared to a well-tuned linear controller.

1.3 Optimisation for control

Towards the development of more systematic procedures for reactive distillation control, a number of contributions have discussed optimisation strategies to efficiently design the control structure. Kookos (2011) developed an MINLP problem to find the optimal control structure for an ideal system aiming to minimise the cost associated with over-purification (reflux ratio), and found that a systematic and model-based control structure selection outperforms heuristics for reactive distillation systems. Later, Haβkerl et al. (Haßkerl et al. 2018a) investigated control based on cost optimisation of a multi-product reactive distillation process under model uncertainty. They were able to design robust controllers, however, the authors faced technical limitations (e.g. conflicting constraints between controllers which cannot be overcome unless relaxing or removing the relevant constraints) which they aimed to resolve in order to validate their work experimentally. This was later achieved, as the same authors (Haßkerl et al. 2018b) successfully applied nonlinear model-predictive control based on cost optimization in their pilot plant facilities for the production of diethyl carbonate.

The integration of optimal process design and control for chemical processes, including intensified processes, has been the subject of various contributions (e.g. Pistikopoulos and Diangelakis 2016, Dias and Ierapetritou 2019, Rafiei and Ricardez-Sandoval 2020 etc.) where the associated challenges and need for deeper understanding and more established methodologies are identified. Current literature suggests that the design of the reactive distillation process impacts on its controllability, and this has been the subject of several contributions. Mansouri et al. (Mansouri et al. 2015) suggested that designing the 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, using as an example the production of MTBE. In addition, Contreras-Zarazúa and their colleagues (Contreras-Zarazúa et al. 2017) performed multi-objective optimisation to determine the optimal design and control of the process and found that by altering the design (e.g. adding interlinking streams, larger column diameter etc.), controllability can be improved. Moreover, Georgiadis and their colleagues (Georgiadis et al. 2002) suggested that simultaneous, and not sequential, optimisation of the design and control of a reactive distillation column is a more economically beneficial approach. Bernal et al. (2018) discussed a methodology for the simultaneous design and control of catalytic distillation columns, using comprehensive rigorous dynamic modelling, taking into account economic and set-point tracking considerations.

Based on the above, although the impact of design on controllability has been previously discussed in the context of integrated design and control, most studies focus on specific design parameters, such as the total number of stages or the feed stage locations for reactive distillation columns. The existing literature therefore provides a limited insight into the impact of reaction and separation parameters in particular, on the controllability of the process using a systematic methodology, as well as understanding of how this interaction can be taken into consideration, both for the design of a rigorous dynamic process, as well as for the design and implementation of an effective control strategy. This, as mentioned above, is therefore the aim of this work. To achieve this, first, the evaluation of the controllability and interpretation of the control behaviour of reactive distillation systems using a systematic methodology and the applicability of proposed control strategies will be presented and discussed; then the methodology will be applied to several case studies to evaluate how reaction and separation characteristics impact on the controllability of the reactive distillation

process; and finally, it will be shown how process design can be taken into consideration to improve the control performance. The methodology developed is general and can be applied to any reactive distillation system, however, is demonstrated in this work using three general case studies so as to focus on general, rather than specific, process characteristics for the investigation of process controllability.

2. Methodology

This section describes how controllability analysis was performed in the time domain using gPROMS ProcessBuilder v1.3.1 (Process Systems Enterprise 2020) and MATLAB R2018a (The MathWorks Inc. 2019). The section also includes a description of how the dynamic models were set up in gPROMS ProcessBuilder along with the conventional control scheme configurations, as well as how state-space representation of a linearised model was used in order to consider advanced control strategies in MATLAB. A description of the criteria used for the evaluation of the control responses is also included.

Figure 1 presents the methodology with the left-half plane (Steps L4-L8) focusing on the configuration and evaluation of conventional control schemes within gPROMS ProcessBuilder, whilst the right-half plane (Steps R4-R10) focuses on the derivation of the state-space representation and the application of Model Predictive Control on the linear model using both gPROMS ProcessBuilder and MATLAB. The methodology can be repeated when new processes or conventional control schemes are considered. Comparison between the performance of conventional and advanced control schemes is also possible when results are generated from both half-planes.

Overall, the methodology presented has the following objectives:

1. Systematically evaluate the suitability of proposed control strategies as well as the controllability characteristics of reactive distillation systems.
2. Evaluate the impact of separation and reaction on the controllability of the reactive distillation process for both conventional and advanced control strategies by considering case studies with different reaction/separation characteristics.
3. Evaluate the impact of design parameters (e.g. number of stages, tray liquid holdup) on the controllability of reactive distillation columns.
4. Show that the conclusions drawn with regards to the impact of reaction and separation characteristics on process controllability are generic, regardless of the method used for the tuning of the conventional PI controllers by either using typical tuning parameters or the optimised tuning parameters using the methodology in this work.

The novelty of this work mainly relates to objectives 2 and 3. For objective 2, the methodology presented in Figure 1 should be repeated for several case studies with different reaction and/or separation characteristics in order to obtain insight into the relevant impact of the latter on the controllability of reactive distillation. For objective 3, the methodology should be repeated for several column designs, where only one design parameter is varied each time, in order to gain insight into the impact of the design parameter considered on process controllability. Although the methodology presented in Figure 1 consists of individual steps that have already been considered in the open literature (e.g. application of conventional control schemes etc.), these steps are in this work for the first time combined into an overall systematic methodology which can be applied to meet the four objectives listed above.

2.1 Dynamic model configuration

All the dynamic models used in this work are first configured at steady state in gPROMS ProcessBuilder. For the set-up of the steady state models (Tsatse et al. 2021), 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 was assumed. This assumption is considered valid at small or medium scales (Vora and Daoutidis 2001) as in the case studies considered, however, at industrial scale, detailed mass transfer and reactant conversion analysis may be required to describe the process more accurately.
3) Constant relative volatilities were assumed as generic components are considered.
4) Pressure drop was considered negligible for the steady state model, but was considered for the dynamic model as will be explained below.
5) Reaction occurs only in the liquid phase which holds for various esterification systems for which reactive distillation has been successfully applied.
6) All column stages (stages 2 to N-1) were considered reactive in the reactive column, with the same liquid holdup per reactive tray (0.1 m^3/tray).
7) There was no heat loss or gain from the environment in any of the equipment used, therefore all models were assumed to operate adiabatically.

Once the model is set up in steady state, the model is transformed into dynamic mode. The steps the user has to take in order to complete the transition from steady state to dynamic mode in gPROMS ProcessBuilder are (Steps 1-3 in Figure 1):

- Specification of reactive distillation column diameter: In steady state, column diameter is calculated based on the flooding limit of the column (e.g. 80%), however, for the dynamic model the user has to specify a column diameter (which can of course be taken from the steady state simulation) so that the latter is kept fixed during the dynamic simulations (and not varied based on the flooding factor which may vary as a function of time).
- Sizing of reflux drum and sump vessels: Heuristics are used for the sizing of the reflux drum and sump of the column, and 5 min of liquid holdup when the vessel is half-full was assumed in this work, based on the total liquid entering or leaving the vessel (Luyben 2006).
- Transition from flow-mode to pressure-driven mode: Steady state models are flow-driven simulations in gPROMS ProcessBuilder whilst dynamic models are pressure-driven simulations. In the latter, the pressure in the first and last unit of the process is fixed and flows are calculated based on flow-pressure correlations (i.e. flows are calculated based on the pressure drop between the inlet and outlet pressures). Pressure changers (i.e. valves and/or pumps), which operate adiabatically, are also added in the dynamic model. For these units, pressure and mass flowrates are specified by the user and the sizing of the units is therefore not performed by the user but rather by the software directly.
- Column pressure drop calculation: A linear column pressure profile cannot sufficiently describe column performance, therefore pressure drop needs to be considered properly. In this work a heuristics value of 0.0069 bar/stage (Luyben 2006) is used for initialisation purposes, whilst the actual pressure drop inside the column is not a direct specification by the user but is instead calculated by gPROMS ProcessBuilder based on column hydraulics using Bennett's correlation for clear liquid height calculation and a simple Bernoulli correlation for pressure drop calculation (Process Systems Enterprise 2020). This means that the solution shows that the columns can be operated in sub-atmospheric pressures (as in this work where pressure is slightly below 1 atm) given process specifications and column hydraulics.

When dynamic modelling is complete, reflux drum and sump liquid level control loops must be configured otherwise the dynamic model cannot initialise. For these two control loops, P-only controllers (no integral and/or derivative action) are used as level control does not need to be perfect. When the two liquid level controllers are installed, with the rest of the loops (pressure and quality control) open, the dynamic simulation can run with the remaining system in open loop. The user can then add the remaining control loops (pressure and composition controllers, here all PI controllers) one at a time to ensure smooth operation and good convergence (Step L4).

For the consideration of disturbances required for the evaluation of the controllability of the process, these can be added to the dynamic model next (Step L5). In this work, disturbances were assumed to be sharp ramps instead of steps, mainly for numerical reasons, but also because this is a more realistic and industrially relevant scenario. More details regarding the controllers (e.g. loop pairing, controller parameters etc.) and disturbances considered (type, direction etc.) are included in Section 3.

2.2 Closed-loop control performance evaluation

For the evaluation of the performance of control strategies following a disturbance in the system (Step L6 in Figure 1), there is a range of criteria used in literature (e.g. Stephanopoulos 1984, Luyben and Luyben 1997). In this work, three of these metrics will be used, which describe the response of the controlled variables following a disturbance in the system.

- **Overshoot** is the maximum amount by which the response differs from the steady state final value, often expressed as a percentage.
- **Settling time** is the time required by the response to reach the final steady state value given a calculation tolerance in the order of 10^{-5} .
- **Offset** is the error between the final steady state value and the desired set point.

An alternative method to evaluate the control performance of a control configuration is by calculating the error, i.e. the deviation from the set point. One error metric often used in controllability investigations is the Integral Absolute Error (IAE). The IAE calculates the sum of areas above and below the set point, and therefore penalises all errors equally regardless of the direction:

$$IAE = \int_0^{time} |e(t)| dt \qquad (Eq. 1)$$

Whilst the control evaluation could have been done based on the IAE rather than by considering overshoot, setting time and offset, we will instead use the IAE criterion for the tuning of the controllers, and the overshoot, settling time and offset to evaluate the control performance (Step L7 in Figure 1). More specifically, the tuning parameters of the PI controllers (excluding the level controllers) will be optimised in order to minimise the set point deviation, i.e. the product loss defined as the product mass flow that is below and above (within a tolerance of 0.001) the quality specification. To evaluate the benefits of this optimal controller tuning, the controllability evaluation will first take place using typical tuning parameters which were found to work sufficiently well for all the conventional controllers. Then, the evaluation will be repeated using optimal parameters found as described above, and the performances will then be compared and for both situations based on overshoot, settling time and offset (Step L8 in Figure 1).

2.3 State-space representation and Model Predictive Control

The following section describes how state-space representation of the reactive distillation model can be performed using a linearised form of the model. The aim of this strategy is to create the state-space model for use as a basis for application of linear Model Predictive Control within MATLAB R2018a (The MathWorks Inc. 2019), i.e. for advanced control.

Reactive distillation can be modelled and represented using mixed sets of non-linear differential and algebraic equations (Process Systems Enterprise 2020). These can be written in the general form (Skogestad and Postlethwaite 2005):

$$\boldsymbol{f}(\boldsymbol{x}, \dot{\boldsymbol{x}}, \boldsymbol{y}, \boldsymbol{u}) = 0 \qquad (Eq. 2)$$

Here **x***(t)* and **y***(t)* are the sets of differential and algebraic variables, respectively, whilst **ẋ** (t) are the derivatives of ***x(t)*** with respect to time, *t*. In addition, ***u(t)*** is the set of time-dependent input variables

(e.g. reflux ratio). The linearised expression (around the desired operating point $\left(\boldsymbol{x}^*(t), \dot{\boldsymbol{x}}^*(t),\ \boldsymbol{y}^*(t), \boldsymbol{u}^*(t)\right)$ of the original non-linear system can be re-written as follows:

$$\begin{pmatrix} \delta\dot{\mathrm{x}} \\ \delta\boldsymbol{y} \end{pmatrix} = -\begin{bmatrix} \frac{\theta \boldsymbol{f}}{\theta \dot{\mathrm{x}},} & \frac{\theta \boldsymbol{f}}{\theta \boldsymbol{y}} \end{bmatrix}^{-1} \begin{bmatrix} \frac{\theta \boldsymbol{f}}{\theta \boldsymbol{x}} & \frac{\theta \boldsymbol{f}}{\theta \boldsymbol{u}} \end{bmatrix} \begin{pmatrix} \delta \boldsymbol{x} \\ \delta \boldsymbol{y} \end{pmatrix} \qquad (Eq. 3)$$

Using the linearised model ***f***, a vector of input variables **U** (subset of **u**) and a vector of output variables **Y (**subset of **y)**, the state-space representation of the systems is as follows:

$$\dot{\mathbf{X}} = [A]\boldsymbol{X} + [B]\boldsymbol{U} \qquad (Eq. 4)$$
$$\boldsymbol{Y} = [C]\boldsymbol{X} + [D]\boldsymbol{U} \qquad (Eq. 5)$$

where $\dot{\mathbf{X}}$ is the vector of state variables that characterise the system and *[A], [B], [C], [D]* are real matrices based on the size of the problem. For a distillation column for instance, $\dot{\mathbf{X}}$ would be a vector including system states such as component holdups per stage; **U** would be a vector of the manipulated variables (e.g. condenser and reboiler duties); whilst **Y** would be a vector of the controlled variables (e.g. pressure, product composition etc.). For a system with *n* number of states, *i* number of inputs and *j* number of outputs then [A]=[*n* x *n*], [B]=[*n* x *i*], [C]=[*j* x *n*] and [D=[*j* x *i*]. At this point, it is worth stressing that this model should, as long as the system does not deviate too far from the linearised operating point, behave in exactly the same way as the non-linear model (Corriou 2018). As the purpose of control is to keep the system at the set point given by the operating point, and the system will therefore not be deviating far from this point, the use of a linearised system is in most cases reasonably close to the operating point.

Once the state-space representation is obtained (Eq. 4-5), the representation can be used for a number of different applications, including the application of linear Model Predictive Control (MPC). Below is a description of how this procedure can be performed using a combination of simulation tools, in this work, gPROMS ProcessBuilder and MATLAB.

Once the two level control loops are closed in gPROMS ProcessBuilder, and the dynamic simulation can initialise without any additional control loops or disturbances, the input/output variables are selected (Step R4 in Figure 1) and the *LINEARISE* task is added in the Scheduling tasks of the gPROMS process. This task, which will be performed once the simulation has reached steady state, linearises the dynamic, non-linear, model at a specific operating point (i.e. steady state in our case) as explained above and in addition, generates the matrices [A], [B], [C] and [D] which characterise the process (Step R5 in Figure 1). After the dynamic simulation has completed, the user can access the abovementioned matrices in the gPROMS results output file and transfer the matrices to MATLAB (Step R6 in Figure 1). It is important that within the LINEARISE task, the input and output variables are introduced using exactly the same variable paths (names) used for the configuration of the conventional control loops to ensure consistency between the two control strategies.

After transferring the matrices [A], [B], [C] and [D] to MATLAB, scaling of the input and output variables is sometimes required (Step R7 in Figure 1) if the order of magnitude of the variables varies considerably (Skogestad and Postlethwaite 2005). In this work, however, the magnitude of all manipulated variables and the magnitude of all outputs were not significantly different, therefore scaling was not applied. Once the scaling (if any) is complete, the user is ready to generate the state-space representation of the system using matrices [A] and [D] and the matrices [B] and [C] (updated if scaling is applied) (Step R8 in Figure 1).

After the state-space model is generated within MATLAB, the user can (optionally) perform model reduction (Skogestad and Postlethwaite 2005) in order to reduce the number of states (through the generation of fewer, new synthetic states via projection-based methods) which will speed up the subsequent calculations (Step R9 in Figure 1). Model reduction is useful when complex models with a large number of states are considered, given that input-output behaviour changes are small. In this work, model reduction was not performed as calculations were found to be very fast even for the full-scale model.

Finally, Model Predictive Control can be applied in the model (Step R10 in Figure 1), using the mpcDesigner platform within MATLAB (The MathWorks Inc. 2019). In this platform, the model (***f***) is imported into mpcDesigner and the plant inputs and outputs can be categorised as manipulated variables, controlled outputs etc. After that, the user can manipulate the type of disturbance introduced (set point change, load disturbance etc.), as well as the tuning parameters of the MPC controller (sample time, prediction horizon, control horizon and variable weights) and directly see the impact of the changes on the performance of the controller. Once the tuning has been completed and the controller shows satisfactory behaviour, the user can export the controller settings only (as a set of parameters); export the overall controlled process (i.e. model, MPC controller and disturbance introduced) as a script for further investigation; or export the controlled process as a Simulink model. In this work, once the controller was properly configured, the script was exported in order to run it in MATLAB and extract the values of the manipulated and controlled variables of each simulation scenario.

In the following, the methodology developed for both conventional and non-conventional control strategies will be applied to a series of case studies, and it will be demonstrated how the methodology can be used to evaluate the controllability, of the reactive distillation system which is the main objective of this work. The dynamic behaviour of the different cases is compared to obtain a preliminary insight into the impact of the reaction and separation parameters, as well as the column design, on the controllability of a reactive distillation process. The methodology can easily be extended to also consider other systems, i.e. real rather than general reactive distillation systems, and it is worth noting that the methodology not limited to only reactive distillation but could also be applied to conventional distillation (although not shown).

3. Case studies

In previous work (Tsatse et al. 2021), a methodology was proposed for how to find the optimal design (e.g. total number of stages, feed stage locations) and operating parameters (e.g. reflux ratio, bottoms flow rate) for a reactive distillation process, and the methodology was illustrated using a number of case studies. For consistency, three of those case studies are also used in this work (Case studies 1, 2 and 15 from our previous work as mentioned in Table 1). The controllability of the optimal design in the case studies is investigated in order to explore how reaction and separation characteristics impact on the dynamic operation of the process. The case studies consider systems of different separation difficulty, as well as different kinetic characteristics, to identify how these two different phenomena contribute to the overall control performance of the system. For this reason, the three case studies were specifically selected as Case study 1 and Case study 2 having the same relative volatilities but different kinetics, whilst Case study 1 and Case study 3 (Case study 15 in previous work) having the same kinetics but different relative volatilities. It should be noted that the three case studies have different design and operational parameters, as determined by the steady state optimisation. Using the same design and operational parameters for all case studies would possibly result in over-designing at least one of the columns (i.e. the system with fast kinetics and favourable relative volatilities), which is expected to not be relevant from a practical and industrial point of view. To further clarify this point, if all three case studies had the same design (e.g. total number of stages, feed stage locations etc.) and operational (e.g. reflux ratio, bottoms flow rate) parameters, then it would be unlikely that the three systems would meet the same bottom product purity, therefore no

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comparisons could have been made. Fixing only the design (i.e. not the operational) parameters for the three case studies would result in an overdesigned column for Case study 1 (which would then have 27 stages instead of the 18 which is the optimal, i.e. 9 stages more) and as a result, no meaningful insight could be obtained regarding its control behaviour. It was therefore decided to use the optimised designs instead, being aware that this would increase the complexity of interpreting the control behaviour of the systems though, as a number of design and operational parameters would vary between the three cases.

The three case studies are based on a quaternary system, in which the following non-catalysed reversible reaction occurring in the liquid phase is considered:

$$A + B \leftrightarrow C + D \qquad \text{(Eq. 6)}$$

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

$$r_f = k_{f0} e^{-Ea_f/RT} C_A C_B \qquad \text{(Eq. 7)}$$

$$r_b = k_{b0} e^{-Ea_b/RT} C_C C_D \qquad \text{(Eq. 8)}$$

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, Eα, is expressed in kJ/mol (assumed to be 80 kJ/mol for both directions); and component concentration C 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.

The separation difficulty is defined based on the relative volatilities between the components, and for each alternative, fast and/or slower kinetic expressions were investigated. For all 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). This boiling point was assumed to be fixed and all other volatilities were calculated using the heavy reactant as the reference (Tsatse et al. 2021) in order to create the desired relative volatilities. Note that for Case study 3, although the VLE parameters are different compared to Case study 1 and Case study 2, the relative volatility between the products (α_{CD}) is the same, and equal to 6. Thus, it is the individual separation difficulties that change (α_{CA}, α_{AB} etc.) in this case. 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 and the relative volatilities were selected based on industrial interest and the reader is directed to our previous work (Tsatse et al. 2021) for further justification with regards to the choice of reaction kinetics. The assumptions of relative volatility etc. are not generally representative of any real system, however, had the study been conducted using real rather than generic systems then the analysis would have been specific to those systems only, and drawing any general conclusions on the impact of reaction vs separation performance would have been very difficult if not impossible. The methodology considered in this work can of course easily be applied to real and specific systems.

The feed temperatures were assumed to be at the corresponding boiling points given their composition. More information related to the vapor pressure of the components and their corresponding boiling points, as well as the underlying assumptions for the calculations, can be found in our previous work (Tsatse et al. 2021). In addition, liquid hold-up of all reactive distillation columns was assumed equal for all reactive stages and fixed at 0.1 m^3/reactive tray (in gPROMS ProcessBuilder, holdup is specified for reactive columns only and not for normal columns). For more information on the selected value of liquid holdup, the reader is directed to our previous work (Tsatse et al. 2021).

Conventional (decentralised) control schemes

For the evaluation of controllability, two conventional control schemes were considered: V-only and LV control (Figure 2). These two control schemes were selected as a) they are commonly used in industry for distillation processes and b) are successfully studied in various relevant investigations in

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literature (e.g. Skogestad and Morari 1987, Luyben and Yu 2008 etc.). In addition, as in LV control the loops remain the same as in V-only control, with only one additional loop included in the flowsheet, the application of these two control schemes will aid the understanding of process controllability. In both control schemes, the pressure at the top of the column (stage 2) is controlled using condenser duty and the liquid levels of the reflux drum and the sump are controlled using distillate and bottoms rate, respectively. In addition, in V-only control scheme, reboiler duty is manipulated in order to control bottom product purity (composition of component D). In the LV control scheme, bottom product purity is controlled in the same way as in the V-only scheme, and additionally the top product purity (composition of component C) is controlled by manipulating reflux ratio, thus expending all degrees of freedom of the system in this case. Table 3 summarises the controlled and manipulated variables for each of the two control schemes. Note that the methodology proposed in this work is not limited to the control configurations considered in these case studies and could easily be applied also to other control schemes such as DB, (L/D V/B), ratio control etc. Should both product streams be controlled in terms of purity, then feed ratio control is a sensible choice, however, in this investigation it was assumed that only the bottom product (component D) is of interest and that any impurity in the top stream (component C) will be taken care of downstream, e.g. in waste water after-treatment. For more information on the choice of product of interest and the aqueous nature of component C, the reader is directed to our previous work (Tsatse et al. 2021).

For the two control configurations considered in the case studies, two different disturbances were introduced to illustrate the methodology and meet the objectives of this work: a) a flow rate disturbance in the heavy feed (5% increase), and b) a feed composition disturbance (5% flow increase in heavy feed and in parallel, 5% flow decrease in light feed). Both disturbances were introduced as sharp ramps over 500s and were chosen as they are commonly considered in relevant academic contributions (e.g. Agachi 2006, Pham and Engell 2011, Zhang et al. 2020 etc.) as well as often encountered in real-plant operation. However, for the reactive distillation systems considered which are designed for 1:1 feed ratio (i.e. stoichiometric feed), it is expected that they will lead to incomplete reactant conversion and therefore difficulty to control both product purities, a difficulty which is characteristic for reactive distillation systems (and not conventional columns). Other disturbances that could have been introduced include, but are not limited to, disturbance in reboiler heating input, disturbance in feed temperature etc. Dead time for concentration measurements was not considered in this work.

The two disturbances mentioned above (feed flow rate and feed composition disturbance) were considered in sections 4.1 and 4.2. For consistency, the same two disturbances were used for all the investigations throughout this work, including for the revised designs (see later Section 4.3). For the linear MPC investigation (Section 4.5), the disturbances considered were: a) the same feed flow rate disturbance (5% increase in heavy feed) and b) a set point change (0.5% step increase in bottom product purity set point, i.e. product purity of 0.99 to product purity of 0.995), in order to also investigate the efficiency of MPC under set point change.

4. Results

This section includes the results generated from the application of the methodology developed in this work to the three case studies considered, for the investigation of the controllability of reactive distillation and the impact of key system and process parameters on the latter. First, a detailed description of how V-only and LV control behaves following a feed flow rate disturbance in a reactive distillation column will be presented (Section 4.1), followed by an investigation of the impact of reaction and separation characteristics on control performance (Section 4.2). This is followed by considering how design parameters, such as total number of stages and reactive tray liquid holdup can impact on control behaviour (Section 4.3). Section 4.4 investigates the impact of tuning parameters, whilst the last section (Section 4.5) evaluates the performance using advanced control.

4.1 Impact of disturbances

Before proceeding to the evaluation of the impact of reaction and separation parameters on the controllability of reactive distillation columns, it is important to obtain a detailed insight into the control behaviour of the column. In this section, the impact of a feed flow rate disturbance on the dynamic behaviour of the reactive distillation column under V-only and LV control, respectively, will be evaluated and explained by considering Case study 2. Although the case studies considered include only one product of interest, both V-only and LV control are investigated in order to understand what changes the column undertakes in order to tackle a disturbance, as well as the impact of an additional control loop, which potentially further increases the complexity of the control performance, especially when reaction is present within the column. For each control scheme, the responses of the controlled and manipulated variables will be presented (Figure 3 and Figure 7, respectively), along with figures which will demonstrate how pressure, temperature, vapour and liquid flow rates change within the column as a function of time, after the introduction of the disturbance and until the system reaches the new steady state (Figure 4 and Figure 8, respectively). Similar figures will be considered to illustrate the changes in reaction rates (in both reaction directions, Figure 5 and Figure 9, respectively) and composition profiles within the column (Figure 6 and Figure 10, respectively).

V-only control scheme

A detailed analysis is initially performed for Case study 2 and the V-only control configuration, and considering a feed B (heavy reactant) flow rate disturbance (5% increase from steady state value) at t = 1.4 hrs. The tuning parameters of all controllers in this section were based on typical values as presented in Table 4 and these values were specific for each type of control loop and therefore did not vary with control configuration (i.e. pressure control loop had the same tuning parameters for V-only and LV control).

The graphs in Figure 3 show the responses of the manipulated (D, B, Q_C and Q_D) and controlled (M_C, M_R, P, $x_{B,D}$) variables for each of the four control loops. Top product composition ($x_{D,C}$) is also shown although it is not controlled (i.e. reflux ratio, RR, is not manipulated), in order to see how this loop behaves. In order to obtain a better understanding of the changes the column undertakes in order to reject the disturbance, Figure 4 shows how the pressure, temperature, vapour and liquid mass flow rates, respectively, change in the column over time (in hrs) as a function of stage number. As the disturbance hits the column, product purity decreases due to the accumulation of component B at the bottom of the column (Figure 3), therefore reboiler duty increases from 426.9 kW to 463.0 kW (Figure 3) to bring purity back to the set-point value (above 99 mol%). This leads to a small increase in vapour mass flow rate (Figure 4 bottom, left), which has the highest value at stage 2 (where due to condensation of the entering reflux mostly liquid can be found) after which it gradually decreases as vapour tends to concentrate at the top of the column (lighter components in the vapour phase) in contrast to the bottom of the column where the heavier components can be mainly found (in the liquid phase). As a result of the vapour flow rate increase (more intense evaporation), pressure at the top of the column increases (Figure 3). The condenser duty then increases from -540.3 kW to -576.2 kW in order to bring pressure back to the steady-state value (impact on pressure is minimal and the control is efficient and relatively fast), increasing liquid flows (Figure 4 bottom, right). In general, liquid flows decrease from the upper to the lower stages of the column as expected due to the vapourisation of the light components. Stage 25 has a very low value as this is the stage where the vapour generated in the reboiler goes back into the column. Once the increased reboiler duty has brought purity back to the set-point (Figure 3), leading to a general pressure increase towards the bottom of the column as the pressure is controlled at the top (Figure 4 top, left), and to a temperature increase at the top of the column (Figure 4 top, right), the bottoms flow rate (Figure 3) drops back down to almost the steady state value (0.175 kg/s). In contrast, the distillate rate needs to stabilise at a higher value (from 0.175 kg/s to 0.185 kg/s) in order to accommodate the removal of the excess of reactant B (Figure 3 top, left). As can be seen, the impact on the reflux drum liquid level is minimal. Overall, after the

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disturbance has settled in the column, the amount of component D has not changed because the amount of reactant A has not changed and top product composition, which is not controlled, decreases as the excess of component B is removed from the distillate.

The reaction rates for the forward and backward reactions are given in Figure 5 for different times during the run, whilst Figure 6 shows the concentration profiles in the column initially (dashed lines) and at the new steady state following the disturbance (solid lines). It can be seen that due to the changes in concentrations through the column (Figure 6), the reaction rates change as well (Figure 5). Figure 6 shows that the additional amount of reactant B is mainly pushed towards the top and middle of the reactive column due to the increased reboiler duty. As a result, the amount of reactant A within the column decreases and the concentration gradient of component C is sharper at the top of the column. The composition at the bottom of the column has a relatively limited change, as the purity of component D is controlled. A change in composition, and therefore temperature (Figure 4 top, right), is expected to impact on reaction rates as well (Figure 5). Figure 5 shows that changes indeed occur, although they are relatively small. As a result, the conversion of component A remains almost complete and the amount of component D produced is not significantly affected.

LV control scheme

The same investigation was performed for the LV control configuration, using the same case study (Case study 2) and considering the same disturbance (feed flow rate increase) in order to investigate the differences in the responses under the two different control schemes. The tuning parameters of all controllers in this section were again based on typical values as presented in Table 4.

The graphs in Figure 7 show the responses of the manipulated (D, B, Q_C, Q_D, and RR) and controlled (M_C, M_R, P, $x_{B,D}$ and $x_{D,C}$) variables for each of the five control loops. Figure 8 shows how the pressure, temperature, vapour and liquid mass flow rates change in the column over time as a function of stage number. As the disturbance hits the column, the behaviour of the system is similar to the behaviour when V-only control is applied. In more detail, the change in feed B flow rate leads to a decrease in bottom product purity, which in turn leads to a significant increase in reboiler duty (to remove component B over the top) from 426.9 kW to 1003.7 kW (Figure 7) to retain bottom product purity at the set point (above 99 mol). The significantly increased vapour flows (Figure 8 bottom, left) due to the increased reboiler duty, lead to a pressure increase at the top (Figure 7) which triggers an increase in condenser duty from -540.3 kW to -1114.9 kW (Figure 7), in order to bring pressure back to the steady state value. The impact on pressure is minimal and the control is efficient and relatively fast. As can be seen, the level responses are also similar to for V-only control. Oscillations observed in the control responses are due to the tuning of the controllers, which at this stage was based on typical values. At the same time, the decrease in top product purity leads to an increase in reflux ratio (Figure 7), which in turn leads to a significant increase in liquid flow rates (Figure 8 bottom, right) and increase in reboiler duty. The increased reboiler duty, which brings bottom product purity back to the set-point (Figure 7) after a while, leads to a general pressure increase towards the bottom of the column as the pressure is controlled at the top (Figure 8 top, left), and to a significant temperature increase at the top of the column (Figure 8 top, right). This shows that in general, the feed flow rate disturbance leads to a temperature increase in the entire column. This observation is different between the two control schemes. In V-only, temperature was maintained at the bottom of the column due to the single point control whilst under LV control, temperature increases in the entire column due to the dual-point control. As the bottom product purity has returned to the steady-state value, bottom flow rate returns to the set-point (Figure 7). In contrast, the distillate rate needs to stabilise at a higher value in order to accommodate the removal of the excess of reactant B (Figure 7) although this leads to violating the top product purity specification (Figure 7). Top product purity cannot be maintained (as its final value is 0.945) and the reflux ratio reaches its upper bound (RR=10). In case the manipulated variable was valve opening, the limiting value would then be 100%.

Simulations with relaxed upper bounds (i.e. reflux ratio up to 150) were performed (results not shown), confirming that the system simply cannot meet the top product purity set-point regardless of the upper bound of reflux ratio, as it is impossible for the system to maintain both product purities due to the additional amount of component B which has to be removed from the top. This behaviour is typical for reactive distillation systems which operate with stoichiometric feeds and is a distinct characteristic compared to conventional distillation columns. If reactants are fed to the reactive column in a 1:1 ratio, then imbalance of reactants (quite easily effected by feed flow rate disturbance) will result in incomplete reactant conversion, and therefore unreacted feed which should be removed from the column as product stream, reducing product purity in one or both outlet streams. Even at very strict feed ratio control, this issue might occur, requiring alternative correction methods, e.g. in post-treatment sections of the product streams.

The system is able to control bottom, and not top, product purity as the reboiler heat duty (vapour dynamics) exhibits quicker dynamics than the reflux ratio (liquid dynamics) (Stewart 1981, Cao et al. 2017). For this case study, the disturbance introduced in the LV control scheme is rejected with more difficulty than in the V-only control scheme, as shown by the changes that the manipulated variables have to undertake, which is expected since the LV control scheme is aiming to control both ends of the column and therefore introduces more interactions between the top and the bottom of the column, leading to higher overshoot and larger settling times. This difficulty of LV control is also attributed to the nature of the disturbance, for which maintaining both product purities is impossible. It should be noted that for a different type of disturbance (e.g. reboiler heat input failure), meeting both product purities could still be possible. The control behaviour discussed so far does not provide sufficient insight so in order to enhance our understanding, further analysis is required.

The reaction rates for the forward and backward reactions are given in Figure 9 as a function of stage number and for different times during the run, whilst Figure 10 shows the concentration profiles in the column initially and at the new steady state following the disturbance. Figure 10 shows that the additional amount of reactant B is mainly pushed towards the top and middle of the reactive column due to the increased reboiler duty and reflux ratio. As a result, the amount of reactant A within the column decreases and the concentration gradient of component C is sharper at the top of the column. The composition at the bottom of the column has a relatively limited change, as the purity of component D is controlled. A change in composition, and therefore temperature (Figure 8 top, right), is expected to impact on reaction rates as well (Figure 9). Figure 9 shows that changes indeed occur (e.g. increase in final forward reaction rate), due to the significant temperature changes. Overall, the conversion of component A remains almost complete and as a result, the amount of component D produced is not significantly affected.

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Comparison

Overall, V-only control was found successful in controlling the system for the feed disturbance considered. This is due to the fact that the decrease in top product purity, due to the feed stoichiometric balance which was no longer met, was accepted (i.e. $x_{D,C}$ was not controlled). This would in practice be acceptable as long as this (top) stream was considered waste or was processed downstream, in a subsequent unit where this quality variation could be tolerated. Dual-point or LV control, on the other hand, was not able to control all the controlled variables, in particular, was not able to maintain the top product specification due to the overall material balance and the imbalance of feed stoichiometry. The impact of the feed disturbance on reaction rates was also more visible (profile shift, maximum values), and the column temperature and composition profiles changed more significantly, under LV control which leads to a higher, although not the desired, top product purity at the expense of high reflux ratio. This is of course expected as both ends of the columns are then controlled (significant change of reboiler duty and reflux ratio), although as mentioned the distillate composition specification cannot be reached. As already discussed, the nature of the disturbance (imbalance of feed flow rates which results in incomplete conversion of reactant B) was expected to have such an impact on the performance for LV control, hence was the focus of investigation. For

other types of disturbances, for instance a disturbance in reboiler heat input or steam flow rate, LV control might well have been successful (not shown).

4.2 Impact of reaction and separation on controllability

In this section, the impact of reaction and separation characteristics on the controllability of reactive distillation will be considered for LV control and towards both feed flow rate and feed composition disturbances (Figure 11). As mentioned earlier, the three processes considered have different design and operational characteristics, as determined by optimisation. For further justification of this choice, the reader is directed to return to Section 3. The responses presented in the previous section indicate that the behaviour of the process is more complex when LV control is considered (i.e. temperature, pressure, flow rates and key control variables undertake more significant changes), therefore the impact of the disturbances and the derived conclusions would be more visible. As a result, the latter was selected for the analysis of this section as well, instead of V-only control. Performing the same investigation using V-only control led to similar conclusions, however, in order not to distract the reader from the focus of the section, detailed results are only shown for LV control.

Figure 11 shows the key control variables responses towards the disturbances introduced under LV control for all three case studies, with the feed flow rate disturbance to the left and the feed composition disturbance to the right. Both disturbances are introduced at 1.4 hrs. All responses are shown as % difference from their original steady state values to allow for easier comparison. Figure 11 shows responses for all three cases and as the absolute values for the three case studies were different, % difference from the steady state value was used instead to facilitate comparisons. In the previous section, Figures 3 and 7 showed results for a single case study, so demonstrating the results in composition units was preferred instead. For the feed flow rate disturbance (left), it can be seen that all case studies have similar responses in terms of settling time (approximately 5.92 hrs), and that this settling time is quite long. Case study 1 (easy separation, fast kinetics) and Case study 3 (difficult separation, fast kinetics) have an overshoot of approximately 0.07% in pressure (top figures) whilst Case study 2 (easy separation, slower kinetics) has a slightly higher overshoot of about 0.1%. For the feed composition disturbance (right), it can be seen that the three systems have similar response in terms of settling time (3.26 hrs) and that this is shorter than for the flow rate disturbance. Case study 2 (easy separation, slower kinetics) has a marginally higher overshoot (0.23%), whilst Case study 1 (easy separation, fast kinetics) and Case study 3 (difficult separation, fast kinetics) show more similar behaviour in terms of overshoot (0.20% and 0.18%, respectively). Pressure is maintained for all case studies and, as a PI controller is used, there is no offset observed.

Figure 11 (middle) shows the bottom product purity response. For the feed flow rate disturbance (left), Case study 1 (easy separation, fast kinetics) and Case study 3 (difficult separation, fast kinetics) have similar responses in terms of settling time (6.61 hrs) and very small overshoot (-0.5%). Case study 2 (easy separation, slower kinetics) has a shorter settling time (5.06 hrs) but a slightly higher overshoot (-0.7%). For the feed composition disturbance (right), the response is similar in terms of settling times (3.86 hrs) for all case studies. Case study 2 (easy separation, slower kinetics) has a slightly increased overshoot (loss of off-spec product) with a value of -1.44%. Again, no offset is observed as a PI controller was used.

Figure 11 (bottom) shows the top product purity response. It can be seen that none of the systems considered are able to maintain the top product purity using two-point control for either of the two disturbances as discussed above, since bottom purity is controlled and mass balances must be respected as the excess of (unreacted) component B needs to be removed from the top of the column. In this case, an additional column would be needed to mitigate this disturbance, such that product C can be separated in the additional column and the remaining feed can be recycled back to the reactive column. Again, Case study 2 (easy separation, slower kinetics) shows a slightly worst control

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performance in terms of offset, although none of the case studies are able to maintain the distillate composition.

From Figure 11 it is found that Case study 2 (easy separation, slow kinetics) has slightly worst responses (in terms of settling time and/or overshoot/offset) compared to Case study 1 (easy separation, fast kinetics) and Case study 3 (difficult separation, fast kinetics), which indicates that for dynamic operation and process control, kinetics may have a more dominant impact compared to relative volatilities, although the impact is quite modest in the three cases considered. Also, the similar behaviour of Case study 1 and Case study 3 shows that, although the two processes have different optimal steady-state designs, the fact that they have the same kinetics might contribute to their similar behaviour. This contrasts with steady state operation where it was shown that relative volatilities had a stronger impact on design and operation (Tsatse et al. 2021). As the inlet flows (feed flow rates) and steady-state bottoms flow rates were the same for the three case studies considered, the sizes of the reflux drum and sump were very similar. In addition, the controller tuning parameters in section 4.2 were the same for all three case studies, hence any differences in control behaviour mainly stem from kinetics and thermodynamics. However, for the case studies considered, the responses do not show any major differences which indicates that the impact of reaction kinetics and separation characteristics on control performance, although existing, is limited.

4.3 Impact of design considerations

As mentioned in Section 1, the number of stages and the reactive tray liquid holdup has been found to impact on the controllability of a reactive distillation column (Al-Arfaj and Luyben 2000b). The impact of increasing the total number of stages, as well as of changing the reactive tray liquid holdup (both at the design stage of the process), on the control performance of the reactive distillation column, will therefore be investigated in this section as follows: a) the base case total number of stages for Case study 1 as found during optimisation in our previous work (Tsatse et al. 2021) (i.e. the minimum required to achieve the specified level of reaction/separation); and b) the tray liquid holdup (which was fixed during optimisation) for Case study 2. As mentioned already, the focus of this section is on bottom product purity as this is often the main product industrially (Tsatse et al. 2021), and it has already been shown that liquid levels and pressure are sufficiently controlled using the control schemes considered. As a result, in the following, the impact of these two design variables on product purity control performance will be considered for both feed disturbances and under both control schemes (Figure 12 for total number of stages and Figure 13 for liquid holdup). Both V-only and LV control are considered in order to investigate whether the impact of design considerations depends on the selected control strategy.

Impact of total number of stages

The impact of increasing the number of stages on the controllability of the process was investigated for Case study 1 (Figure 12). This parameter was investigated since by increasing the optimal number of stages (found during optimisation) slightly, the overall cost is not significantly affected (Tsatse et al. 2021), and the tolerance to failures due to inadequate separation and/or reaction is expected to improve. Adding a number of additional trays is a common strategy in conventional distillation to mitigate production failures and it is therefore interesting to investigate whether adding a number of stages also improves dynamic performance.

Figure 12 shows the bottom product purity response under V-only (Figure 12a) and LV (Figure 12b) control. The responses are shown towards both disturbances for the base case total number of stages as well as for an additional two and four stages (added evenly in the stripping and rectifying section), respectively, for Case study 1. In general, increasing the total number of stages had a minor impact on component D production rate showing that the impact on reaction only, was not significant and any differences mainly stem from the separation task. From Figure 12a, it is shown that under V-only control, increasing the total number of stages deteriorates the performance in terms of settling time

and overshoot. This is sensible for a reactive column as increasing the number of stages, and thereby the overall liquid holdup, leads to longer response times, delaying the control action given that control takes place only at the bottom of the column, and therefore increasing the overshoot. Oscillations observed in all responses are due to controllers tuning parameters as explained earlier. For the LV control scheme (Figure 12b), on the other hand, the responses are very similar, and the base case design is only slightly better in terms of settling time. This is reasonable since increasing the number of stages, although leading to control loop decoupling, introduces some delays in responses which are, however, minimal as there is parallel control action at both column ends. Overall, it is shown that the impact of an increased total number of stages is more significant under V-only control and actually makes the performance worse rather than better.

Impact of liquid holdup

Similarly, the impact of increasing liquid holdup, practically by increasing the tray weir height, on the controllability of the process is investigated. A 20% and 50% increase from the base case value (0.1 m^3/reactive tray) was considered. Case study 2 was considered this time, as it included slower kinetics, which are more dependent on tray liquid holdup in terms of reaction residence time. It is expected that increased holdup will increase pressure drop across the column, however, the focus of this section is the impact of the holdup on the controllability of the process so the impact on column hydraulics is not considered in further detail.

Figure 13 shows the bottom product purity response under V-only control scheme (Figure 13a) and LV control (Figure 13b). For the V-only control scheme (Figure 13a), it was found that an increase of liquid holdup may also deteriorate control performance. This is sensible as increasing liquid holdup leads to longer response times, thus delaying the control action (i.e. reboiler duty increase to evaporate the excess of component B, given that control takes place only at the bottom of the column) and therefore also increasing the overshoot. This observation is in agreement with the previous investigation, where the overall liquid holdup was increased through the addition of reactive stages in the column and similarly to the previous investigation, the differences mainly stem from separation behaviour (and not reaction differences). From Figure 13b, it can be seen that for LV control increasing the liquid holdup (especially for feed flow rate disturbance) improves overshoot slightly, given that control action takes place at both ends, therefore the manipulation of reflux ratio and reboiler duty reduce overshoot for bottom product purity control as they both increase separation performance. Increasing tray liquid holdup, however, increases slightly settling times in all responses, due to the longer residence time (increased production rate) and, therefore larger response times. In order to investigate whether lower holdup is, in general, easier to control, the same simulations were performed using lower values of liquid holdup (down to 0.07 m^3/reactive tray), however, the results (not shown) were fairly similar to the base case results, indicating that the behaviour does not stem from the exact value of holdup, but from the system characteristics.

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Comparison

Overall, when V-only control is considered, the initial optimal design responds better to feed flow rate and feed composition disturbances. Having a larger overall holdup (i.e. reaction residence time, through adding more stages or having larger holdup per stage) leads to slower responses and larger overshoot. When both product purities need to be controlled, however, (i.e. LV control is applied), designing a column with a number of additional stages and/or increased tray liquid holdup may be beneficial for the controllability of the column, mainly in terms of overshoot. In addition, larger liquid holdup improves reaction performance, however, this is not reflected to the results, showing in turn that the control behaviours presented mainly depend on the separation, and not reaction, task.

4.4 Impact of tuning parameters of controllers

This section will provide insight into whether the conclusions drawn so far depend on the choice of tuning parameters for the controllers. The improvement in bottom product purity control due to

optimisation of the controller tuning parameters will be indicatively shown for Case study 1 (Figure 14). In addition, the findings of the previous sections with regards to the impact of reaction kinetics (Figure 15) on control performance, which were obtained using parameters based on typical values, will be compared to the performance using optimised control parameters.

As the tuning parameters considered so far were based on typical values, optimising the tuning parameters for all PI controllers (not level controllers as levels are not tightly controlled) was considered using as optimisation criterion the minimisation of the off-spec amount as described earlier. The optimised tuning parameters, as found for the case studies and disturbances considered in this section under LV control, are presented in Table 5. Figure 14 shows that the control responses can be improved, using as an example the bottom product purity response to a feed flow rate disturbance for Case study 1 under LV control configuration. The settling time was reduced from 6.26 hrs to 2.86 hrs and the overshoot decreased slightly from -0.52% to -0.48%. However, the improved controller was also more aggressive and introduced some oscillations in the control behaviour.

Next, results are repeated to show that the conclusions drawn so far are independent of the controller tuning parameters. In an effort to confirm that slower kinetics will have an impact on control performance, regardless of tuning parameters, Figure 15 (top) shows the pressure responses for Case study 1 and Case study 2 towards a feed composition disturbance under LV control scheme. It is shown that the settling time of Case study 1 (easy separation, fast kinetics) is 1.86 hrs and the overshoot is almost 0.12% whilst for Case study 2 (easy separation, slower kinetics) settling time is 2.36 hrs and overshoot is almost 0.4%. The equivalent plot, generated with literature tuning parameters (Figure 11 top, right) shows that Case study 1 has similar settling time (4.3 hrs) with Case study 2 (larger settling time compared to the improved performance of Figure 15), however, the overshoot of Case study 1 is almost 0.20% whilst the overshoot of Case study 2 is 0.23%. This shows that using both the literature and the optimised parameters, the conclusion that slower kinetics hinder reactive distillation process controllability still holds.

4.5 Linear MPC results

In this section, the performance of linear MPC will be evaluated and compared to the conventional control schemes applied so far, indicatively for Case study 1 (Figure 16). In addition, the control behaviour for the three case studies will be evaluated using MPC and considering a bottom product purity set-point change (Figure 17) and load disturbance (Figure 18) in order to investigate whether the abovementioned findings with regards to the impact of reaction kinetics on the controllability of the reactive distillation column are valid, even when advanced control is considered.

For all case studies, the non-linear dynamic models were linearised in gPROMS ProcessBuilder and, following the procedure described previously, the state-space representation was generated and an MPC controller was designed in MATLAB using the mpcDesigner tool. The condenser and reboiler duties were considered as manipulated variables and the remaining three inputs (both feed flow rates and reflux ratio) were considered measured disturbances. Reflux ratio was considered a measured disturbance (as the alternative in the mpcDesigner tool would be unmeasured disturbance), however, its value was kept fixed at the steady state value and was therefore practically considered a constant. In addition, pressure and bottom product purity were considered measured outputs whilst top product purity was considered an unmeasured output. This decision was made since it was previously (based on conventional control) shown that the reactive column cannot maintain both product purities, at least not for the cases considered in this work. It was therefore decided that the MPC would have two control goals, maintain pressure at the top of the column and bottom product purity, instead of three. Testing this decision and adding a third control goal in the MPC scheme (i.e. top product purity control) led indeed to unsuccessful control for both product purities i.e. both product

purities could not return to their set-point after the introduction of the disturbance. In addition, the agreement between the linear and non-linear model around the operating point was tested before the implementation of the linear MPC and for all case studies, the agreement was very good. The linear model is nevertheless just an approximation, and will only be valid very close to the linearisation point. Therefore, as operation is moved away from this point the linear MPC prediction may not follow the non-linear behaviour exactly but can nevertheless still provide good control, and will in practical implementation not violate any physical limitations. Although this would be beyond the scope of this work which is the investigation of controllability rather than control, the performance of the linear MPC could be further compared to the performance of the equivalent, non-linear MPC (i.e. using the original, non-linear model), however, the latter is not currently supported within the mpcDesigner tool and therefore the application of non-linear MPC would require developing the controller in the command line. This would potentially introduce inconsistencies between the two approaches and as a result, non-linear MPC and its performance is not considered in this work. In addition, although this would again be beyond the scope of this work, the performance of the linear MPC could be evaluated on the original, non-linear model. However, this was not possible within gPROMS ProcessBuilder and the mpcDesigner tool and it was therefore not considered.

For all case studies, the same MPC tuning parameters were used: a sample time of 30 s, a prediction horizon of 120 s and a control horizon of 30 s, as these parameters were found to work well for all the systems. The sample time was chosen based on the desired closed-loop response. In addition, usually, the prediction horizon is selected to be longer than the control horizon as then the control system is less sensitive to model error. Also, the weights of the variables (i.e. factors which penalise deviations from the relevant target values) were kept at their default values, and instead a beta parameter which is related to how aggressive or closed-loop stable the controller is was manipulated. This beta parameter adjusts all weights in order to make the controller more or less aggressive. As the beta parameter increases, the weights of manipulated and controlled variables (i.e. set-point tracking) increase whilst the manipulated variables increment suppression decreases. In this work, a beta parameter of approximately 2.23 was chosen, which would mean that in the controller's objective function, the manipulated variables increment suppression would be halved whilst the output variable tracking would be twice as important, in order to penalise any significant deviation from the product quality specification. In the mpcDesigner platform, the user can manipulate the value of the beta parameter through the relevant tuning sliding bar thus in this work the bar was fixed just above 2, which was the desired point.

First, for Case study 1, the performance of the conventional V-only control versus the performance of the MPC for a feed B flow rate disturbance (5% increase) was evaluated and shown in Figure 16. It is shown that although the MPC leads to similar settling time as under V-only control, it eliminates the oscillations observed for conventional control and also reduces the overshoot of the bottom product purity, therefore improves the response significantly.

Next, the performance of all case studies using MPC was evaluated for two different disturbances: a) a set point change in bottom product purity for component D (0.5% increase) and b) a feed B flow rate disturbance (5% as considered so far).

Figure 17 shows the control performance of MPC for all case studies towards the bottom product purity set point change. From Figure 17 (top) it is shown that all systems are able to follow the set point change. Case study 1 (easy separation, fast kinetics) and Case study 3 (difficult separation, fast kinetics) meet the new bottom product purity set point faster (approximately 4.5 hrs) whilst Case study 2 has a significantly larger settling time (51 hrs). This is also expected by looking at the behaviour of reboiler duty (Figure 17, bottom). For Case study 1 and Case study 3, reboiler duty quickly reaches a new steady state value (after about 2.6 and 4.5 hrs, respectively), however, this is not the case for Case study 2, where reboiler duty shows instability, in fact requiring approximately 55 hrs before it finally stabilises, therefore leading to larger settling times for the control variables (condenser duty

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has similar behaviour, not shown). Increasing the beta parameter for Case study 2, keeping the rest of the tuning parameters (i.e. sample time, prediction and control horizons) the same as they did not significantly improve the performance, to a value of approximately 4.57 (i.e. making the controller more aggressive), reduces the settling time for reboiler duty to approximately 39 hrs. This indicates that even with improved controller settings (variable weights), Case study 2 requires more time to reach the new steady state, due to the slower kinetics, as observed and discussed in Section 4.2 for the conventional control schemes as well. The unstable behaviour of Case study 2 may indicate a potential state transition (i.e. multiple steady states), which should be investigated further in a separate investigation.

Figure 18 shows the control performance of MPC for all case studies towards the feed B flow rate disturbance. From Figure 18 it can be seen that Case study 2 (easy separation, slow kinetics) shows a more increased difficulty in rejecting the load disturbance introduced. Case study 1 (easy separation, fast kinetics) and Case study 3 (difficult separation, fast kinetics) show successful rejection of feed B flow rate increase and the manipulated variables settle to the new set points within 3.5 hr. However, this is not the case for Case study 2 where slow response is observed for bottom product purity (more than 30 hrs required to completely eliminate the offset) and instability is observed for condenser duty as it needs almost 55 hrs before it finally stabilises (reboiler duty has similar behaviour, not shown). A comment needs to be made regarding pressure response. Case studies 1 and 3 show an increase in pressure before dropping it back to its set point. However, for Case study 2, a decrease in pressure is observed (reverse behaviour). This is due to the unstable behaviour of the controller, as both condenser and reboiler duties show an initial increase (absolute increase for condenser duty) and then decrease which cannot be easily stabilised, suggesting that, again, the tuning of the MPC for Case study 2 would potentially need revision (e.g. change of variable weights) in order to be more stable and successfully reject faster the changes introduced. As a result, it is shown that the same tuning which leads to a successful control strategy (MPC) for Case study 1 and Case study 3 (fast kinetics), is not sufficient for the control of Case study 2 (slower kinetics) which requires more careful tuning and further investigation with regards to the possibility of state transition.

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5. Conclusions

In this work, the controllability of reactive distillation processes has been evaluated using a developed methodology. The latter was applied to three different case studies with varying difficulty of separation in terms of volatilities and reaction characteristics in terms of kinetics to obtain insight into how key system characteristics impact on control behaviour. Based on these three case studies, it was shown that for conventional distillation control schemes, kinetics (for the ranges considered) may have a more determining effect towards the obtained controlled performance than relative volatilities. This is in contrast to previous findings (Tsatse et al. 2021) for steady state design and operation, where relative volatilities were found to have a more significant impact on the optimal process design and operation.

A significant observation was made with regards to the importance of feed ratio control when the reactive column operates with stoichiometric feed. When two-point control is required, feed flow rate changes and/or feed composition changes will result in incomplete conversion, leading to unsuccessful quality control. This indicates the increased sensitivity of reactive distillation systems operating in stoichiometric mode towards feed ratio disturbances, comparing to conventional distillation columns.

Although the performance of two-point control was not satisfactory in terms of distillate control, it was nevertheless included as the primary goal of this manuscript was not finding the most suitable control strategy, but rather to investigate the interactions between reaction and separation characteristics and their impact on the controllability of reactive distillation. More importantly, the component of interest was only component D (bottom product stream). Many common industrial

examples are of this type, i.e. have one desired component (often bottom component) and one waste component (often distillate component), and the control of these cases is therefore of great industrial interest. By performing the simulations for both V-only and LV control, the behaviour of such systems was studied and explained in detail, and the impact of the additional control loop in LV control was discussed as it is of relevance to reactive distillation, more so than regular distillation, and for these cases tight control of the distillate is not generally required.

The importance of design variables on the controllability of reactive distillation was also investigated by studying the effect of increased total number of stages and the tray liquid holdup. Revising column design led to benefits in terms of controlled variables settling time, overshoot and offset, however, these benefits depended on the control strategy and therefore the impact of process design on controllability should be carefully investigated when various control alternatives are considered .

The more determining effect of reaction kinetics on the controllability of the column, previously found using typical values for the tuning of the controllers, was also confirmed using optimised control parameters based on the minimization of the loss of off-spec bottom product. The optimised parameters led to improved controller performance and established the impact of the reaction on control behaviour, which was independent of tuning parameters selection.

Finally, linear model predictive control (MPC) was considered to demonstrate how linear MPC can improve the control performance compared to conventional control schemes. It was also demonstrated that the relative impact of reaction and separation on the controllability of reactive distillation was the same using either conventional or advanced control. Other control configurations, such as feed ratio control, could also have been considered but was beyond the scope of this work which focused on investigating controllability rather than control.

The systems considered in this work are ideal and generic, and therefore the derived conclusions cannot be automatically expanded to real chemical systems as this would require the additional consideration of the latter and comparison of the associated control behaviour, which was beyond the scope of this work. Future work could focus on considering non-ideal systems based on specific rather than generic components in order to investigate whether the conclusions drawn from this investigation also apply to real chemical systems (i.e. with no underlying assumptions such as constant chemical equilibrium etc.). Furthermore, the methodology proposed in this work can easily be applied to other intensified distillation processes (e.g. dividing-wall columns etc.) to obtain further insight into the controllability of the latter.

6. Notation list

B	Bottoms flow rate (kg/s)
CCB	Bottom product composition controller
CCT	Top product composition controller
D	Distillate flow rate (kg/s)
e	Error
Eα	Activation energy (kJ/mol)
f	Model
IAE	Integral absolute error
k_{b0}	Backward pre-exponential factor (m^3/(kmol·s))
K_{eq}	Chemical equilibrium (-)
k_{f0}	Forward pre-exponential factor (m^3/(kmol·s))
LCB	Sump liquid level controller
LCT	Reflux drum liquid level controller
M_C	Reflux drum liquid holdup (m/m)
MPC	Model Predictive Control
M_R	Sump liquid holdup (m/m)
P	Proportional (controller)
PC	Pressure controller
PI	Proportional integral (controller)
PID	Proportional integral derivative (controller)
P_T	Pressure at stage 2 (bar)
Q_C	Condenser duty (kw)
Q_R	Reboiler duty (kW)
r_b	Backward reaction rate (kmol/(m^3·s))
r_f	Forward reaction rate (kmol/(m^3·s))
u	Time-dependent input variables
x	Set of differential variables
$x_{B,D}$	Bottom product purity (mol/mol)
$x_{D,C}$	Top product purity (mol/mol)
y	Set of algebraic variables
α	Relative volatility (-)

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8. Figures and Tables

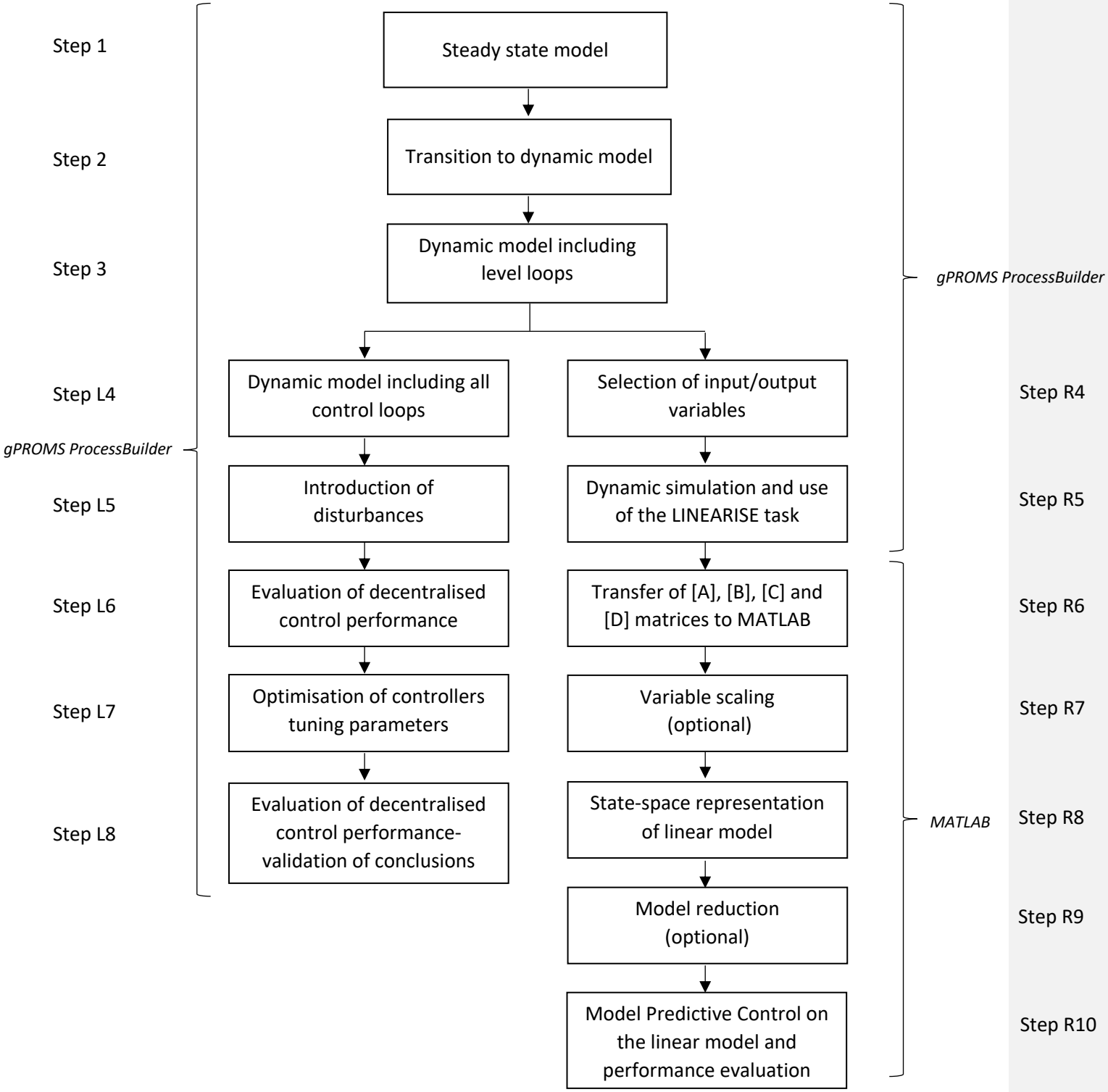

Figure 1: Methodology proposed in this work for the evaluation of controllability using conventional and advanced control strategies. Left: evaluation of conventional control schemes within gPROMS ProcessBuilder, Right: evaluation of Model Predictive Control on a linearised model using both gPROMS ProcessBuilder and MATLAB. The methodology should be repeated several times based on the purpose of the investigation as explained in section 2.

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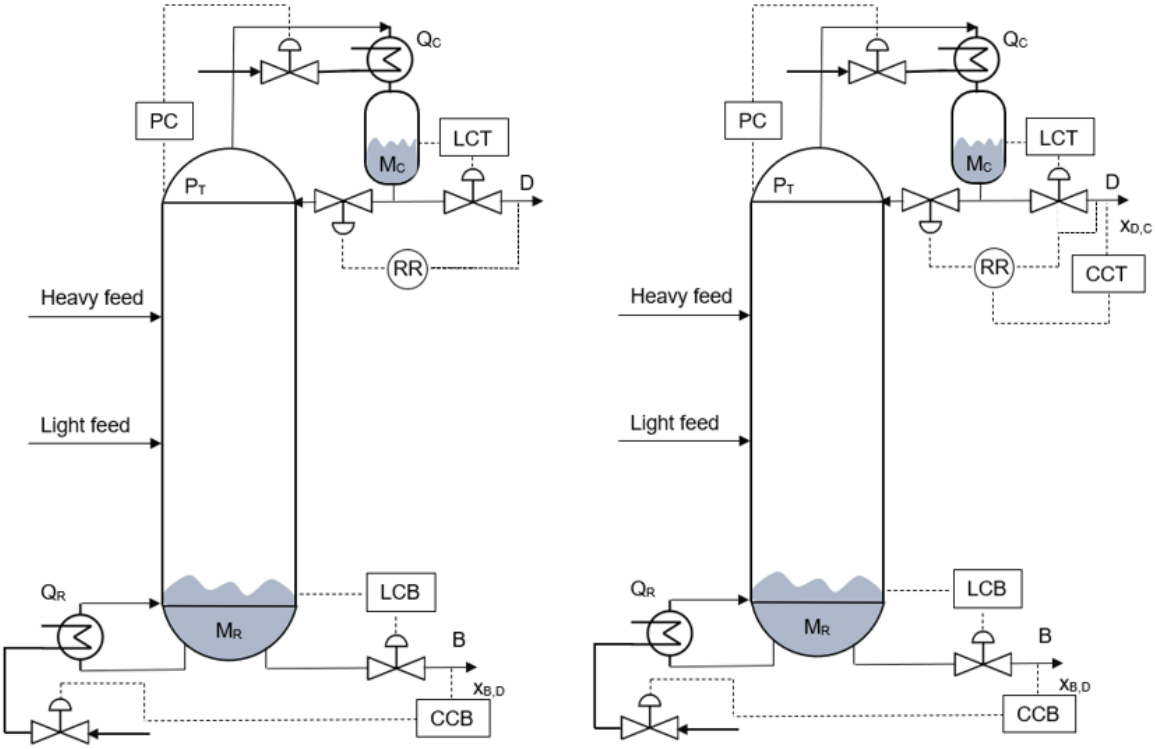

Figure 2: V-only (left) and LV (right) control configurations.

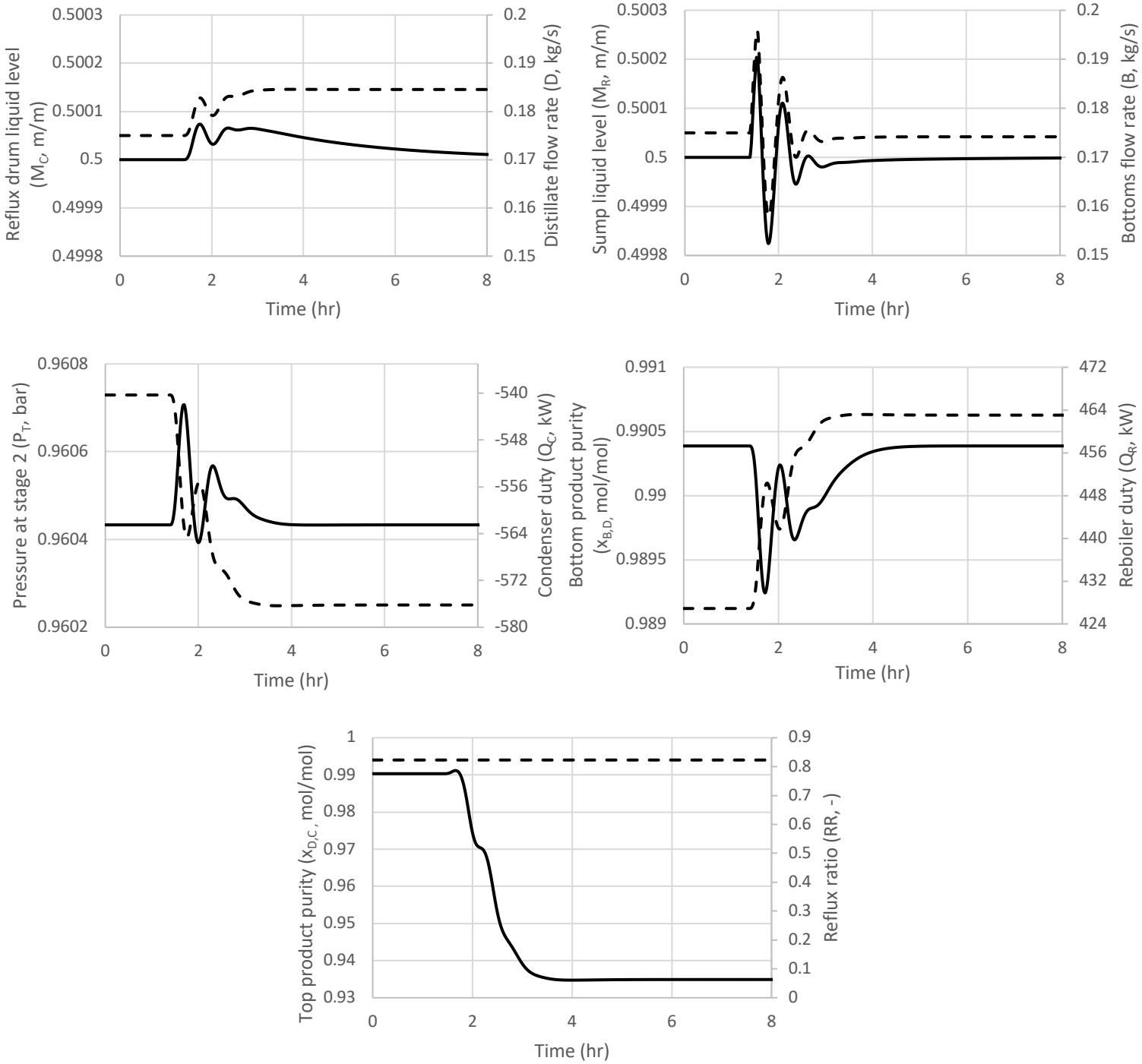

Figure 3: Closed-loop responses for feed B flow rate disturbance (5% increase). Disturbance introduced at t=1.4 hrs. Left axis is controlled variable (solid line) and right axis is manipulated variable (dashed line).
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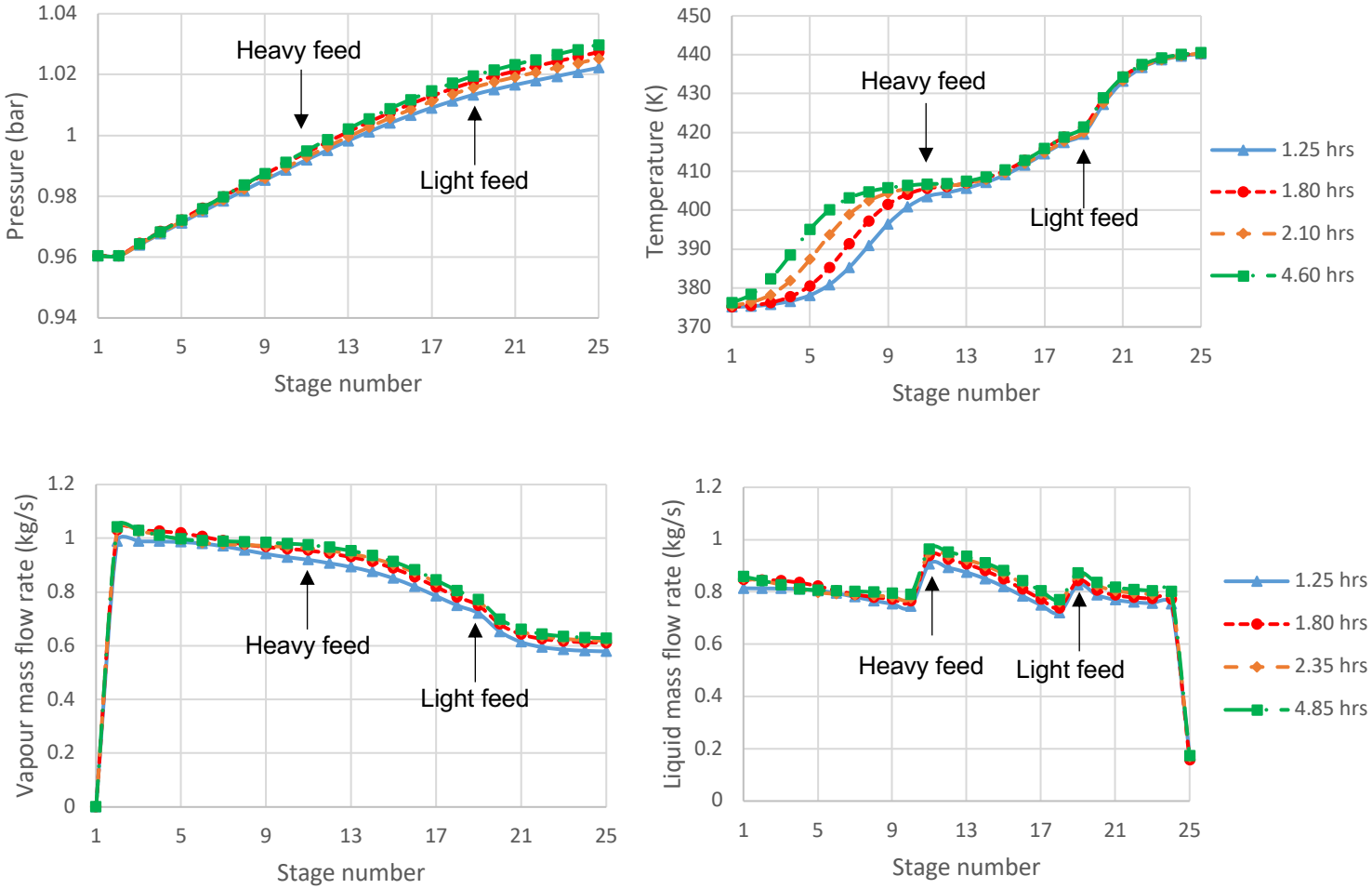


Figure 4: Pressure (top, left), temperature (top, right), vapour mass flow rate (bottom, left) and liquid mass flow rate (bottom, right) change due to the introduction of feed B flow rate disturbance (5% increase). Disturbance introduced at t=1.4 hrs.
(Case study 2, V-only control).

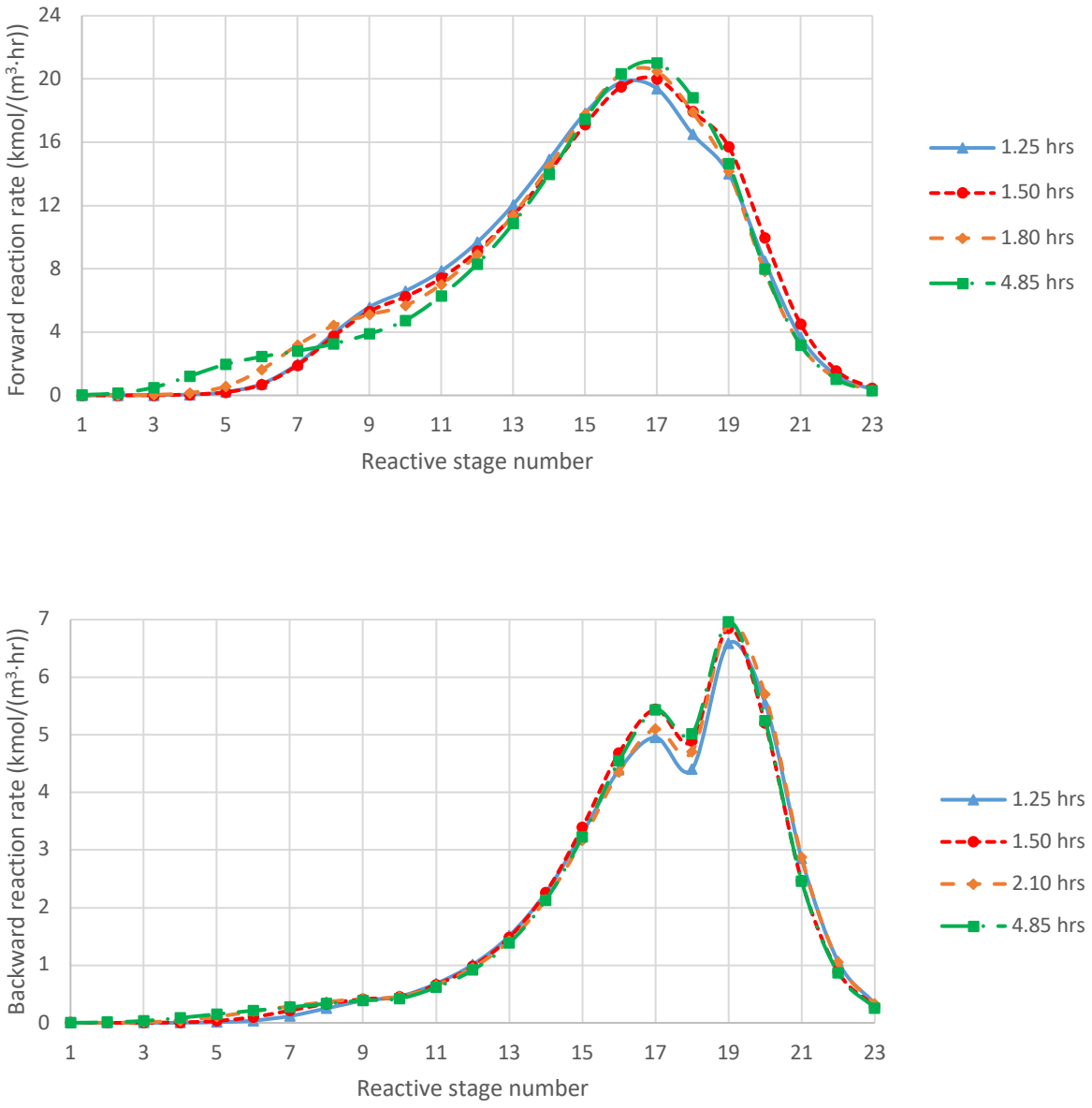


Figure 5: Reaction rate (forward-top and backward-bottom) change due to the introduction of feed B flow rate disturbance (5% increase). Disturbance introduced at t=1.4 hrs.
Stages 1 (condenser) and 25 (reboiler) are not considered reactive, therefore reactive stages only are shown. (Case study 2, V-only control).

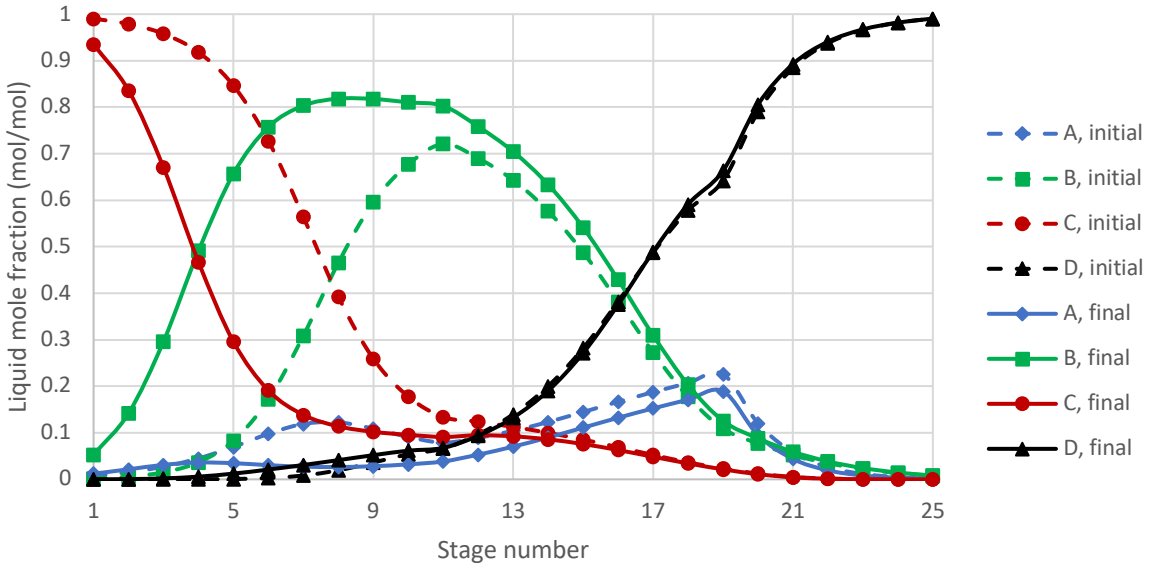


Figure 6: Composition profiles change due to feed B flow rate disturbance (5% increase).
Initial: steady state value before the introduction of the disturbance, Final: indicates the new steady state value after the disturbance has settled in the column.
(Case study 2, V-only control).

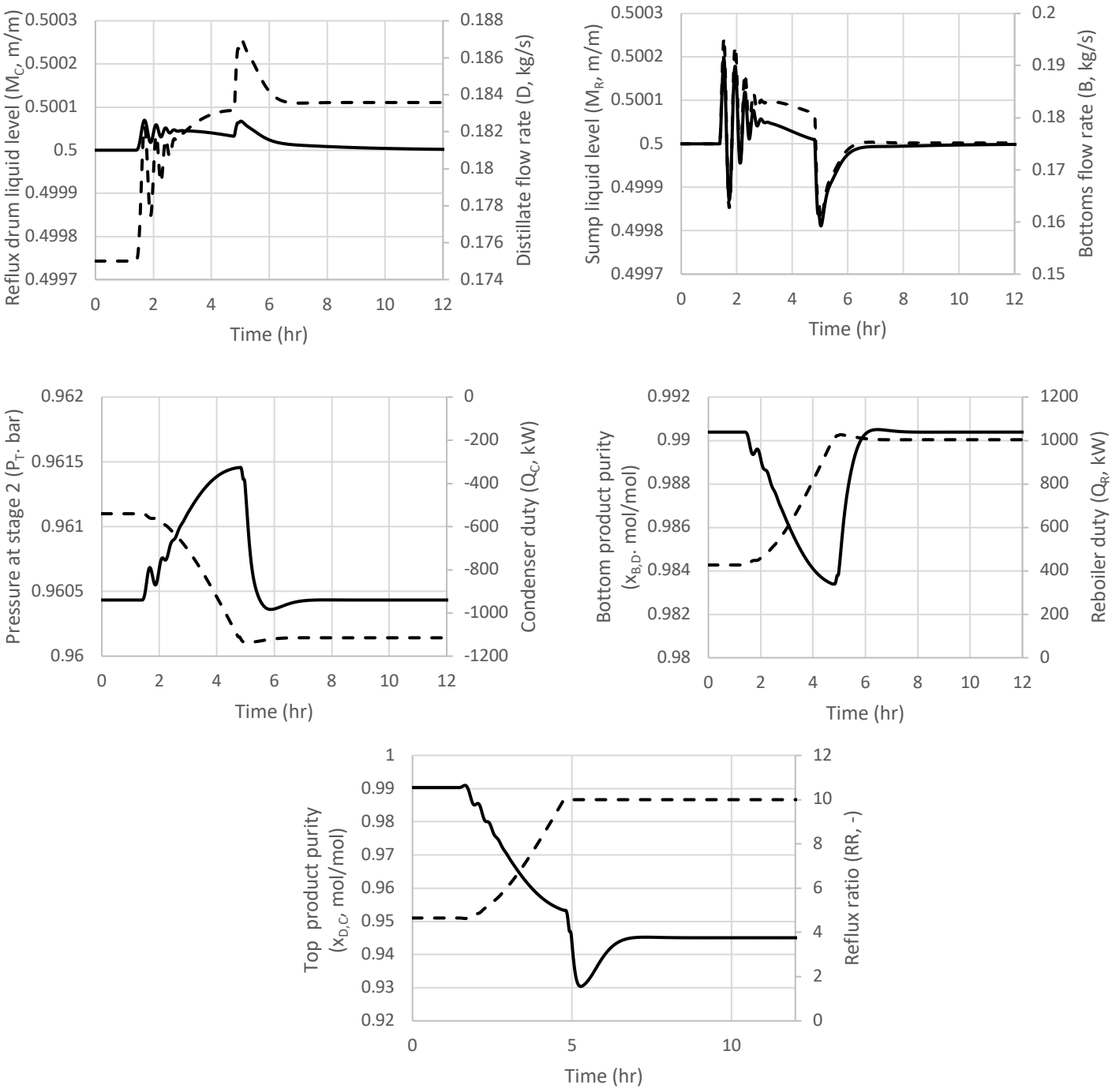


Figure 7: Closed-loop responses for feed B flow rate disturbance (5% increase). Disturbance introduced at t=1.4 hrs. Left axis is controlled variable (solid line) and right axis is manipulated variable (dashed line). (Case study 2, LV control).

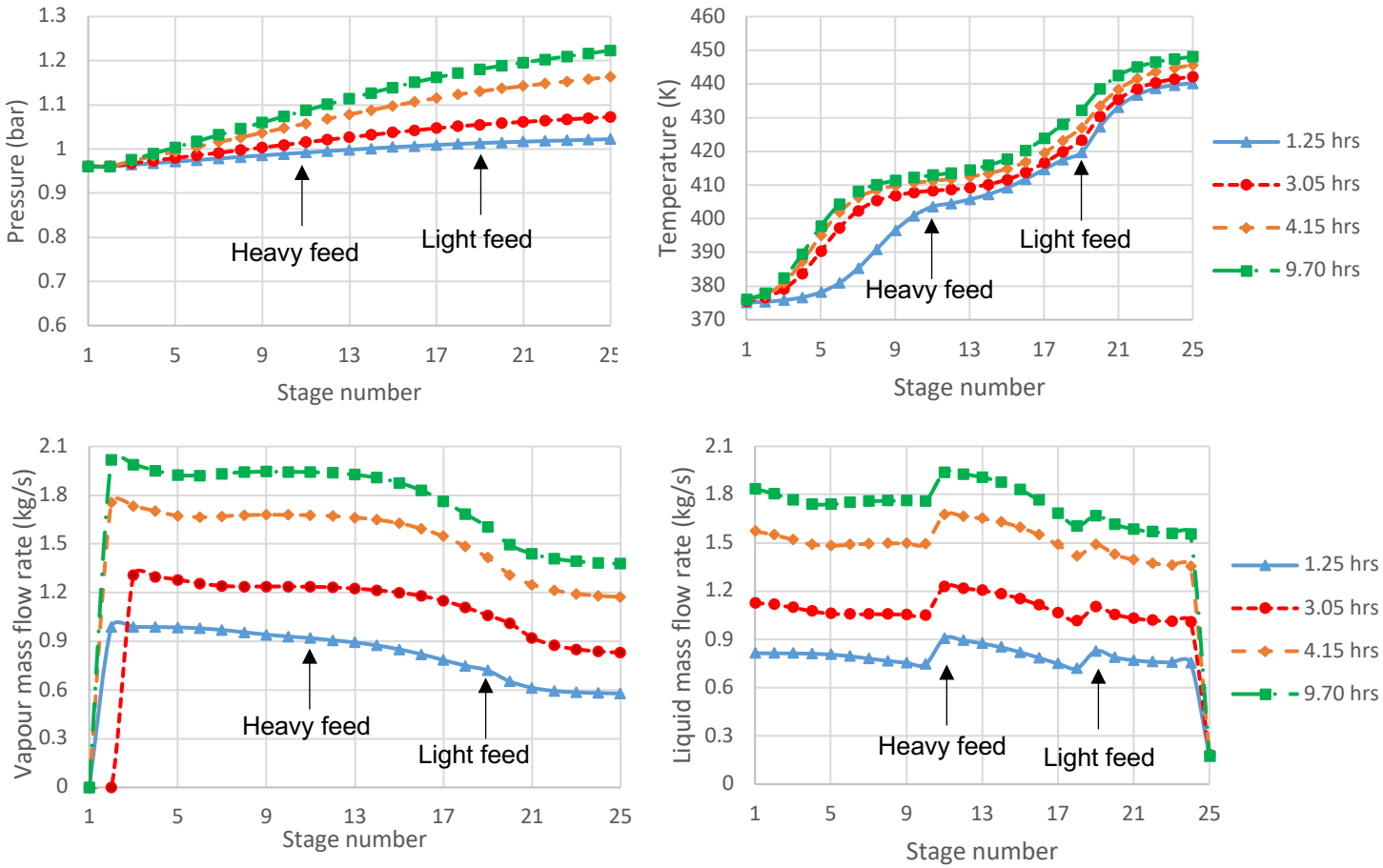


Figure 8: Pressure (top, left), temperature (top, right), vapour mass flow rate (bottom, left) and liquid mass flow rate (bottom, right) change due to the introduction of feed B flow rate disturbance (5% increase). Disturbance introduced at t=1.4 hrs. (Case study 2, LV control).

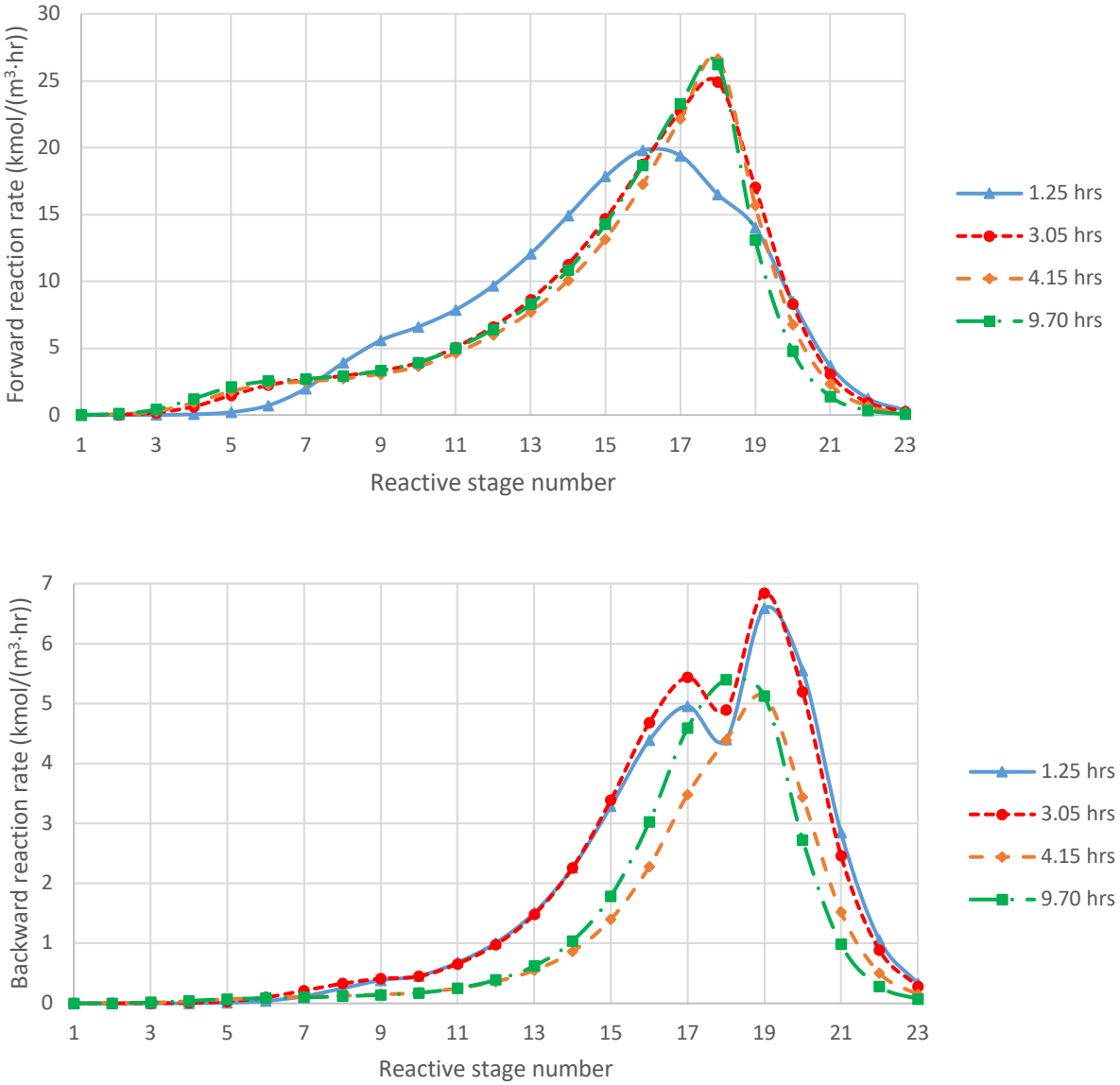


Figure 9: Reaction rate (forward-top and backward-bottom) change due to the introduction of feed B flow rate disturbance (5% increase). Disturbance introduced at t=1.4 hrs.
Stages 1 (condenser) and 25 (reboiler) are not considered reactive, therefore reactive stages only are shown. (Case study 2, LV control).

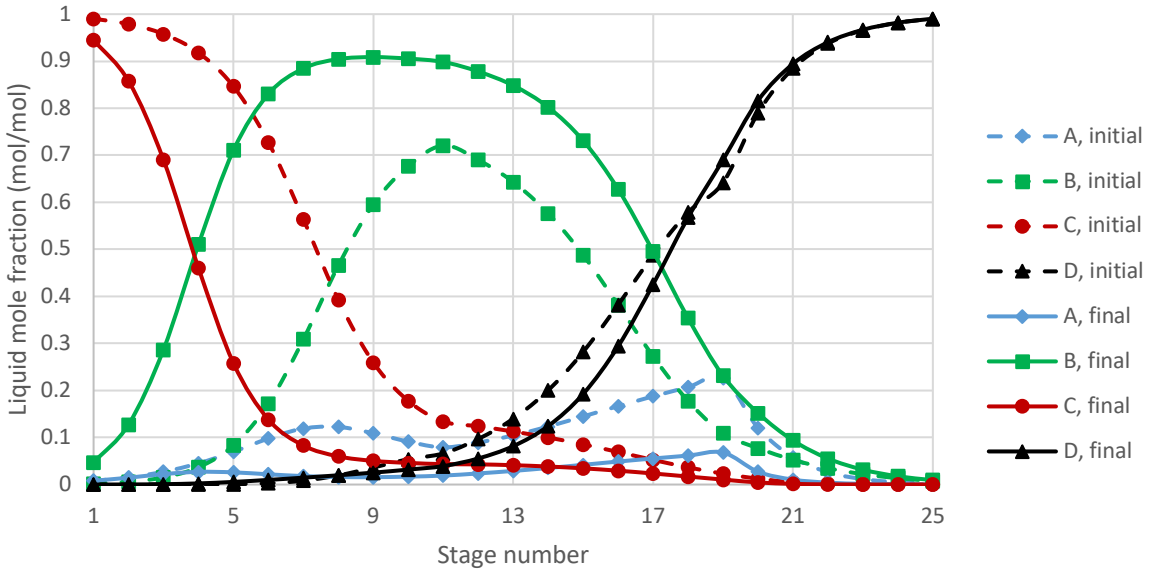


Figure 10: Composition profiles change due to feed B flow rate disturbance (5% increase).
Initial: steady state value before the introduction of the disturbance, Final: indicates the new steady state value after the disturbance has settled in the column.
(Case study 2, LV control).

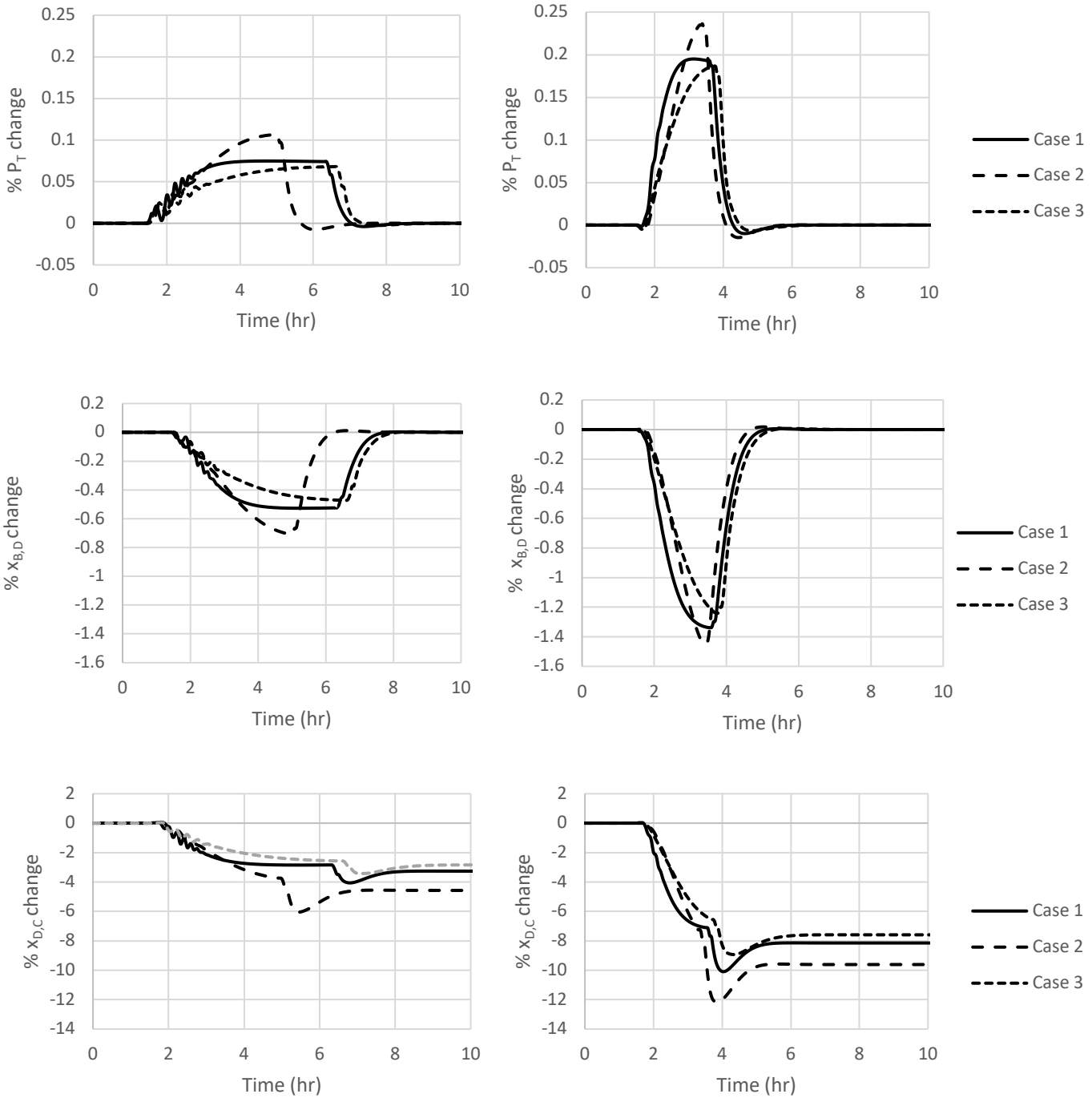
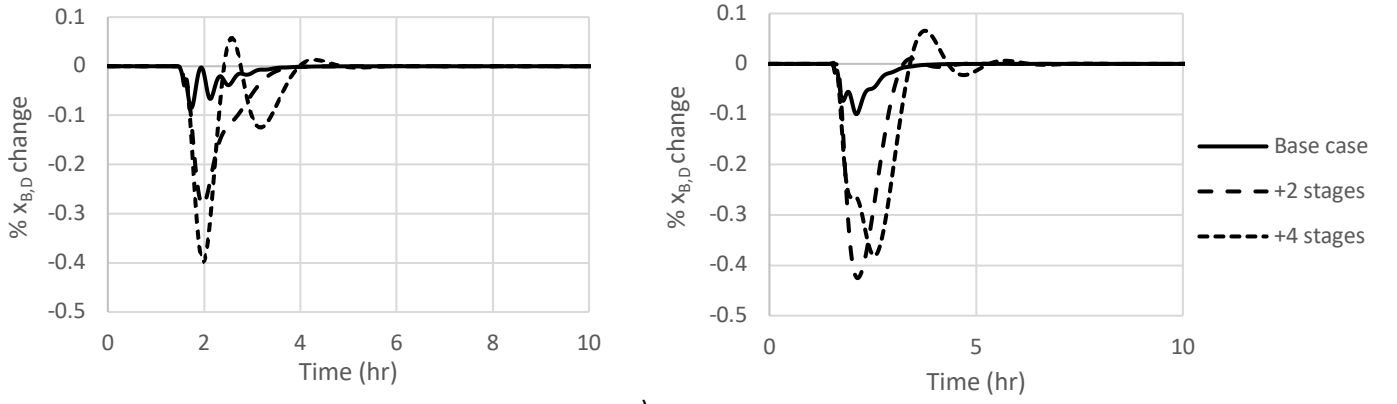
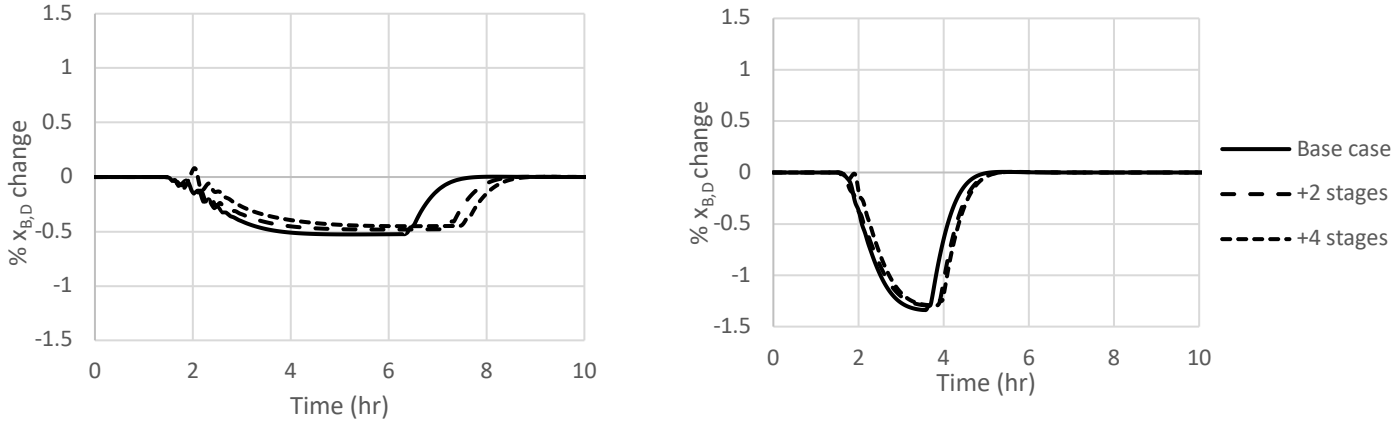


Figure 11: Response to feed flow rate disturbance (5% Feed B increase) (left) and feed composition disturbance (5% Feed B increase and 5% Feed A decrease) (right) for all case studies. Disturbance introduced at t=1.4 hrs. Top: pressure; Middle: Bottom product purity; Bottom: Top product purity. (LV control).



a)



b)

Figure 12: Bottom product purity response to feed flow rate (left) and feed composition (right) disturbance for additional number of stages of reactive column. Disturbance introduced at t=1.4 hrs. (Case study 1, a) V-only control; b) LV control).

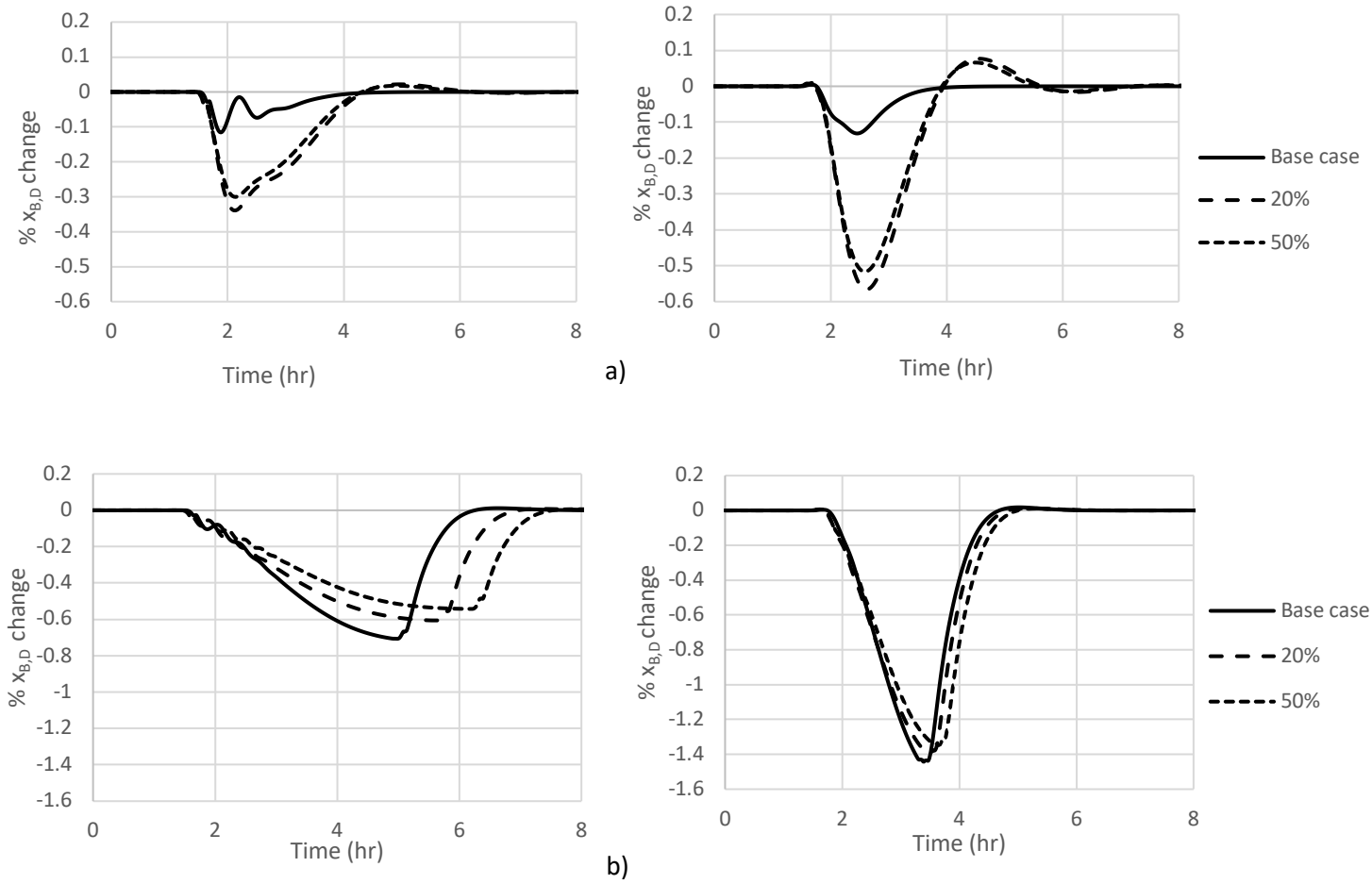


Figure 13: Bottom product purity response to feed flow rate (left) and feed composition (right) disturbance for increased tray liquid holdup. Disturbance introduced at t=1.4 hrs. (Case study 2, V-only (a) and LV (b) control).

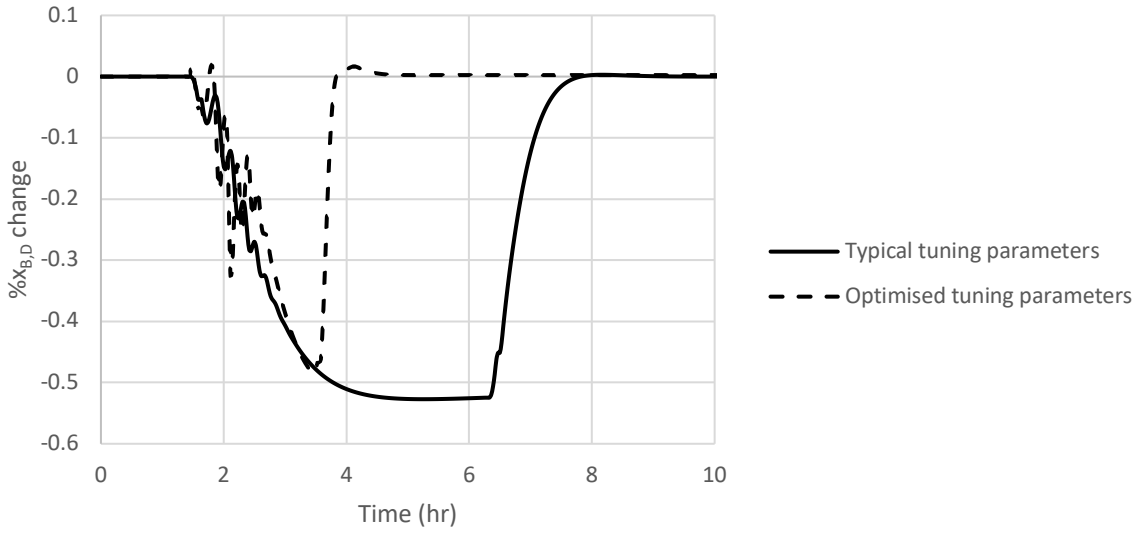


Figure 14: Bottom product purity response to feed flow rate disturbance (Case study 1, LV control) for typical and optimal tuning parameters. Disturbance introduced at t=1.4 hrs. Optimised tuning parameters are shown in Table 5.

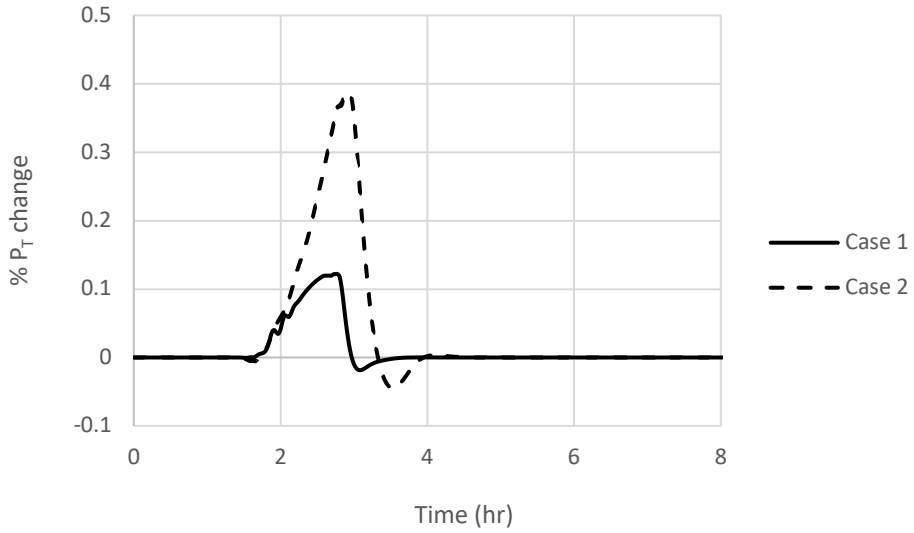


Figure 15: Control responses to feed composition disturbance using optimised tuning parameters as shown in Table 5 (Case study 1 and Case study 2, LV control). Disturbance introduced at t=1.4 hrs.

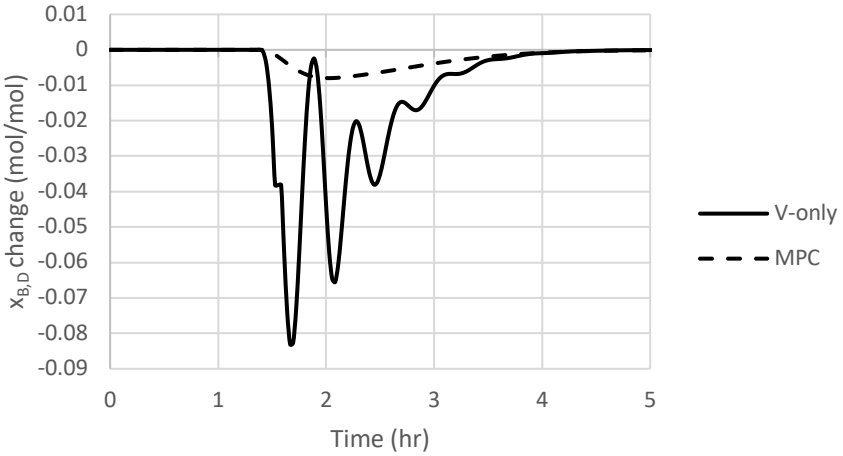


Figure 16: Difference in bottom product purity response to feed flow rate disturbance using conventional V-only control (solid line) and linear MPC (dashed line) for Case study 1. Disturbance introduced at t=1.4 hrs.

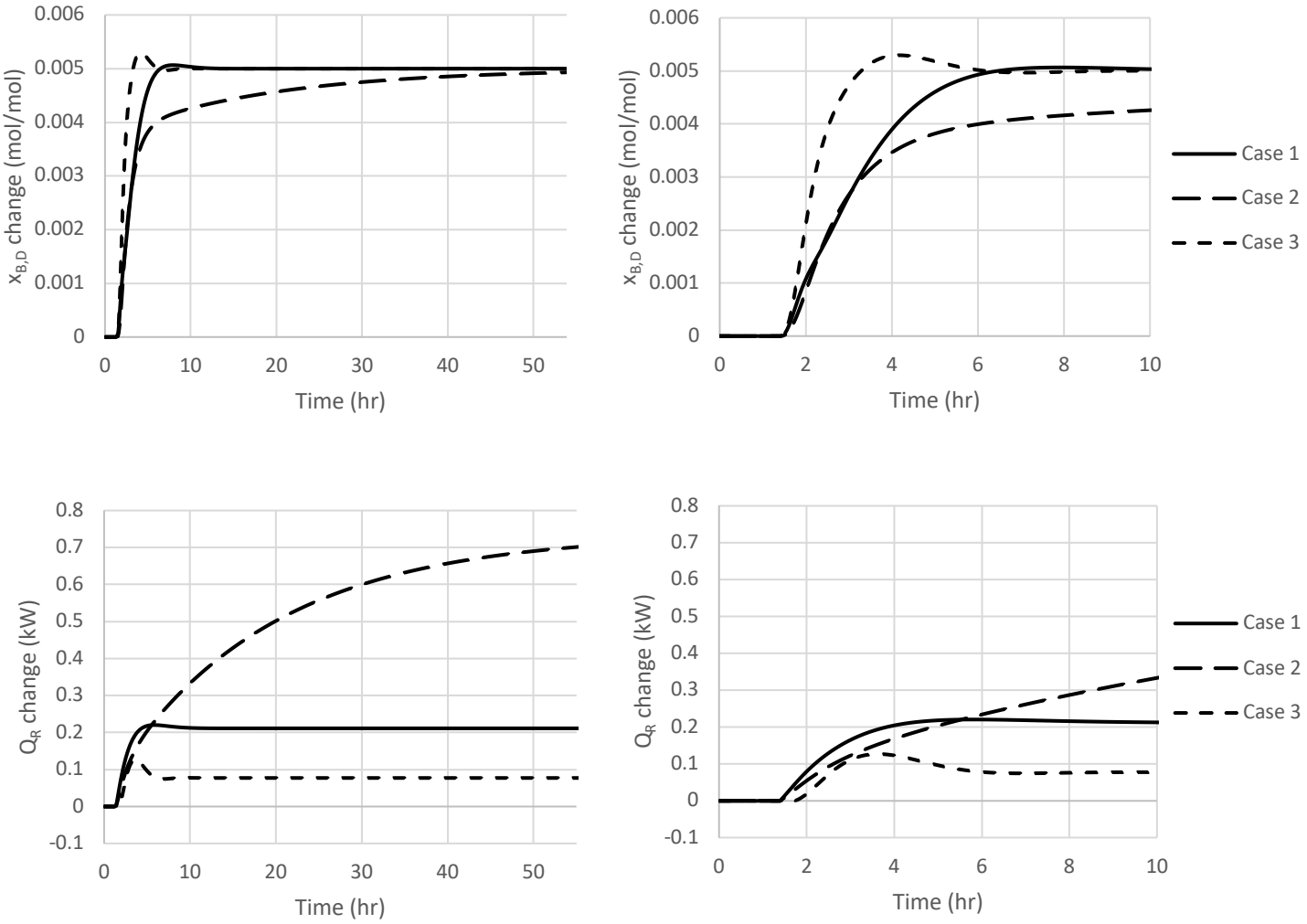


Figure 17: Control performance of MPC for all case studies towards bottom product purity set point change. Bottom product purity response and reboiler duty are presented from top to bottom, respectively. Left figures show full time scale whilst figures on the right focus on initial responses. Disturbance introduced at t=1.4 hrs.

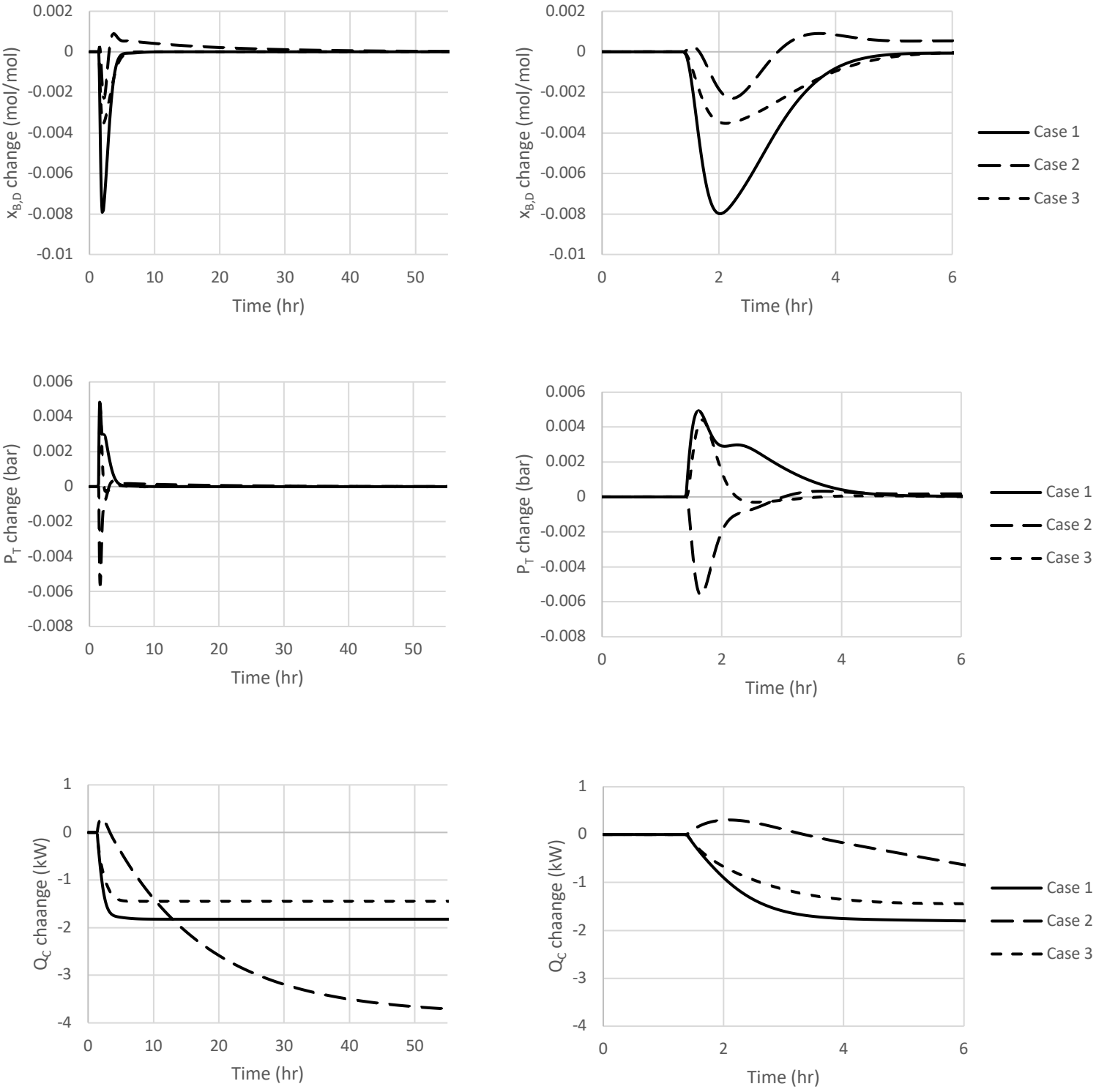


Figure 18: Control performance of MPC for all case studies towards feed B flow rate disturbance. Bottom product purity, pressure and condenser duty are presented from top to bottom, respectively. Left figures show full time scale whilst figures on the right focus on initial responses. Disturbance introduced at t=1.4 hrs.

Table 1: Reaction (k_{f0}-forward pre-exponential kinetic factor and K_{eq}-reaction chemical equilibrium) and separation (α-relative volatility) characteristics for the case studies considered and their optimal design and operational variables (Tsatse et al. 2021). Case study 1 (easy separation, fast kinetics) and Case study 2 (easy separation, slower kinetics) had the same numbering whilst Case study 3 (difficult separation, fast kinetics) in this work was Case study 15 in the previous work (Tsatse et al. 2021). For all case studies, bottom flow rate is shown on a mass basis (0.175 kg/s) which is equivalent to 12.6 kmol/hr on a mole basis.

	Case study 1	Case study 2	Case study 3
System parameters			
α_{CA}	2	2	1.2
α_{AB}	1.5	1.5	2.5
α_{BD}	2	2	2
k_{f0} (m^3/(kmol·s))	$8.41 \cdot 10^6$	$2.1 \cdot 10^6$	$8.41 \cdot 10^6$
K_{eq}	81	2.25	2.25
Optimal design and operation variables			
Number of stages*	18	25	27
Light feed (A) stage**	13	19	23
Heavy feed (B) stage**	12	11	9
Reflux ratio	2.59	4.65	3.7
Bottoms flow rate (kg/s)	0.175	0.175	0.175
Reactive zone by stages	2-17	2-24	2-26
Column diameter (m)	0.62	0.78	0.71
Bottom purity	0.99	0.99	0.99
Top purity	0.99	0.99	0.99

* Stage 1 is the condenser and stage N is the reboiler

** Counted from the top

Table 2: Feed input for the reactive distillation case studies.

	Case 1	Case 2	Case 3
	Light feed		
Composition (mol)	100% A	100% A	100% A
Flow rate (kg/s)	0.175	0.175	0.175
Temperature (K)	389.5	389.5	381.2
Pressure (bar)	1.01325	1.01325	1.01325
	Heavy feed		
Composition (mol)	100% B	100% B	100% B
Flow rate (kg/s)	0.175	0.175	0.175
Temperature (K)	412	412	412
Pressure (bar)	1.01325	1.01325	1.01325

Table 3: Manipulated-controlled variable pairings for V-only and LV control schemes (Figure 2).

	V- only		LV	
Controller	**Manipulated**	**Controlled**	**Manipulated**	**Controlled**
LCT	D	M_C	D	M_C
LCB	B	M_R	B	M_R
PC	Q_C	P_T	Q_C	P_T
CCB	Q_R	$x_{B,D}$	Q_R	$x_{B,D}$
CCT	--	--	RR	$x_{D,C}$

Table 4: Initial control parameters based on typical values (see Figure 2).

Controller	**Gain (Kc)**	**Integral time constant (τ)**
LCT/LCB	2 [(kg/s)/(m/m)]	167 (min)
PC	20 (kW/bar)	12 (min)
CCB/CCT	3 (kW/-)	25 (min)

Table 5: Optimised control parameters based on off-spec product loss minimisation tuning for Case studies 1 and 2 under LV control (see Figure 2).

System	**Case study 1**		**Case study 2**	
Parameter	**Kc**	**τ**	**Kc**	**τ**
PC	33.27 (kW/bar)	6.72 (min)	19.75 (kW/bar)	11.14 (min)
CCB	4.13 (kW/-)	9.08 (min)	3.20 (kW/-)	11.95 (min)
CCT	3.88 (kW/-)	9.11 (min)	3.38 (kW/-)	10.64 (min)