



Modelling, Design, Operability and Analysis of Reaction-Separation Systems

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Modelling, Design,
Operability and
Analysis of
Reaction-Separation
with Recycle Systems

Ph.D. Thesis

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August 2005

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Preface

This thesis is submitted as partial fulfillment of the requirements for the Ph.D. degree at Danmarks Tekniske Universitet (The Technical University of Denmark). The work has been carried out in the CAPEC group at Institut for Kemiteknik (Department of Chemical Engineering) from September 2002 to August 2005 under the supervision of Prof. Rafiqul Gani.

I would like to thank all the students and co-workers at CAPEC at the Department of Chemical Engineering at DTU with whom I had the big opportunity to work during this period. I would like to thank Prof. Sten-Bay Jørgensen for his affability and time for discussion, his comments were always welcome. Prof. John Villadsen for his offer of help. To my supervisor for the opportunity to work in this project. I would like to thank Prof. Diane Hildebrandt and Prof. David Glasser and all their group at COMPS at the School of Process and Materials Engineering at the University of Witwatersrand, South Africa, where I spent a 3-month stay for their kindness and the knowledge (not only in Attainable Regions) they gently shared, it was a wonderful experience working with them. My deepest gratitude to Mauricio with whom I spent countless hours of joy and fruitful discussion and, above all, because of his willingness in helping me, as well as to Dr. Teresa López Arenas that without her help and knowledge, this work in the final stage would not be possible to carry it out. Many Thanks to both! Thank you Erik for your advices. Thanks Núria for being supportive. To my Professors in México. I am grateful for the financial support provided to this project by El Consejo Nacional de Ciencia y Tecnología de México (CONACyT).

Finally, I would like to thank my Family: my Dad as the biggest source of tenacity, my Mom for her unconditional loving care, my Sister for her well-known support, my Aunt for always being with us. My Friends: I would not like to leave any one of you without mention, so please, allow me to do that in person. I hope someday I can make up for all this time.

Lyngby, August 2005.

Edgar Ramírez Jiménez

Abstract

This thesis presents a model-based Methodology for the design and analysis of chemical processes involving a Reaction-Separation with Recycle (RSR) scheme. At the core of this Methodology, a *model-based* analysis of first-principles models of different complexity identifies the important interactions between design and process variables, so that specified design targets may be achieved. Based on this, flexible operating policies are developed together with the corresponding control structure in order to maintain the specified design targets. The model-based Methodology divides the analysis into three stages. *Stage 1* simplifies the design-control problem such that only the main operations are analysed. The corresponding model, developed in terms of dimensionless variables, helps to identify the limiting values of a set of lumped (design-process) variables and locates operational windows where process feasibility can be assessed. In *Stage 2*, more detailed models are developed by delumping the set of lumped variables and relaxing the assumptions that were considered in *Stage 1*. The only solutions to be considered are those lying within the bounds (operational window) defined in *Stage 1*. The objective of *Stage 2* is to identify the location of an optimal operation based on a specified design target. The final *Stage 3* is employed as a verification step by means of more rigorous models in steady-state and dynamic modes. The information generated through *Stages 1* and *2* serves as the initial estimates for the needed rigorous simulations in *Stage 3*. The *Stage 3* simulations validate the design decisions made from the earlier stages. Through the solution of a number of hierarchical sub-problems, the solution of a complex design-control problem is therefore obtained systematically along with an understanding of the process behaviour.

The model-based Methodology has been applied to a series of RSR systems (case studies) varying in complexity and ranging from first-order reactions with perfect separators to multiple (isothermal and no-isothermal) reaction systems with more elaborate separation section (distillation-based, strippers or flash units). Through the analysis of theoretical RSR systems, it was possible to demonstrate different process behaviours (*input* and *output* multiplicities) under different scenarios of process operation. These issues are of major importance when an operating policy or control structure needs to be developed. For more complex RSR systems, the model-based Methodology has shown its potential to address the important issues related to the integrated design and control problem. Note that the important design and process variables, once identified, lead to the proposal of a simple control structure that maintains the design specifications and provides the basis for a more thorough analysis.

Resumé på Dansk

Denne afhandling præsenterer en modelbaseret metode til design og analyse af kemiske processer som involverer en enhed for Reaktion-Separation med recykling (RSR). Det centrale i denne metode er at en *modelbaseret* analyse af (masse og energibalance) modeller af varierende kompleksitet identificerer de vigtigste interaktioner mellem design og procesvariable således at det specificerede designmål kan opnåes. Baseret herpå udvikles fleksible operationsstrategier sammen med den tilsvarende kontrolstruktur for at holde de specificerede designmål.

Den modelbaserede metode inddeler analysen i tre trin. *Trin 1* simplificerer design-kontrol problemet så kun de vigtigste operationer analyseres. Den hertil svarende model i dimensionsløse variable bruges til at identificere grænseværdierne for et sæt kombinerede (design-proces) variable og bestemme operationsvinduer hvor processen er realisabel. Kun løsninger indenfor disse operationsvinduer går videre til *Trin 2*, som sigter på at finde det optimale operationspunkt samt den optimale kontrolstrategi for det specificerede designmål. Hertil udvikles mere detaljerede modeller ved at udrede sættet af kombinerede variable og løse de antagelser som blev anvendt i *Trin 1*. Afslutningsvis verificerer *Trin 3* designbeslutningerne fra de foregående trin samt det optimale operationspunkt og kontrolstrategi ved hjælp af mere rigoristiske steady-state og dynamiske modeller. Informationerne fra *Trin 1* og *2* bruges som startgæt. Denne modelbaserede metode betyder at et komplekst design-kontrol problem løses systematisk gennem løsningen af et antal hierarkiske underproblemer hvorved processens opførsel bedre forstås.

Ovenstående metode har været anvendt på en række af RSR processer (case studier) af varierende kompleksitet lige fra førsteordens reaktion med perfekt separation til multiple (isoterme og ikke-isoterme) reaktionssystemer med komplicerede separationssektioner (distillation, stripping eller flash). Procesopførsel såsom input og outputmultipliciteter er påvist ved analyse af teoretiske RSR processer for forskellige scenarier. Viden om sådan opførsel er essentiel for bedste valg af operationsstrategi og kontrolstruktur. Denne modelbaserede metode har vist sit potentiale for mere komplekse RSR processer til at identificere de vigtigste problemer fra det integrerede design og kontrolproblem. Bemærk at identifikationen af de vigtige design og procesvariable medfører forslag af en simpel kontrolstruktur som holder designspecifikationerne samt giver grundlaget for en mere grundig analyse.

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1

Introduction

Some of the main objectives in the development of integrated process design and plantwide control are to achieve a reliable operation, low energy consumption and high profitability. Therefore, a (unified) framework for the integrated process design and control system will have to involve the determination of a large set of decisions that are linked to the process topology, equipment design specifications, operating conditions, control structure configuration and controller tuning.

An integrated design methodology requires a good qualitative and quantitative description of those process characteristics that have, not only a dominant effect on the dynamic behaviour of the process but also their relationship to the design decisions required to be made in order to obtain an 'optimal' operation.

The nonlinearity of chemical processes manifests as parametric sensitivity, state multiplicity, instability or oscillatory behavior, which in terms of a process design and operational point of view needs to be understood. These behaviors may be due to, e.g., the nonlinearity in the reaction kinetics, the performance of the separation units and/or the presence of recycle streams (including mass or energy recycle). All these operations by themselves may also exhibit complex behavior. However, when they are integrated, mainly through recycle streams, the difficulty for modelling (and simulation) increases together with their operation.

Nevertheless, it is common and also most of the times convenient that, in order to achieve the above mentioned objectives, to find or end up in designs of chemical processes involving the recycle of one or more streams to different unit operations, introducing with this parametric sensitivity in the system, complex dynamics, instability, induce non-minimum phase behaviour and affect disturbance sensitivity.

It is in this context that a typical recycle scheme of a chemical plant is the one relating the Reaction and Separation operations (**R**eaction-**S**eparation with **R**ecycle, *RSR*) and its study becomes relevant not only once a flowsheet has been established, but also at the early stages of the conceptual design in order to evaluate the overall performance. Moreover, for the design and control issues, it is important to find the most appropriate set of parameters and conditions, in order to identify the possible reasons for disturbances and/or sensitivity of the process to the disturbances such that the process can be operated in an efficient and reliable manner.

At the same time, a computer-aided integrated process design relies on the existence of model-based systems. Therefore, there is the possibility to develop a systematic model-based analysis that contributes to the formulation and solution of problems related to integrated process design. These model-based systems contain sets of parameters which need to be identified, not only to find and/or ease their solution but also, when translated to a computer (by an in-house or process simulator) allow their analysis due to the complexity of the system.

Therefore, the objective of this Ph.D. thesis is to present a model-based Methodology to carry out the design and analysis (for control and operation) of integrated processes involving a RSR scheme.

On the other hand, it is important to remark that it is not the objective in this Ph.D. thesis to carry out the final control action for the control structure that, as one of the results from the model-based Methodology can be sketched.

The core of the Methodology will be a hierarchical sequence of *model-based* analyses. Hence, the development and analysis of first principles models for the RSR system becomes a key aspect for the Methodology. The development and application of these models is divided into three stages, where the different design and control aspects can be identified, analysed and resolved at each stage, thereby reaching the total solution in a systematic way.

The objective of *Stage 1* (Simplified Models) is to identify the variables (design parameters) through which the limiting conditions in the systems can be determined (e.g. critical conversions or operational constraints). With this aim, a 'simple' (or reduced) model using grouped but representative parameters of the system (e.g. Da , Pr , Pe numbers) and state variables (e.g. reactant conversion) that are able to capture the important linear/non-linear behaviours is a convenient way for this part of the analysis. Consequently, an operating window is established such that design and control of the system can be done in a reliable and integrated manner.

Stage 2 (Detailed Models) deals with the identification of the important operational/design parameters and the location of the optimal design. In order to do so, the key feature at this stage is the development of more detailed models. This time, unlike *Stage 1*, the grouped parameters are delumped, permitting the assessment and contributions of the key design variables of the system but within the range established by the grouped parameters for a feasible operation. The final objective at *Stage 2* is to reach a complete characterization of the system so that further analysis can be performed without additional data.

A final verification stage (*Stage 3*) involves the results from *Stages 1* and *2* using rigorous simulation (steady state and dynamic) with process simulators (if available). Using the results from the earlier stages a better starting point is obtained for simulation of the flowsheet which ensures a feasible operation.

Consequently, having obtained information from *Stage 1* related to the sensitivity of the process, as well as identified the set of (design-process) variables that have a major influence in its performance, it will be possible to outline a control structure that maintains the set of design target values (pro-

cess/controlled variables) that were defined at *Stage 2*. In this way, the design and control problem for the RSR system can be considered resolved.

The advantages of the proposed approach is that the analysis provides the integration of design and control of the process without involving rigorous modeling or optimization (*Stages 1-2*). At the same time, the important design-control related variables are identified together with their limiting values. This knowledge, which is obtained through the model analysis, helps to define “design” targets that when matched render the design-control of the reactor-separator system at least near optimal. Thus, near optimal design-control of complex non-linear processes can be achieved at the early stages of the design of a process. Moreover, the analysis and the determination of the design and process variables are done systematically, which allows the possibility to identify the important design and control issues such that the process performs in its *designed* condition.

Given the above discussion, this Ph.D. thesis is divided into the following chapters. In Chapter 2, theoretical considerations are made regarding issues on integrated processes as well as the design and control problems with the objective to establish a framework for the integrated design-analysis problem. Chapter 2 also presents a review of the different approaches that have dealt with RSR systems. In Chapter 3 the model-based Methodology proposed for the solution of integrated processes with a RSR scheme is presented. An illustrative example highlighting the main features of the Methodology is also presented. In Chapter 4 the different RSR systems studied through the application of the proposed Methodology are discussed. These case studies are intended to be presented in a sequential order of ‘complexity’, starting with simple theoretical-based compounds (case studies 1 and 2). Case Study 3 helps to highlight the identification of *design targets* and the characterization of a process (in terms of flowrates, T , P , etc.) that can be obtained from the model-based Methodology. Case Study 4 is an example of the successful application of the model-based design and analysis approach to identify the control structure needed to maintain the design targets of a complex process. Finally, Chapter 5 draws the conclusions of this Ph.D. thesis and with that, the perspectives for the work in the future.

Theoretical Background

We shall start this chapter by defining some basic concepts with the aim to establish an appropriate theoretical framework throughout this work. Important considerations on process integration related to integration of design and control are presented next, followed by a discussion on the different approaches tackling RSR (reaction-separation-recycle) systems.

2.1 Definitions

The following definitions are given with a view to establishing the terminology and concepts that will be used throughout this work.

System.— Hangos and Cameron (2001) define a system as *a* part of the real world with well-defined physical boundaries, which is influenced by its surroundings or environment via its *inputs* and generates influences on its surroundings by its *outputs* which occur through its boundary.

From the notion of a system follows the notion of a *process system*. A process system could then be considered a system in which physical and chemical processes are taking place. Process systems are usually specified in terms of a flowsheet which defines the boundaries together with inputs and outputs.

Model.— A *model* is an image or abstraction of reality; a mental, physical or mathematical representation or description of an actual system (Sage 1992).

Process Design.— Douglas (1988) defines process and plant design as the creative activity whereby ideas are generated and then translated into equipment and processes for producing new material or for *significantly upgrading* the value of existing materials.

Process Analysis.— *Process analysis* is the application of scientific methods to the inspection and definition of problems as well as to the development of procedures to their solution (Himmelblau and Bischoff 1992). This means (1) mathematical specification of the problem for the given physical situation, (2) detailed analysis to obtain mathematical models, and (3) synthesis and presentation of the results in order to ensure the full understanding.

Operational Conditions.— The set of variables, i.e., temperatures, flow rates, holdups, etc. that describe the operation of the process are defined as ‘operational conditions’.

A chemical process is characterized by a large number of inputs and disturbances that might have an impact in the performance of the system. Thus, a model analysis will also help to determine which inputs and parameters have a significant effect on plant’s performance.

Operability.— Operability is the ability of the plant (together with its control system) to achieve acceptable operation (both statically and dynamically). Operability includes flexibility, switchability and controllability as well as many other issues (Larsson and Skogestad 2000).

The goal of the (process) operability analysis is to ensure that there is an adequate equipment overdesign so that the process constraints can be satisfied while a combination of the operation costs and overdesign cost is minimized over the entire range of anticipated process disturbances (Fisher, Doherty and Douglas 1988b).

Controllability.— One of the key issues to ensure in the design of a RSR system is the controllability. According to Cui and Jacobsen (2002) the *controllability* concerns the inherent ability to achieve acceptable dynamic performance of a process system by means of feedback control. Controllability is a property of the process itself only. The performance may be related to attenuation of disturbances and/or tracking of setpoint changes. The plant design can impact the controllability through equipment size, flowsheet layout, and other decisions that affect the dynamic behaviour of the plant.

In contrast, Lyman, Luyben and Tyréus (1996) define a property concerning robustness to disturbances which is a function of the process design parameters as well as the control structure and algorithm used. This property should be labeled as *controllability robustness*. However this concept is less useful than controllability itself since controllability robustness also depends upon control structure and on the actual controller algorithm and its design.

2.2 Process Integration

The International Energy Agency (1993) (IEA) gives the following definition:

“Systematic and General Methods for Designing Integrated production Systems, ranging from Individual Processes to Total Sites, with special emphasis on the Efficient Use of Energy and reducing Environmental Effects”.

In this sense, an integrated process design will have to look after to satisfy the increasing demand for development of environmentally benign yet operable

process, this is, to select an environmentally friendly chemistry, to minimise material waste, to maximise energy (exergy) efficiency and to ensure that the integrated plant is safely operable.

However, in order to ‘differentiate’ the definition given by the IEA from the context of what *process integration* is used throughout this work, we could argue that: “*process integration is the activity whereby two or more unit operations are combined such that they perform their principal operational tasks simultaneously, involving for example, mass and/or energy transfer operations*”.

Therefore, in an “integrated plant” the presence of recycle of mass and/or energy becomes an important issue with respect to how the different unit operations are linked in order to enhance the process performance (such as yields or conversions specifications) or minimise waste releases or improve the energy demands.

On the other hand, the recycle of material and heat integration may alter the time constants of the plant (Hangos, Hallager, Csaki and Jørgensen 1991, Recke and Jørgensen 1997, Morud and Skogestad 1996) and may give rise to instability or oscillatory behaviour, even when the individual process units are stable by themselves. Also, these interconnections may introduce fundamental limitations to any control system. For example, Morud and Skogestad (1996) studied linear systems considering the recycle of mass and energy as a positive feedback mechanism through an eigenvalue analysis. The feedback effect caused by the recycle, may move the poles of the plant towards the positive side in the complex plane. A unified approach to analyzing recycle systems should look at a) the slower dynamics due to recycle and b) that the unstable poles must be observed and stabilized. Nevertheless, it is recognized that there is a need for a systematic classification of “causes” which may introduce complex behaviour in a plant.

Another issue in process integration is the question of the change in the degrees of freedom for the process to manipulate operational variables as a consequence of integration. This issue can be illustrated in the following example through a model-based analysis. The analysis is shown first for the stand-alone units, followed by the effect of incorporating a recycle stream into the system.

In this example, an isothermal first-order reaction $A \rightarrow P$ is considered to take place in a CSTR and a downstream separation carried out in a sharp component splitter as shown in Fig. 2.1. For illustrative purposes, it is assumed that within the reactor perfect mixing occurs and also that there is equal inflow and outflow from this unit (implying constant liquid volume with $V_r = \text{constant}$). The kinetic rate constant is assumed available. The reaction unit can be fully described by developing only the mass balances for component A . It can be demonstrated that the analysis of degrees of freedom in the reactor does not change by adding the balance of product P . With respect to the splitter, it is assumed that the operation can be carried out through the specification of the corresponding split factors of each component.

Thus, the steady-state mass balance for component A in the reactor leads to

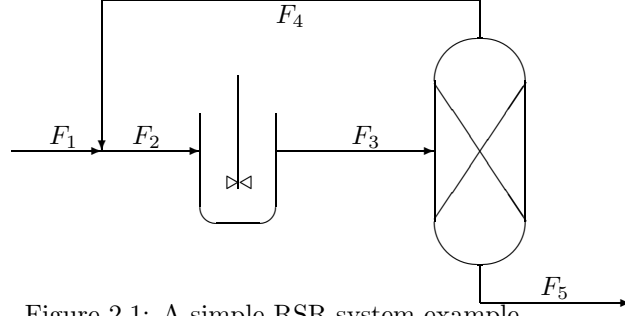


Figure 2.1: A simple RSR system example.

Reaction law

$$R_A = -kC_{A,3} \quad (2.1)$$

Mass-balance equation

$$0 = F_2C_{A,2} - F_3C_{A,3} + R_AV_r \quad (2.2)$$

Based on the above assumptions, the model-based analysis on these equations shows that there are $N_u = 6$ variables, classified as:

- System (equipment) parameters: V_r, k ,
- Algebraic variables: $F_2, C_{A,2}$,
- State (process) variables: $C_{A,3}, R_A$

Hence, since the number of model equations $N_e = 2$, the DOF $N_{DOF,r} = N_u - N_e = 4$. Therefore, it is clear that if values for $[F_2, C_{A,2}, V_r, k]^T$ are assigned the model for the reaction unit can be solved for $[C_{A,3}, R_A]^T$.

With respect to the splitter, the equations describing the operation are:

Component balances

$$0 = F_{A,3} - F_{A,4} - F_{A,5} \quad (2.3)$$

$$0 = F_{P,3} - F_{P,4} - F_{P,5} \quad (2.4)$$

Split factors

$$\sigma_A = F_{A,4}/F_{A,3} \quad (2.5)$$

$$\sigma_P = F_{P,5}/F_{P,3} \quad (2.6)$$

Similar model analysis shows that there are $N_u = 8$ variables, classified as:

- System (equipment) parameters: σ_A, σ_P
- Algebraic variables: $F_{A,3}, F_{P,3}$
- State (process) variables: $F_{A,4}, F_{P,5}, F_{A,5}, F_{P,4}$

Therefore, as the number of model equations $N_e = 4$, the DOF $N_{DOF,s} = N_u - N_e = 4$. Hence, by specifying $[F_{A,3}, F_{P,3}, \sigma_A, \sigma_P]^T$ the model for the component splitter can be solved for $[F_{A,4}, F_{P,5}, F_{A,5}, F_{P,4}]^T$.

However, in order to increase the conversion to product P , the unreacted component A is commonly recycled back to the reactor through the recycle stream F_4 , coupling, thereby, the reactor-splitter units and adding the following expression (see Fig. 2.1):

$$F_1 + F_4 = F_2 \quad (2.7)$$

Consequently, the analysis of degrees of freedom at the mixing point adds two variables (F_1 and F_4) and one equation (Eq. (2.7)), and because of this the DOF for the system increases by one. The later leads to the difficulty of selecting the right set of variables to fulfill the DOF for the entire system. That is, because of the incorporation of the recycle stream, the same set of variables, previously used to satisfy the DOF of each unit is no longer available, since variables, such as F_2 become dependent variables. Although, the example treated here dealt only with algebraic equations, in systems involving differential-algebraic equations (DAE), the selection of an appropriate set of variables that fulfills the DOF may, however, cause high INDEX problems. Therefore, the issues of INDEX as well as DOF will need to be considered simultaneously. On the other hand, the behaviour of the coupled system can be seen modified from that of the individual units since these are no longer isolated and small disturbances, for example, in some flowrates can result in undesired phenomena like the so-called “snowball” effect (Luyben 1994).

Let us now consider the dynamic/control implications of the above example. For the sake of simplicity, it is considered that the separation section has no dynamics and that the time constant τ for the CSTR is given by,

$$\tau = M_{fluid}/F_2 \quad (2.8)$$

where M_{fluid} is the corresponding holdup of fluid within the tank.

From Eq. (2.7) it is clear that as a result of recycle, the reactor inlet F_2 will no longer be an independent variable once the recycle stream F_4 closes the recycle loop. Consequently, the time constant of the system may be seen altered and with that the initial behaviour of the plant due to recycle of mass (and energy; if energy balance was also considered).

Figures 2.2 and 2.3 show the time responses when the recycle is added to the system (for $\sigma_P = 0$) for step disturbances in the inlet concentration of component A in the CSTR and the residence time, respectively. As it can be seen, the positive feedback due to the recycle has in this case made the response slower, and the steady state sensitivity higher.

On the other hand, if it was desired to maintain a given design condition, say the mole fraction of P , $z_{P,r}$ (or conversion), this would mean that the fresh feed F_1 could be now a manipulated variable with the level of the reactor (V_r)

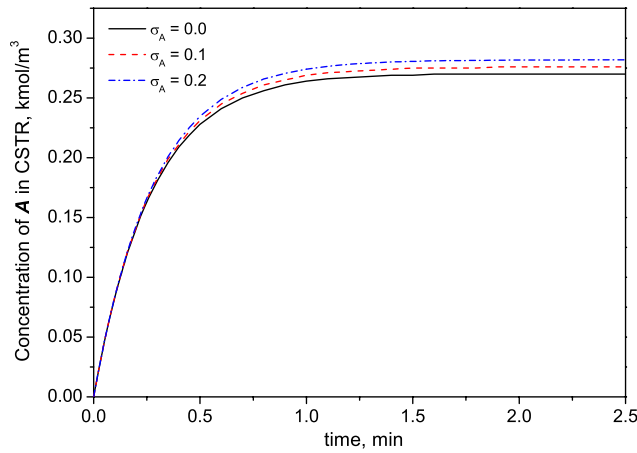


Figure 2.2: Step response for the recycle system example.

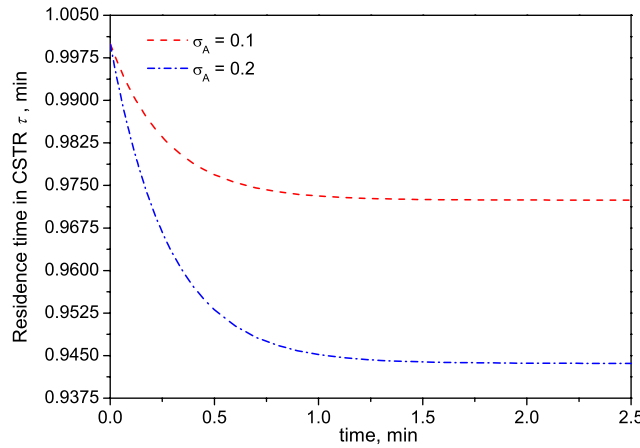


Figure 2.3: Residence time for the recycle system example.

as a corresponding process variable to be controlled in order to maintain the desired design specification. In a process without recycle, on the other hand, a typical control structure for the same design specification would be keeping the reactor outlet on flow control with the reactor inlet as a disturbance to the process. Note again that this variable has become now a dependent variable (via Eq. (2.7)) in the RSR case.

This simple analysis highlights the importance of considering the design and control related tasks in a simultaneous manner in order to obtain a feasible design as well as a feasible operation and control. This also forms the basis of the systematic model-based Methodology developed in this Ph.D.-thesis (described in section [3.2]).

2.3 Design and Control Integration

Integrating issues of design and control of a process together with the effect of (material/energy) recycle streams results in a difficult and complex problem, whose solution requires a good understanding of the inherent non-linear behaviour of the process. One way to achieve such integration is to identify the common issues (set of variables) that have significance both to the design and control problems and to determine their values, so that,

1. the specified design objectives (optimal performance criteria) satisfying a set of process/operation constraints can be achieved through a set of design (optimisation) variables
2. the specified control objectives (optimal controllability and operation characteristics defined through a set of process/operational constraints) can be achieved by maintaining the same set of design (optimisation) variables and thereby leading to an optimal control structure.

Two sets of variables have dual roles in process design and control (Russel, Henriksen, Jørgensen and Gani 2002). The first set is the *process variables* that define the process constraints in the design problem and the operational constraints in the control problem. That is, in design, these variables define if a process is feasible, while, in control, they are the variables that need to be measured/controlled in order to keep the process feasible (operating) at the desired design. The second set is the *design variables* whose specified values lead the process to attain its optimal design characterized through specified process constraints. In design, they are usually regarded as optimisation (*design*) variables while in control, they are usually regarded as manipulated/variables or actuators.

Based on the above discussion, it becomes clear that integration of design and control can be achieved by

- identifying the important process/operation variables (\mathbf{x}) and their connection to optimisation/manipulated (\mathbf{u}) variables,
- determining operational windows defined by the two sets of variables \mathbf{x} and \mathbf{u} ,
- determining the optimal values for \mathbf{u} and \mathbf{x} (\mathbf{u}_{opt} , \mathbf{x}_{opt}).

The identification of these sets of (significant) variables can be performed through a model-based analysis. That is, through the development of simple yet appropriate models and their corresponding analysis, it will be possible to recognize the impact of their process-design variables on the performance of the process. It should be noted, however, that the objective of this work is not to determine the final control action but to provide sufficient support in order to outline an appropriate control structure to be utilized, i.e., to recognize the variables needed to be controlled (process variables, \mathbf{x}) paired with the appropriate manipulated variables (design variables, \mathbf{u}).

2.4 State of the Art

The objective of this section is to provide an overview of some of the most representative approaches in the literature for the design, synthesis or control of chemical processes involving a recycle structure.

Given the inherent complexity of the integrated design-control problem, the development of a methodology able to address both issues requires a systematic and detailed analysis in order to obtain an adequate balance between the important design and control issues. A significant research effort has been dedicated to the design and control of individual process units, e.g., reactors or distillation columns. However, as a result of more stringent environmental regulations and economic considerations, today's chemical plants tend to be highly integrated and interconnected. Different lines of thinking can be found in the literature when it comes to tackling the problem of integrated (heat/mass) plants. The following literature review is divided into those approaches that propose the solution of plantwide problems mainly from a control perspective; methodologies that are heuristic-based; and those that are optimisation-based. Also, the problem of integrating the design and control with respect to variables selection is reviewed. Comprehensive reviews and similar topics can also be found in Wu and Yu (1996) and Seferlis and Georgiadis (2004).

2.4.1 Plantwide control and heuristic-based approaches.

One of the pioneer works on this area is the one from Prof. William Luyben and coworkers. In Luyben, et al. (1993a, 1994), the different effects of recycle loops on process dynamics ranging from one to two recycle streams are addressed. On the other hand, Tyr us and Luyben (1993) and Luyben and Luyben (1995) analyse the effect of different stoichiometric schemes. From the above-mentioned works, a series of heuristic rules applicable to recycle systems were derived as well as to define what has come to be known as the "snowball effect" (Luyben 1993a) (i.e., a small disturbance results in a very large increase in the recycle flowrate). Also from this perspective the work by Wu and Yu (1996) deals with the control structure of plantwide systems classifying them as *unbalanced schemes* and *balanced schemes*. In the *unbalanced schemes*, if load changes are handled mostly by a single unit in a plantwide system, some of the process variables (e.g. flowrates, level, etc.) can reach operating constraints with very small changes. On the other hand, in the *balanced schemes* if a load disturbance is not handled evenly by the units, the imbalance grows exponentially via the recycle structure (also known as "snowball" effect) and limits the rejection capability. The whole plant is treated as a complete process unit and the control systems are designed accordingly, e.g., the recycle flow is adjusted by measuring the reactor level. Thus, the *balanced* control scheme handles disturbances by changing conditions in several units in the process, not just one. However, the balanced scheme may lead to rather complex control

configurations, especially for composition control.

Zheng, Mahajanam and Douglas (1999) developed a hierarchical procedure for synthesizing an optimal plantwide control system for an existing continuous chemical process. Alternative plantwide control systems are synthesized and compared based on economics. The cost associated with dynamic controllability is quantified by a controllability index ν introduced by Zheng and Mahajanam (1999). The procedure comprises of six steps: (1) Steady-state robust feasibility (flexibility), (2) controlled variables selection, (3) steady-state control structure screening, (4) dynamic control structure synthesis, (5) economic ranking, and (6) dynamic simulations. There are, however, a number of practical issues that need to be resolved in carrying out the procedure. For example, the problem of selecting a set of controlled variables is a combinatorial problem which requires an efficient selection method; an appropriate tool for estimating the controllability index ν quickly is also needed; quantitative guidelines for deciding when feedforward and cascade structures are economically justified are needed; and so on.

Wu, Yu, Luyben and Skogestad (2002) present a method for the design of a control structure based on ratio schemes. The basic idea here is to distribute the actuator load evenly among process units as the production rate changes. This is done through a steady-state disturbance analysis by solving component balances with intensive variables fixed as changes in the disturbance variables are made. The resulting required changes in the dependent variables are examined to analyse the resulting pattern. Thus, the dependent variables are expressed in terms of ratios that should remain constant for feed flow disturbances. The disturbance analysis gives the relationship between the manipulated input and load variables while keeping controlled variables constant. The disturbance sensitivity matrix obtained gives the relationship between inputs and loads. However, the control structure proposal is left to designer's experience and some of the proposals given, are derived from steady-state disturbance analysis which may not be (dynamically) preferable.

Through an asymptotic analysis, Kumar and Daoutidis (2002) address the dynamic analysis and control of process systems with recycle to establish that (i) small recycle flowrates induce a weak coupling among individual processes, whereas (ii) large recycle flowrates induce a time scale separation. Thus, from this time scale separation, it was observed that the dynamics of individual processes evolve in a fast time scale with weak interactions, and, the dynamics of the overall systems evolves in a slow time scale when these interactions become significant. This slow dynamics is usually nonlinear and of low order. Based on such conclusions a model reduction methodology is proposed for deriving nonlinear low-order models of the slow dynamics induced by large recycle streams, and a controller design framework consisting of properly coordinated controllers in the fast and the slow time scales. This approach follows

from the Vora and Daoutidis's (2001) method of nonlinear model reduction to reaction systems that exhibit dynamics in two different time scales owing to the presence of fast and slow reactions. The method identifies the independent algebraic constraints that define a low-dimensional state space where the slow dynamics of the reaction system are constrained to evolve.

Bildea and Dimian (2003), supported by nonlinear analysis, present an approach where Luyben's rule ("*...use a control structure that fixes the flowrate of one stream somewhere in a liquid recycle loop...*") for avoiding the "snowball" effect is revisited. The main conclusion derived from this work is that the most convenient way for avoiding such phenomenon is to set the streams entering to the reactor (fresh plus recycle reactants) on flow control such that stable controllable plantwide control structures are obtained. These insights also validate the results obtained by Pushpavanam and Kienle (2001) and Zeyer, Pushpavanam and Kienle (2003) where the behavior of a coupled reactor-flash system is analyzed. Here, it was shown that even for simple models, more complex patterns of behavior -involving infeasibility, multiple steady states, and limit cycles, can be observed when a recycle stream is incorporated into the system. Therefore, the plant's behaviour crucially depends on the flow and the flash control strategy. Stability criteria are derived for different flow and flash control strategies, depending on the operating conditions and on the basic physicochemical properties of the mixture.

Steady-state disturbance sensitivity analysis (Luyben 1975, Luyben 1993a, Luyben 1994, Yi and Luyben 1995, Semino and Giuliani 1997) has also been used for screening different control structure proposals that might arise for a system. These approaches focus their attention, among other things, on the snowball effect; the selection of the different proposals is chosen on the basis of experience and engineering judgement. McAvoy and Miller (1999) present an approach to use steady-state simulators in order to obtain a gain matrix as in Arkun and Downs (1990) for determining input-output sensitivities and asymptotic properties (see also Weitz and Lewin (1996)).

2.4.2 Optimisation-based approaches

Optimisation-based methods have been applied to address the plantwide control problem where the main objective has been to synthesize a design and a control structure that satisfies a set of economic constraints and operability issues. Luyben and Floudas (1994a, 1994b) proposed a method to consider simultaneously steady-state economics and open-loop controllability objectives within the mathematical programming framework of process synthesis. Using a superstructure of possible design alternatives, a multiobjective mixed-integer nonlinear programming (MINLP) problem is formulated. With the flowsheet unknown *a priori*, this formulation requires expressions for the steady-state economic and control objectives in terms of the unknown design variables to

be determined solving the optimisation problem. After generating the noninferior solution set by applying the ε -constraint method within the framework of the Generalized Benders Decomposition algorithm, the trade-offs among the competing objectives are assessed using a cutting-plane algorithm to determine a best-compromise solution.

In the Mohideen, Perkins and Pistikopoulos (1996) framework, the process system is modeled using dynamic mathematical models where variations include both uncertain parameters and time-varying disturbances while control structure selection and controller design is considered as part of the optimisation problem. This framework requires the following key considerations: a) control scheme definition, b) feasibility of operation in the presence of any possible realization of parametric uncertainty and disturbances, c) stability of the dynamic system in the presence of parametric uncertainty and disturbances, and d) efficient numerical scheme for the resulting stochastic mixed-integer optimal control mathematical formulation, also known as mixed-integer dynamic optimisation (MIDO) problem. The disadvantage of this approach is that the resulting MINLPs are very large, even for relatively small-scale DAE systems, which potentially prohibits the solution of large, realistically-modelled systems.

McAvoy (1999) presented an alternative to some of the steps in Luyben, Tyr us and Luyben's (1998) algorithm where a MILP problem is solved to minimise valve movement for disturbance compensation. The various components include (1) development of a gain matrix that includes integrating variables; (2) use of optimisation to select candidate control architectures for variables that must be controlled for safety reasons; (3) screening of the architectures for the safety variables using controllability tools; (4) use of optimisation to select candidate control architectures for controlling product flow and quality; and (5) controlling chemical components and unit operations using standard approaches (as in Luyben et al.'s (1998)). This approach looks only at steady-state considerations assuming that it is not always possible to address all the important issues with a dynamic model for the whole process. It is argued, however, that there exists the possibility to expand the procedure when dynamics are available.

Bansal, Perkins, Pistikopoulos, Ross and van Schijndel (2000) showed a procedure where process design and control involving both discrete and continuous decisions can be simultaneously optimised for systems using rigorous mixed-integer dynamic optimization models, which in spirit, is similar to Mohideen et al.'s (1996) earlier approach. The algorithm is based on variant-2 of the Generalised Benders Decomposition (v2-GBD) for MINLPs. The limitations of this approach is that although a locally optimal solution is guaranteed when the integer variables are chosen as the complicating variables, the convexity conditions required for the algorithm to converge to the global optimum will not be satisfied by most process problems. Bansal, Perkins and Pistikopou-

los (2002) present an algorithm using the same framework of Mohideen et al. (1996) that, even when the binary variables participate within the DAE system, a master problem does not require any explicit dual information with respect to the DAE system and so no intermediate adjoint problem is required for its construction. Furthermore, the MIDO approach is independent of the type of method used for solving the dynamic optimisation primal problems. It should be noted, however, that since the algorithm is based on v2-GBD, like the MIDO approaches of Mohideen et al. (1996) and Schweiger and Floudas (1999), it shares its limitations. In particular, although a locally optimal solution is guaranteed when the integer variables are chosen as the complicating variables, the convexity conditions required for the algorithm to converge to the global optimum will not be satisfied by most processes.

Mönnigmann and Marquardt (2002) presented an approach to incorporate constraints in the system dynamics into the optimisation based design of nonlinear systems. In this approach, boundaries in the parameters space of the nonlinear system where desired dynamics characteristics of the system are lost, are considered. Parametric robustness is guaranteed by staying off the boundaries at a user specified distance in the parameter space, which ensures that the desired dynamic characteristics will be met despite parametric uncertainty or parameter drift. In a successive work, Mönnigmann and Marquardt (2003) used an approach to the steady-state optimisation of continuous processes in the presence of parametric uncertainty. The approach identifies an optimal nominal point of operation which is exponentially stable, and which is feasible with respect to inequality constraints such as physical operating limits or product specifications. The approach is based on enforcing a lower bound on the distance between the optimal point of operation and *critical* points, that is, those points at which feasibility or stability is lost.

The self-optimizing control concept has lead to a number of studies. The basic idea was formulated by Morari et al. (1980): ‘... in attempting to synthesize a feedback optimising control structure, our main objective is to translate the economic objectives into process control objectives. In other words, “we want to find a function c of the process variables which when held constant, leads automatically to the optimal adjustments of the manipulated variables, and with it, the optimal operating conditions.[...]” This means that by keeping the function $c(u, d)$ at the setpoint c_s , through the use of the manipulated variables u , for various disturbances d , it follows uniquely that the process is operating at the optimal steady-state’. On the other hand, Skogestad (2000) restates the *self-optimizing control* concept as: ‘... when we can achieve acceptable loss with constant setpoint values for the controlled variables (without the need to reoptimise when disturbances occur)’. Self-optimizing control is a direct generalization to the case where we can achieve acceptable (economic) performance with constant controlled variables. Skogestad (2000) presented a procedure for finding suitable controlled variables based on only steady-state information.

The procedure consists of analysis of degrees of freedom, definition of optimal operation (cost and constraints), and evaluation of the loss when the controlled variables are kept constant rather than optimally adjusted (see also Larsson et al. (2001, 2003), Halvorsen et al. (2003)). Likewise, Skogestad (2004) extends the Skogestad's (2000) earlier procedure in order to design the control structure for a chemical plant where several tools are applied like decentralized control or multivariable control. One difficulty with this approach is that in general it is not clear if a self-optimizing structure exists, and going through the various alternatives using the procedure can be quite tedious. On the other hand, the issue of finding good controlled variables is a structural problem. That is, if a good structure is found for a particular case, it might also work on another similar process with different parameters values, thereby creating an 'invention' process.

2.4.3 Design and Control integration approaches

An important assumption in many of the methods discussed above is that an appropriate set of design (manipulated) and process (controlled) variables have already been selected. However, such assumption is not always valid. In this respect, several attempts have been made for integrating design and control into a systematic framework through which a conceptual design leading to an optimally operated process (with respect to design and control and their interconnection) can be obtained during the early stages of design. Nishida, et al. (1981) state that the development of a control system requires the specification of (1) a set of control objectives, (2) a set of controlled variables, (3) a set of measured variables, (4) a set of manipulated variables, and (5) a structure interconnecting the measured and manipulated variables. Therefore, the interface between design and control should be based on the translation of the results from the design study into a corresponding set of specifications.

Fisher et al. (1988a, 1988b, 1988c) presented a hierarchical methodology for the synthesis of a control system based on a series of heuristic rules. This procedure follows the same decision hierarchy for process design proposed by Douglas (1988). In the first part of the method (Fisher et al. (1988a)), a controllability analysis is performed in order to determine which of the different process alternatives has the smallest cost penalty, such that some of the economic penalties associated with control can be used as an additional criterion for screening process alternatives. Furthermore, it is evaluated whether there is an adequate number of manipulative variables to satisfy the process constraints and to optimise all the operating variables.

In the second part of the method (Fisher et al. 1988b), an assessment on process operability is carried out. The goal of the operability analysis is to ensure that there is an adequate amount of equipment overdesign (flexibility) such that the process constraints can be satisfied and minimise the combination of the operating costs and overdesign costs over the entire anticipated operating

windows. This operability analysis relies also on the decision hierarchy for process design proposed by Douglas (1988). It is important to keep in mind that this controllability analysis is only based on steady state considerations. Hence, when process dynamics are considered, new controllability limitations might arise.

In the third part of the framework (Fisher et al. (1988c)), the goal is to select a set of controlled variables that satisfies the active process constraints and, in addition, give close to optimum steady-state performance after dynamic transients have decayed. The primary control objective is the profitable operation of the process. Other control objectives include product quality specifications, production goals, safety and environmental regulations. The results from the optimum steady-state control analyses are used to generate heuristics for plant control in much the same way that heuristics have been developed for setting the values of certain design variables to aid in flowsheet design and synthesis. The selection of the controlled variables normally correspond to constraints on the recycle flows or some other quantity, therefore these constrained optimisation variables can be used as controlled variables. If one (or more) of the operating variables are not specified as a controlled variable(s) by this procedure and if the operating costs are sensitive to optimisation of this (or these) variable(s), then an on-line optimiser should be used.

Newell and Lee (1988) give a qualitative criteria to guide the selection of controlled and manipulated variables which are suitable for an initial analysis in the design of a plantwide control system. These guidelines are driven by the plant and control objective(s).

Skogestad (2004) also presents a systematic procedure for the plantwide control structure design, the selection of the manipulated and controlled variables is based on process insights, although some (heuristic/knowledge-based) guidelines are given in order to determine them. Given the objectives of this thesis, it is worth to remark the importance that Skogestad (2004) gives to the use of models, i.e., ‘generic’ models where the structural part is correct, even though all the parameters may not match the true plant in question. A first-principles model, based on material and energy balances is recommended given that a good control structure is generally insensitive to parameter changes.

Kiss (2004) and Kiss, Bildea, Dimian and Iedema (2005) have recently proposed a somewhat ‘similar’ approach to the one that has been developed in this work (see Chapter 3). In their approach, the non-linear analysis plays a key role in analyzing RSR systems, aiming to identify regions in the parameters space where the system has a desired behaviour (robust with respect to disturbances). Feasible plantwide control structures are identified through the use of a simple plant model. Within this framework and given the interaction between the design and control of recycle systems, the type of behaviour exhibited by the whole system is influenced by the plantwide control structure.

Consequently, the overall control strategy is decided before performing the design of the operating units. Detailed modelling (as in this work) is not fully developed, but carried out using commercial process simulators, hence relying on their modelling and control experience for the model construction and analysis.

2.4.4 Synthesis of Reaction-Separation systems

In this section some of the most representative approaches for the synthesis of chemical processes (implicitly including reaction-separation operations and recycle streams) is presented. The main objective is to present how the design and process variables are treated in each approach.

One of the most well-known procedures for the synthesis (and design) of chemical processes is the one from Douglas (1985). This procedure comprises of 5 hierarchical layers where the complete process is always considered at each decision level. Heuristics guides the decisions making. By accumulating the decisions made by the designer for cases where there are no heuristics, or where the designer overrides the heuristics, a list of process alternatives is developed for further consideration. Each decision level terminates with an economic analysis. The input information required is: a) Reactions: stoichiometry, T , P , catalysts, etc., b) Products: production rate, purity, etc., c) Raw materials: composition, T , P of all raw materials as well as their prices, d) Constraints: safety considerations, explosive limits, etc., e) Plant and site data: utilities, disposal facilities, etc. The five decision levels are:

1. Batch vs. Continuous.
2. Input-Output structure of the flowsheet. At this level, decisions concerning feed impurities, number of product streams, recycle and purge are made and the corresponding heuristic rules are given.
3. Recycle structure of the flowsheet. At this level, guidelines are given concerning the number of reactors (according to their conditions), reactor feed streams and for the number and destinations for recycle streams having identified at Level 2 the components that would be recycled.
4. General Structure of the Separation System. Liquid and vapour recovery systems are considered initially and the way to determine them depending on the phase conditions from the reactor. The corresponding heuristics are given also concerning the type of operations for each of the recovery systems to be used.
5. Heat Exchanger Network. Even though an extensive research has been carried out for the development of heat exchanger networks, it is recognized the need of optimisation procedures due to the lack of rules of thumb that can be used to fix the process flows since they are as such variables to be optimised in order to develop the best heat exchanger network.

This procedure depends on the designer having to guess values for the design variables and process alternatives which may lead to the best possible design. Nevertheless, it can be used as a starting point. This procedure also relies on the existence of heuristics and designer's experience which sometimes might not be available.

Floquet, Pibouleau and Domenech (1985) develop a tree search algorithm to synthesize chemical processes according to a technical-economic criterion involving reactors-separators sequences interlinked with recycle streams. The basic points of this Branch and Bound method are respectively the definition of the finite sequential search space and the use of heuristic lower and upper bounds to reduce the enumeration of all possible flowsheets. The main assumptions taken are that each separation unit is a distillation column operating at a high recovery of the key components, each reaction unit is an ideal isothermic reactor (e.g., CSTR or PFR), after the reaction each component of the mixture is either recycled or separated and the running continuous parameters (operating pressure and reflux ratio for distillation columns, operating pressure, temperature and conversion for reactors) are not considered as optimisation variables, which are fixed at nominal values (given by the user) before each execution of the search procedure. Later, Pibouleau, Floquet and Domenech (1988) proposed the use of Lagrangian-based algorithm for the optimisation of the superstructure and the operating conditions, where a linearized subproblem is solved with a large-scale projected reduced gradient procedure. In this procedure, the operating conditions, component molar flowrates and structural parameters defining the split fraction in the distillation columns are now incorporated into the optimisation problem. The structural parameters defining the process structure are the split fractions of streams (connectors reactor-reactor or column-reactor) and the recovery rates of the feed components in the distillate product of each column. The technico-economic criterion is based on cost correlations that might not be available sometimes.

Mizsey and Fonyo (1990) used a combined approach of hierarchical and algorithmic methods for the synthesis of chemical processes. Some of the features of this methodology are the implication of the *user-driven* synthesis technique to tackle the implicit knowledge derived during the synthesis, and an efficient bounding strategy to account for cross-layer interactions. The main steps are: I) use of *Hierarchical methods* for creating good preliminary flowsheets and screening process alternatives with simple energy integration using short-cut models and simple estimations of the total costs (based on Douglas (1988)); II) the *user-driven* synthesis technique is applied to tackle all the constraints, complex energy integration and the additional implicit knowledge derived during the conceptual design that were unknown from the outset; III) a *bounding strategy* based on performance targets is developed to reduce the usually enormously huge search space; IV) *Algorithmic methods* are suggested to the optional final tuning, the optimisation of the superstructure postulated in the

previous steps, and the the remaining heat exchanger synthesis problem. For final designs the use of rigorous models and optimisation techniques is proposed in order to account more rigorously for features such as interconnections and capital costs. One of the key messages of this approach is the flexibility to incorporate different techniques to the different design steps in order to complete the design process ranging from the use of heuristic rules to optimisation-based solutions and thermodynamic considerations. The procedure has been only applied to continuous processes where ideal vapour-liquid equilibrium can be assumed. Therefore, issues of how the framework might be generic or extendible to non-ideal systems and other phases have to be resolved.

Kokossis and Floudas (1991) proposed a general superstructure of different reactor and separation tasks and features all the potential interconnections among the proposed units resulting in an MINLP formulation where the objective function involves both integer and continuous variables and is subject to a nonlinear set of constraints. The solution strategy comprises the following aspects: 1) *Derivation of cost models via simulation data* given the fact that the specifications of the feed streams of the separation columns are variables. A series of simulations are therefore performed in order to provide cost data for different feed flowrates and compositions. A regression analysis then determines the expressions for the cost of each column as a function of these variables; 2) *Generation of the superstructure*: the reactor network features alternatives for reactors in series, reactors in parallel or series-parallel, reactors with multiple feed and recycles, as well as bypasses around the reactor units; 3) *Formulation of the synthesis problem* as a constrained optimisation problem. The integer variables represent the existence of each particular reactor and separator unit. The continuous variables consist of the flowrates and compositions of all streams, volume of the reactors, the operation time of the plant, and the cost associated with each unit. 4) The *proposed solution algorithm* comprises the decomposition and iteration according to the generalized Benders decomposition algorithm. An offset of the approach is that the solution algorithm is restricted to provide a *local* solution. The solution, which evidently depends on the initial starting point, cannot be claimed to represent the *global* optimum.

A two-level algorithmic approach to the synthesis of RSR systems is proposed by Omtveit, Wah and Lien (1994). At the *upper level* of this approach, the reactor conversion and purge fraction are optimised using a simple direct search method, and the flows among the subsystems such as the reactor system and separation system are calculated. Therefore, for each combination of the purge composition and conversion rate, the annualized profit has to be found. That is, the flows into and out of such (reactor and separator) subsystems are fixed at a given point in the simplex search process, thus for fixed inputs and outputs, the corresponding subsystems that are able to perform the specified input-output transformation in the most profitable manner are synthesized (determined). On the other hand, individual subsystems are optimised at the

lower level for every iteration of the upper level loop. The structure and operating conditions of the subsystems are determined and the cost is returned to the upper level. The reactor network synthesis problem is solved by simulating each one of six different adiabatic reactor configurations given the inlet composition, temperature and pressure with an overall conversion determined by the upper level simplex search algorithm. The sizing and costing is performed and the least expensive reactor system is returned to the upper level. The separation synthesis problem addresses the automated synthesis of heat integrated simple columns, sharp split distillation systems and is formulated as a mixed combinatorial and continuous optimisation problem. Here, again, the cost of the resulting “optimal” separation system is returned to the upper level simplex optimisation procedure. Different computational aspects have to be considered, such as the different optimisation techniques used at each level of solution as well as the synthesizers and the need to incorporate methods for handling more than sharp split distillation.

Omtveit, Tanskanen and Lien (1994) tried to address the synthesis problem in a graphical way by extending the *Attainable Region* concept (Horn 1964) for a larger number of components through the use of the reaction invariance principle and also outlining the possible application to reaction-separation with recycle systems. However, no further development has carried out or reported.

Probably one of the earliest works in the category of rigorous optimisation was that by Umeda, Hirai and Ichikawa (1972) who considered the optimisation of flowsheets comprising a fixed set of reaction and separation unit operations. Complete connectivity between these operations was assumed. Split ratios were treated as continuous optimisation parameters, together with the equipment design variables for each individual unit. A shortcut Fenske-Underwood model was employed for modelling the distillation operations. In the same spirit, detailed unit operation models are considered within the optimisation framework of Smith and Pantelides (1995). This is based on:

- a) differentiating the plant on material states, processing unit operators, and mixing and splitting operators;
- b) each raw material, end and/or intermediate product is described by a state s of material characterised by a single extensive variable m_s (i.e., flowrate, etc.) and a vector of intensive properties x_s (e.g., composition, P , T);
- c) each processing unit operator p corresponds to an instance of a unit operation type transforming a set of input states to a set of output states and is characterised by a set of design and operating parameters as well as a set of internal variables;
- d) the operator input states, and the end product states are made by mixing material from all operator output states and raw material states;
- e) the optimisation determines the actual number of instances of each processing unit operator type in flows, also the values of the design and operating

parameters, and the internal variables for each such instance p as well as the inter-states flowrates.

The objective function is a measure of plant performance and may depend on the design and operating parameters and internal variables of the various processing unit operators included in the flowsheet, as well as the characteristics of the various states. The framework leads to a MINLP problem solved by standard numerical techniques. The existence of any recycles is deduced automatically from the chosen connectivity. This procedure cannot guarantee the global optimality of the solution obtained, which is due to the nonconvexity of the constraints describing the mixing operators.

A framework for applying MINLP optimisation to the successive and iterative decomposition method of process design is presented by Phimister, Fraga and Ponton (1999). In a first stage a MINLP problem is formulated to address the synthesis of multistep processes where limited information is available except from reaction paths, costs of raw materials, expected selling prices and the expected plant production. The MINLP formulation consists of binary decision variables that represent continuous variables such as flowrates and conversions and indicate whether connections or plant sections exist. To address the connectivity and synthesis problem a profit-based objective function is maximised. While not synthesizing the ‘complete process’ with unit operations, the proposed MINLP approach addresses connectivity, provides upper bounds on profitability, and allows insight into the financial and strategic motivations for implementing large scale design modifications. Because each section is incorporated into the MINLP as a ‘black box’, providing an output based on a given feed input, more accurate section modelling and costing can be implemented without loss of generality. The emphasis of the work is to create a systematic framework, which screens a large number of recycle structures and determines initial values for those variables which greatly affect process viability and profitability (‘dominant design variables’). It is important to mention that additional objective function or constraint complexity decreases the likelihood of finding a feasible and optimal solution and increases uncertainty of whether a local minima obtained is also a global minima.

Pahor, Irsic and Kravanja (2000) use a MINLP approach combined by a successive analysis of the *Attainable Region* technique. The first step is to develop a more compact superstructure of the reactor network followed by a modification of the *AR* so that economical criteria are used rather than the conventional performance criteria (conversion, yields, etc.). A further extension is made to consider recycle reactors and intermediate separation, which are chosen in advance by fixing their binary variables to 1. The *AR* analysis could suggest the modification of the superstructure and/or the bounds of the continuous parameters. The multilevel MINLP process synthesis procedure is applied only to the higher level where it is concerned with detailed reactor

network synthesis while the separation is considered as an identification task. The authors claimed that most of the reactor synthesis problems can be highly nonlinear and that global optimality usually cannot be guaranteed, especially when solving problems with a set of parallel-sequential reactions with complex kinetics.

2.5 Summary

In this Chapter, a discussion of the theoretical background addressing the integration of the design and control problems for chemical processes, in particular for those involving a RSR scheme (sections [2.1]–[2.3]), has been given. The state of the art review (section [2.4]) has included some of the most representative methods dealing with recycle systems. These methods have been classified according to the strategy of solution and the objectives pursued. It is important, however, to point out some of the still unsolved issues. For example, most of the plantwide control methodologies start from the basis that a suitable (appropriate) set of manipulated and controlled variables are known (pre-selected) or, their selection is based on heuristics or, designers' experience while very few methodologies address the selection problem itself. Optimisation-based approaches are used not only to find an optimal design but also to perform the synthesis of the process, even incorporating the control problem in it. The resulting number of variables involved in the optimisation problem could limit sometimes their numerical solution or not guarantee the location of a global optimum. Also, the initial estimates and bounds for the optimisation variables can be considered an issue that is not fully understood and needs to be addressed.

In the following chapters (Chapters 3-4) a *model-based* Methodology is presented (and highlighted through case studies) trying to address some of the deficiencies in the reviewed methods. Through a model-based analysis it is possible to recognize the most important design and process variables for the RSR system and thus help to identify feasible regions of operation by determining the bounding values for them. Consequently, the pairing of manipulated-controlled variables should be easier, ensuring with this an optimal operation and feasible dynamic behaviour. On the other hand, if the control problem was only considered, the model-based Methodology would be able to provide the set of manipulated-controlled variables to the methods presented in the review, so that further analyses can be carried out. With respect to the optimisation problem, the bounding values for the optimisation variables could be obtained from the Methodology, thereby, making it easier to obtain a solution that matches the design targets or specified design objectives.

Model-based Methodology for Integrated Design-Analysis

This chapter presents a systematic approach to address the problem of the design and analysis of Reaction-Separation with Recycle systems. In this manner, first, the problem statement is given in order to describe the problem to be addressed by the model-based Methodology. Next, a method of solution to solve the stated problem is proposed together with a discussion on its justification and significance. Finally, the developed systematic methodology for design and analysis of RSR systems is presented and the important steps are highlighted through a simple illustrative example.

3.1 Problem Statement

Figure 3.1 describes what in general can be considered as an RSR system. That is, a *reaction section* which can involve from a single reaction unit (CSTR, PFR, etc.) up to a complex reaction network made up of several reactors (even with different configurations); and a *separation section* utilizing distillation columns, sharp splitters, flash drums, etc. A section for the mixing of the recycle streams, which may be either of material and/or energy, is also taking into account coupling the reaction and separation sections.

Based on the above description of an RSR system, the following **Problem** is formulated:

Given a chemical process with a Reaction-Separation with Recycle (*RSR*) structure,

Determine the ‘optimal process’ through the integration of design and control aspects.

The ‘optimal process’ will be referred to as a process defined by values for a particular set of design variables $\mathbf{u}_{\text{design}}$ that corresponds to a desired condition of operation defined by a set of process variables \mathbf{x}_{spec} . Therefore, the integrated design and control problem will have to find the identities of the above

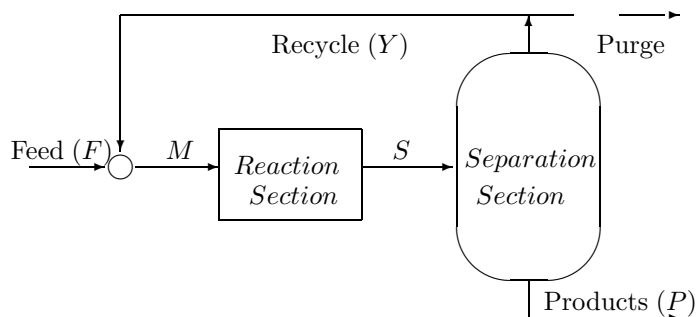


Figure 3.1: General scheme for an RSR system.

mentioned set of variables together with their values such that the *problem statement* as formulated above can be considered as solved.

3.2 Proposed Method of Solution

The proposed methodology comprises of three-successive stages (Ramírez and Gani 2004) that allows the identification and analysis of the behaviour of the process together with its operational conditions from the early stages of the design (see Fig. 3.2). The model-based Methodology also recommends decisions to be taken that could improve the operability of the process.

The objective of *Stage 1* is to identify the (design) variables through which the limiting conditions (design and operation) can be assessed. A simple (or reduced) model (Okino and Mavrovouniotis 1998) with lumped variables that is able to capture the important non-linear behaviours is a very convenient means of analysis at this stage given that they help to characterize the main design issues in the process, such as, reaction conversions or recycle amounts. Moreover, due to the inherent multivariable nature of these processes, a reduction in the dimension of the problem favours the analysis.

In *Stage 2*, a de-lumped model is used to identify the optimal design, that is, the operating window where the optimal values of the important design parameters are likely to be found. Note that, since the limiting values of the state variables are known from the *Stage 1*, the same relationship also determines the state variable values corresponding to the design parameters. Another objective in this stage is to identify the actual design/operating variables, i.e., the variables defining the lumped variables. The reason for de-grouping the model is to obtain a more detailed model with respect to the design and process variables so that their interactions during the operation of the process can be analysed.

The final stage (*Stage 3*) involves verification through rigorous simulation (steady-state and dynamic). These rigorous simulations may be performed through commercial process simulators due to the built-in models available

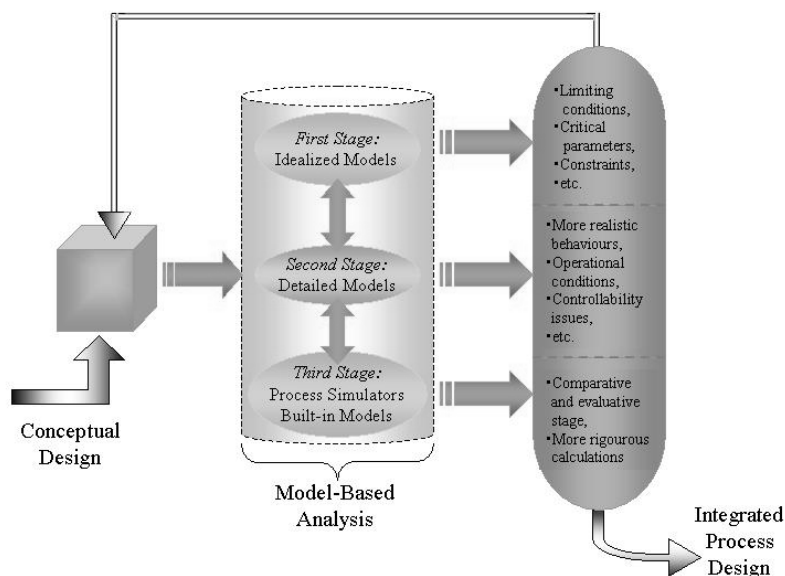


Figure 3.2: Conceptual Representation of the model-based Methodology.

in them. However, the set up of the simulation case should be, in principle, easier since information obtained from the two previous stages serves as initial estimate and, therefore the efficiency and robustness of the model-based solver is improved.

3.2.1 Justification and Significance

Importance is given in this work to the development of process models and, more importantly, to their systematic analysis with the aim to understand the process behaviour so as to identify improved design/operation of complex chemical processes in an easier way. Gani and O'Connell (2001) acknowledge also the importance of process and phenomena models in their *service* role, i.e., providing the needed numerical values for further analysis. In addition, Russel et al. (2002) acknowledge their *advice* role in terms of the insights obtained for the understanding and solution to the process design-control problem from an integrated point of view. It is important to note here that the *optimisation* variables in the *design* problem are the *manipulated* variables for the *control* problem, while the state variables defining the condition of operation (in design) are the variables being controlled. Thus, another objective of the Methodology is to identify the limiting values of the design variables through model analysis in *Stage 1* and to fix (select) values of the state variables that match the desired process specifications through the model analysis in *Stage 2*. The analysis in *Stage 2* also should identify the values of manipulated (design)

variables, within the limits defined in *Stage 1*, that will lead the process to the selected values of the state variables.

According to the ideas on integration given in sections [2.2] and [2.3], the proposed algorithm (model-based Methodology) could also be considered as an *integration tool*, this is, given the objectives of the design-control problem it is necessary to use a set of different instruments (tools) that help to solve the problem. Nevertheless, it is important to remark that the purpose of the present work is not to perform the synthesis of a process but, to lead to a design that also allows a reliable operation in terms of low energy consumption, high profitability and improved flexibility.

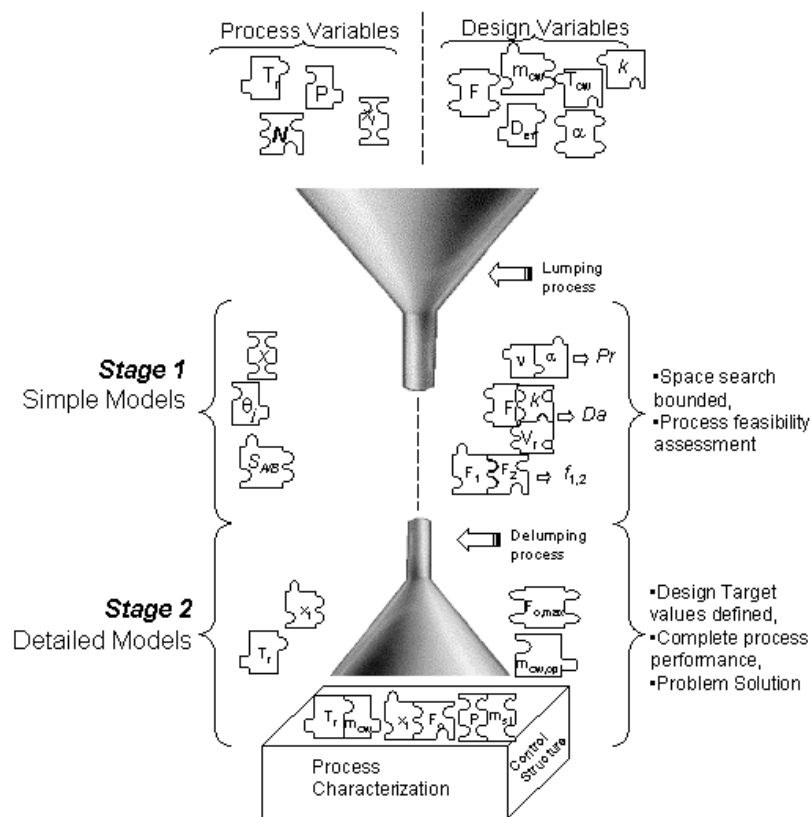


Figure 3.3: Relationship between *design* and *process* variables through the different stages.

A schematic representation highlighting the way the model-based Methodology relates *design* and *process variables* can be seen in Fig. 3.3, wherein variables like flowrates, temperatures, etc. and process parameters such as kinetic

rate constants, enthalpies of reaction, etc. are correlated in *Stage 1* through dimensionless variables, for instance, Da , Pe , Pr , etc. numbers assessing the overall performance of the system. On the contrary, in *Stage 2* the effect of those (design) variables can be evaluated on an individual basis, through the de-lumping of the dimensionless variables, thereby identifying the sensitivity of the process to each variable and simultaneously determining the actual operational conditions of the process.

Mathematically, the analysis carried out in *Stage 1* is represented by Eq. (3.1), which could also be considered a generic form of representation of the process model.

$$\frac{d\mathbf{x}}{dt} = \mathbf{f}(\mathbf{x}, \mathbf{u}, \mathbf{d}) \quad (3.1)$$

In the context of chemical reaction systems, model order reduction refers to the identification of relationships among the reactants, so that fewer species need to be independently tracked (Okino and Mavrouniotis 1998, Hangos and Cameron 2001). The goal of model order reduction is to transform the system of equations (3.1) to one of lower order and still retain the key information of the system. The reduced system becomes

$$\frac{d\hat{\mathbf{x}}}{dt} = \hat{\mathbf{f}}(\hat{\mathbf{x}}, \hat{\mathbf{u}}, \hat{\mathbf{d}}) \quad (3.2)$$

where $\hat{\mathbf{x}}$ is the state vector in the reduced model (dimension $\hat{n} < n$), and $\hat{\mathbf{u}}$ and $\hat{\mathbf{p}}$ are the design and systems parameters vector in the reduced model, respectively. Note that $\hat{\mathbf{x}}$ may refer to a subset of the original states, to groups of original states, or to linear combinations and other mathematical constructs. The transformation relation is

$$\hat{\mathbf{x}} = \mathbf{T}\mathbf{x} \quad (3.3)$$

where $T_{i,j}$ is equal to 1 when x_j contributes to \hat{x}_i and 0 otherwise. It is important to remark that it is possible to find infinite number of transformations for the same input-output set of variables.

3.3 Methodology Description

3.3.1 *Stage 1*. Model-based analysis by Simple Models.

The main purpose at this first stage is to identify the variables through which the limiting conditions of the system can be established (e.g., critical conversions, yields, selectivity or operational constraints). In this respect, the following subproblem is stated:

Given a simplified flowsheet of the process, solve the RSR system by developing a simple model(s) in terms of dimensionless parameters in order to show the overall behaviour of the process and its operability.

In this context, it is logical to identify first the main sources that contributes to such performance, in other words, the identification of the main operations occurring within the process. Hence, instead of dealing with a complete and complex flowsheet, a simplified but representative flow diagram should be utilised; comprising, typically, of a reaction and a separation section interconnected by either a mass or energy (or both) recycle streams.

The next step involves the analysis of the reaction scheme, since it is often one of the major sources of nonlinearities in a process. In this regard, it is important to identify the components that, according to the characteristics of the reaction (e.g., if they are reversible), may have a major impact in the conversion and/or yields while they are recycled. In this way, the model can be developed in terms of recovery factors (design variable) for those components to be recycled, as well as in terms of conversions or yields (process variables) for the products of interest.

In this same context, the thermal effects also play a key role in the model development. For example, if the reaction is known to be highly exothermic, therefore mass and energy balances have to be solved simultaneously since they are linked by the heat and rate of reaction. A relatively simple case is when the reaction operates isothermally, therefore the energy balance should not be taken into account.

From the above discussion, two paths can be recognised: the development of a process model considering mass balances only or a model with coupled mass and energy balances. At this point the models should be built in terms of dimensionless variables, such that variables can be lumped representing a given phenomena or relationship in the process. For instance, in RSR systems a typical parameter that often appears is the plant Da number relating the rate of reaction with respect to the rate of feed to the process, which makes it possible to assess variables such as conversion or yield as a function of Da number. Another important variable commonly appearing is a feed inlet ratio of reactants which helps to measure stoichiometric relationships and consequently their impact on process performance. Assuming that in *Stage 1* the separation section may be modelled as perfect separators, the use of recovery factors to evaluate the amount of unreacted reactants to be recycled back to the reactor so it will be possible to find limiting conditions that could help to identify operational problems such as “snowball” effect (see section [2.4.1] for definition).

By developing dimensionless models it is also possible to reduce the dimension of the process in terms of variables. An initial order reduction is carried out when the main operations were identified, for example, if the original flowsheet comprises of two distillation columns, a simplified scheme would consider only one separation section, hence the number of variables (e.g., flowrates to each column and recycle streams) could be reduced to one recycle stream (if this is the case) and one product stream. Nevertheless, with these models some design and process variables are grouped (lumped) so that the analysis can be carried out in an easier way because of the number of variables that need to be

handled is less.

Once the model has been constructed, numerical and computational aspects related to its solution also needs to be analysed. The model analysis further helps to identify non-linear terms in the balance equations. For example, consider that a model including mass and energy balances has been derived. The rate of reaction in this case is dependent on the reactor temperature T_r and concentration $C_{A,r}$. However, if perfect control of T_r is assumed then mass and energy balances become decoupled and can be solved (analysed) independently. A similar example could be thought for an adiabatic operation of a reactor. Consider the case of a system having a relatively small heat of mixing in comparison to the enthalpy of reaction ($\Delta\hat{H}_r$) and where the ratio of the enthalpy of reaction to the specific heat capacity of the mixture ($\widehat{C}p_m$) is constant. In this case, the following simple algebraic equation can be derived (reduced) from the energy balance equation,

$$T_r = T_b^\circ + T_{ad}(1 - x) \quad (3.4)$$

where x is the conversion, T_{ad} is the adiabatic temperature rise and is equal to $(\Delta\hat{H}_r C_{A,o} / \widehat{C}p_m)$ and T_b° is referred to as the *basis temperature* and is the temperature of the mixture if it was adiabatically reacted to form, say, pure A, i.e., at complete conversion ($x = 1$). Thus by fixing T_b° (reactor inlet temperature), the reactor temperature and concentration (or conversion x) are thus related by Eq. (3.4), therefore T_r becomes a dependent variable. These kind of insights are obtained by the model analysis.

On the other hand, once a solution strategy has been established the process needs to be analysed such that operability and/or feasibility issues can be assessed. In this respect, different tools can be applied and might even depend for each reactive system. For example, Hahn, et al. (2004) and Kiss (2004), among others, have applied bifurcation theory to analyse nonlinear processes, the later specifically to RSR systems. These kind of methods can be implemented, in order to identify regions of stability, or to determine the existence of multiplicities that are likely to be found because of the nonlinearities not only due to the reaction but also for those introduced by the recycle streams. Likewise, a sensitivity analysis of the model (Luyben 1975, Semino and Giuliani 1997) with respect to different parameters (design variables) helps to identify the response of the system to such variations, as in the case of, for example,

- i) feed inlet ratios (which can be interpreted as a process disturbance);
- ii) analysis of recovery factors that can find the limits where the process is capable of handling a given workload to the separation section.

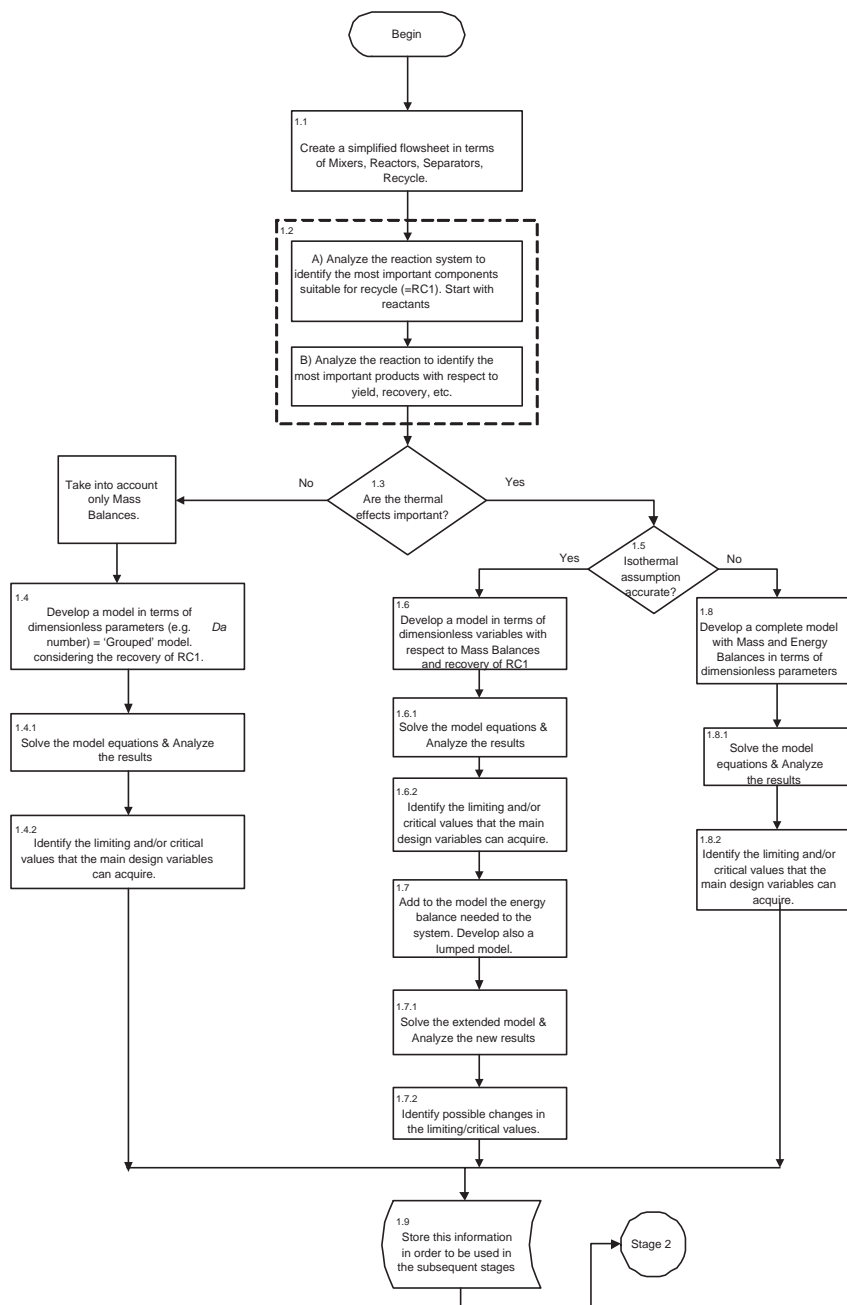
The behaviour that the process exhibits with respect to process/design variables is what it will be called as “operational windows”, i.e., the set of information in terms of phase-plane diagrams or data relating design and process variables in terms of operational limits.

The results of the operability and sensitivity analyses will be the definitions of the conditions of stability, operational windows and also a classification of

the important design variables. Worth mentioning here is that, during the model development and analysis, a set of decisions are taken that definitely will be reflected not only in the performance but also in the control structure configuration.

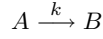
Based on the above discussion, a step-by-step algorithm (see also the flow diagram in Fig. 3.4) is presented for *Stage 1* and highlighted with a simple illustrative example. Note, however, in Chapter 4 more elaborated case studies are presented.

- 1.1** Create a simplified flowsheet in terms of Mixers, Reactors, Separators and Recycle streams.
- 1.2** Reaction Analysis.
 - 1.2.A** Analyze the reaction system to identify the most important components suitable for recycle. Start with reactants (RC1).
 - 1.2.B** Analyze the reaction to identify the most important products with respect to yield, recovery, etc.
- 1.3** Thermal effects consideration. If they are not important, go to step [1.4], otherwise, go to step [1.5] (see page 30 for criteria).
- 1.4** Develop a model considering the recovery of RC1, in terms of dimensionless parameters ('Lumped Models').
 - 1.4.1** Solve the model equations. Analysis of Results. The appropriate set of tools for the analysis should be employed and they will depend on each reactive system (e.g. non-linear analysis).
 - 1.4.2** Identify the limiting values that the main design variables can acquire. Go to Step [1.9].
- 1.5** Is an isothermal assumption sufficient? If 'Yes', go to Step [1.6]. If 'No', go to step [1.8]. Analyse, e.g., the dimensionless heat of reaction β (if $\beta \rightarrow 0$ then isothermal assumption is accurate), also, the Arrhenius number γ (if γ is small also an isothermal assumption is accurate), in catalysts pellets if the Biot number for heat transfer $Bi < 5$ the heat transport inside the pellet is important.
- 1.6** Develop a model in terms of dimensionless variables with respect to Mass Balances and recoveries of RC1.
 - 1.6.1** Solve the model equations. Analyse the results.
 - 1.6.2** Identify limiting and/or critical values for the main design variables.
- 1.7** Add to the model the energy balances needed to the system. Develop as well a dimensionless model.
 - 1.7.1** Solve the extended model and Analyse the new results.
 - 1.7.2** Identify changes in the limiting/critical values. Go to Step [1.9].
- 1.8** Develop a complete model with Mass and Energy Balances in terms of dimensionless variables.
 - 1.8.1** Solve and Analyse the results.
 - 1.8.2** Identify the limiting and/or critical values that the main design variables can acquire. Go to Step [1.9].
- 1.9** Store the information obtained in order to be used in subsequent stages.

Figure 3.4: Flow Diagram for *Stage 1* algorithm.

Illustrative example of *Stage 1*

The example presented here illustrates the *Stage 1* algorithm through the following isothermal first order reaction:



The process flowsheet follows the same configuration as in Fig. 3.1, where the reaction section utilises a CSTR and the separation section consists of a sharp splitter. Thus,

◆ **Step 1.1.** Process flowsheet simplification.

This simple flowsheet includes the reaction section (the CSTR) and a separation section (sharp splitter), therefore, no further simplification is carried out.

◆ **Step 1.2.** Reaction Analysis.

▷ **Step 1.2.A.** A complete conversion of reactant A is not assumed, thus its recycle should be included as a means to enhance the conversion. Consequently, the following main assumptions are: i) Complete recovery of B in the product stream ($\beta_{Y,S} = F_{B,Y}/F_{B,S} = 0$) and, ii) no purge stream ($\sigma = 0$).

▷ **Step 1.2.B.** The main performance variable will be the conversion of component A as to measure the production of product B.

◆ **Step 1.3.** Thermal consideration.

As it was mentioned, the reaction takes place under isothermal conditions, therefore, only mass balances are going to be developed, thus proceeding to step [1.4].

◆ **Step 1.4.** Model Development.

The mass balance around the system in terms of conversion of A, x_A , yields to

$$g(x_A, Da, \alpha_{Y,S}) = Da - \frac{x_A}{(1 - x_A)(1 - \alpha_{Y,S}(1 - x_A))} = 0 \quad (3.5)$$

where

$$Da = \frac{kV_r \rho_m}{F_A} \quad (3.6)$$

is the plant Damköhler number (Da) for a first order reaction based upon inlet flowrate to the plant (Bildea, Dimian and Iedema 2000). Equation (3.6) assumes that the molar density, ρ_m does not depend on composition.

Equation (3.5) counts two design variables, namely, the plant Da number and the recovery factor $\alpha_{Y,S}$ and has to be solved for one process variable, i.e., the conversion of A, x_A . That is, for different values of Da number and $\alpha_{Y,S}$, corresponding values of x_A are calculated and analysed.

▷ **Step 1.4.1.** Model Solution.

In Eq. (3.5) there are two Da -dependent solutions. These are presented in Fig. 3.5 for different values of the recovery of A, $\alpha_{Y,S}$. For a stand-alone CSTR ($\alpha_{Y,S} = 0$) or incomplete reactant recycle ($\alpha_{Y,S} < 1$), the feasible ($0 < x_A \leq 1$) and unfeasible ($x_A < 0$) solution branches do not intersect. When all the reactant is recycled ($\alpha_{Y,S} = 1$), one solution ($x_A = 0$) involves infinite recycle. The other solution has physical significance ($0 < x_A \leq 1$) if and only if, $Da > 1$.

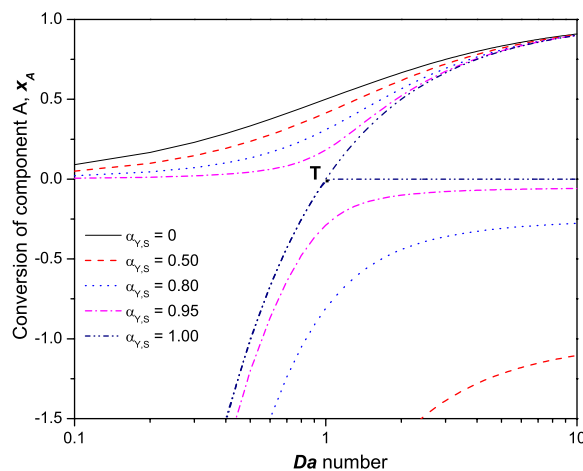


Figure 3.5: Conversion of A as function of Da number for First Order Reaction.

Moreover, the two branches intersect at the point **T** at $(Da, x_A) = (1, 0)$, representing a transcritical bifurcation which is found as follows

$$\frac{\partial g}{\partial x_A} = -\frac{1 - \alpha_{Y,S} + \alpha_{Y,S}x_A^2}{(1 - x_A)^2 (1 - \alpha_{Y,S}(1 - x_A))^2} = 0 \quad (3.7)$$

where the only feasible case ($0 < \alpha_{Y,S} \leq 1$) is when $\alpha_{Y,S} = 1$. The details for these critical conditions are presented in the second approach.

▷ **Step 1.4.2.** Identification of limiting values.

The recycle of reactants might be helpful in some situations, specially for incomplete reactions or multiple reactions, however, as Fig. 3.5 shows, the more reactant A is recycled the lower the conversion becomes. Also, the reactor outlet stream (S) increases considerably, which might also have an effect on the performance of the process since an increasing fraction has to be recovered. The later can be observed in Fig. 3.6.

In RSR systems, the yield enhancement is achieved through separation and increased flow rates, but an operation close to a $Da = 1$ as in the present case produces high flow rates leading also to a “snowball” effect and because of this severe operational problems could be expected.

◆ **Step 1.9.** Storage of Information.

Operational windows have been generated in terms of the plant Da and recovery factor $\alpha_{Y,S}$ where it is possible to determine the conditions where unstable operation is obtained, which will be used later to determine operating conditions and/or complete a design. That is, operating conditions close to a $Da = 1$ and high recoveries ($\alpha_{Y,S} \rightarrow 1$) are expected to lead to unstable operations.

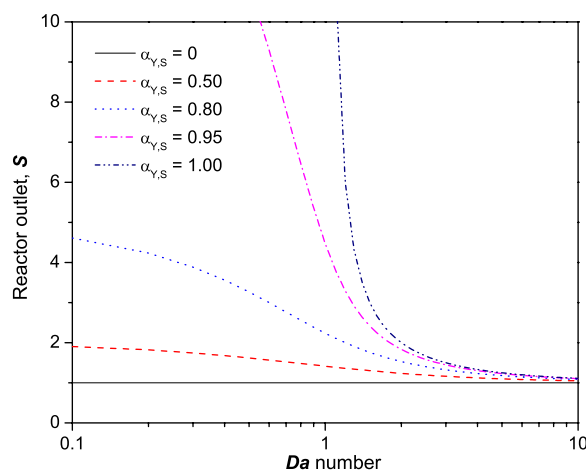


Figure 3.6: Reactor outlet flowrate as a function of Da number.

3.3.2 Stage 2. Model-based analysis by Detailed Models.

This stage deals with the identification of a “near” optimal design. By “near-optimal design” we will be referring to that particular design that achieves a set of design “target” values and also exhibits an adequate operability and control. The set of design “target” values will consider reactor performance variables as conversions, yields, selectivity, etc. and specific recoveries and/or purities in the separation units. Note that the “near” optimal solution will be obtained not through optimisation or simulation but instead, through model-based analysis.

Since we are dealing with multivariable systems, it would not be a straightforward task to develop and solve a model capable of handling all the inherent complexities attached to it. Consequently, from the *Stage 1* analysis, the range of variation for the main design and process variables is now delimited, which makes it possible to perform a ‘search’ much easier and within a region of confidence defined by the dimensionless variables.

At this second stage the *Attainable Region* (AR) concept is used (Horn 1964) in order to determine an optimal reactor design. This technique has proved its utility in terms of finding the optimal reactor network structure that achieves the highest yield (or conversion) of the product of interest in a multiple reaction system. In this respect, recently the AR concept has been applied to RSR systems (Omtveit et al. (1994), Hildebrandt et al. (1998)). Although, this technique has been restricted to obtaining the appropriate reactor network configuration, there have not been sufficient efforts to incorporate it into the analysis and operability of RSR systems. In this sense, Appendix A gives an example of the application of the AR within the framework of the model-based Methodology. Therefore, it is possible to generate a process model as well as to assign the design target for achieving an optimal design through the location

of the maximum of the Attainable Region (or at any other value lying on its boundary according to an objective function, given that the boundary defines the best process layout or sequence and the best operating conditions).

It is worth mentioning that while these models could be simple, they are still accurate and part of the analysis is graphical, providing a visual display of the integrated design process.

As in *Stage 1*, the following subproblem is stated for *Stage 2*:

Considering the complete flowsheet of the process, resolve the RSR system by developing the appropriate model that takes into account all unit operations and carry out the corresponding analysis in order to completely characterise the process.

Given the fact that the process has been bounded, an analysis using more detailed models can be carried out only within these bounds. Firstly, given the objectives of the stage, it is necessary to determine the maximum conversion and/or yield that the reaction scheme can provide. Also, in the case of multiple reactions an *AR* needs to be constructed. If multiple reactions are not present, the selection of an operating point could be made from the operational window(s) obtained in *Stage 1*. Otherwise, a design target can be supplied in advance on the basis, either of a desired production rate or selectivity, environmental restrictions, etc.

Consequently, the main assumptions made in *Stage 1* should be removed (e.g., complete recoveries or constant pressures, etc.). The complete process in terms of unit operations should be included now.

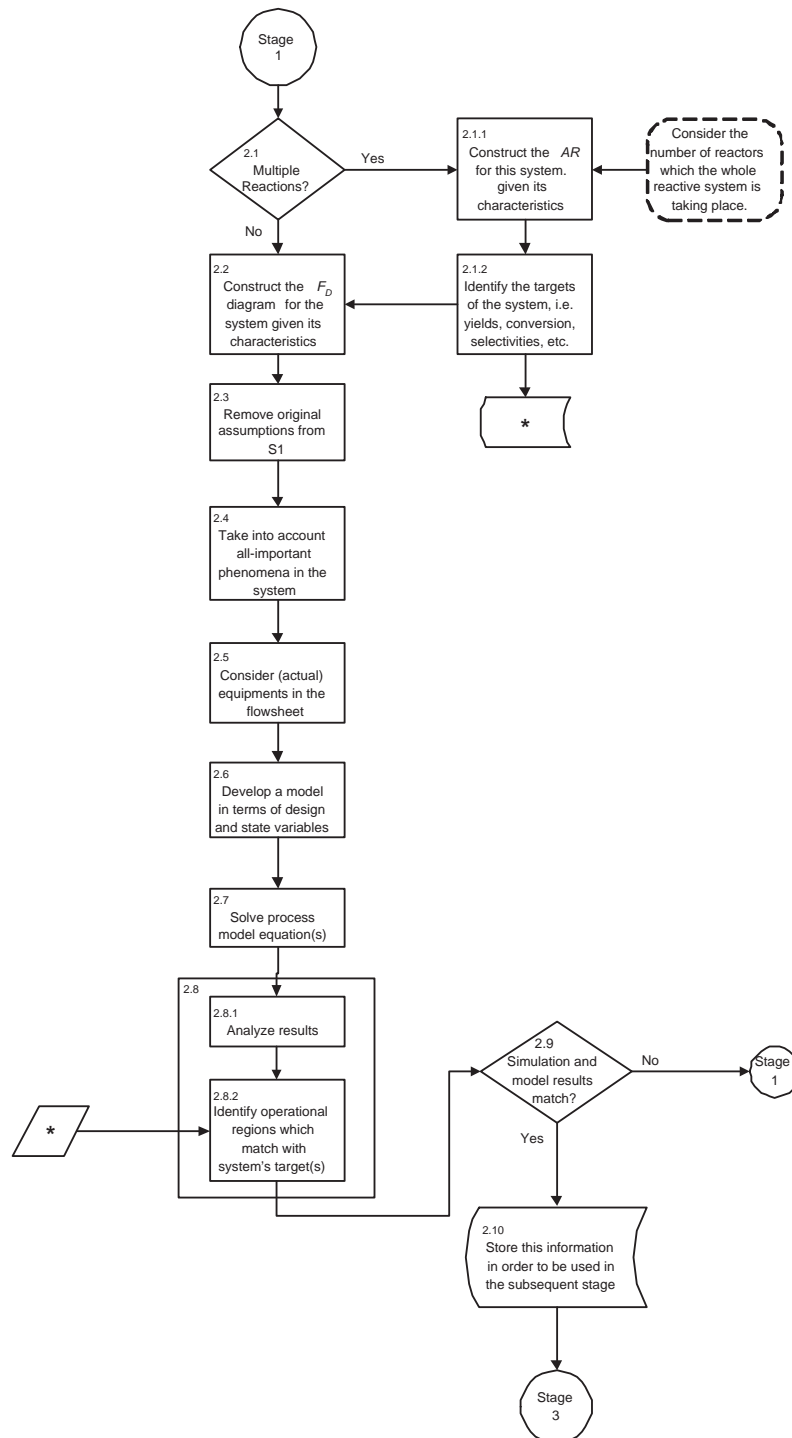
In this way, the detailed model of *Stage 2* will disassemble the lumped variables from *Stage 1* allowing the individual assessment of the effect of the variables involved in them. This, of course, increases the complexity of the model, but then again, the values that such variables can acquire are bounded. The corresponding model now will be in terms of actual design and process variables, i.e., holdups, concentrations, temperatures, etc., instead of dimensionless variables. It is important to remark that if some important phenomena are present, these also should be included in the modelling since they impose operational constraints.

The solution of this detailed model turns out to be more difficult given that all the complexities are considered. The previous stage, however, provides information regarding limiting conditions, for example, values for recycle flowrates, flow ratios, etc., and therefore, good initial estimates can be given to the solver. Similarly, model analysis will help to determine process and operational insights before solution.

It is important to consider that if the results in this stage do not follow or match with *Stage 1* then a ‘recycle’ of information should be made in order to inspect possible reasons for mismatch to subsequently eliminate such mismatch.

Consequently, the results from this stage plus the results from *Stage 1* reach a complete characterization of the process.

The procedure described above is presented in the form of a step-by-step

Figure 3.7: Flow Diagram for *Stage 2* algorithm.

algorithm (see flow diagram in Fig. 3.7):

- 2.1** If multiple reactions are not present in the system go to [2.2],
 - 2.1.1** Construct the Attainable Region for the RSR system (Consider the existing number of reactors and the number of reactions taking place in each of them).
 - 2.1.2** Identify the design targets for the optimal design of the RSR system, i.e., find target values for yields, conversions, etc.
 - 2.1.3** Store this information to be used in [2.8.2].
- 2.2** Construct a Driving Force diagram in order to identify the separation targets for the separation section.
- 2.3** Remove original assumptions from *Stage 1*, such as complete recovery of reactants and/or the use of mass balances.
- 2.4** Take into account all-important phenomena in the system that were not considered at *Stage 1*.
- 2.5** Include the actual equipments in the process.
- 2.6** Develop a model in terms of the *design* and *state* variables. The lumped variables are disassembled.
- 2.7** Solve the process model equation(s). Supply information from *Stage 1* as initial estimates.
- 2.8** Model Analysis.
 - 2.8.1** Once a solution has been obtained, the appropriate analysis of the results needs to be carried out.
 - 2.8.2** Identify operational regions that match with the system's target(s). Use information from [2.1.2]
- 2.9** Results from *Stage 1* and *2* match? If 'Yes' go to step [2.10]. Otherwise, go to [1.2] in order to check the assumptions made.
- 2.10** Store this information in order to be used in the subsequent stage.

This algorithm is applied to the theoretical example.

Illustrative example of *Stage 2*

We continue with the RSR process example used to illustrate the steps of *Stage 1* algorithm. From *Stage 1* it was determined that an operation close to a $Da = 1$ and high recoveries ($\alpha_{Y,S} \rightarrow 1$) will result in an unstable conditions and problems related to control could be expected. This information will be used in *Stage 2*.

◆ **Step 2.1.** Multiple reactions consideration.

The selection of a design target for this simple forward reaction could be made, for example, through the operational window shown in Fig. 3.5. In this way, there will be the interest in the design of an operation that can achieve a conversion $x_A = 0.75$.

◆ **Step 2.2.** Driving force diagram.

We are only interested in showing the properties of the Methodology in terms of determining limiting conditions of operation and it is assumed that not difficulties

will be encountered in the separation section beyond to the operational restrictions that the system might impose (e.g., “snowball” effect), therefore no driving force diagram is drawn.

◆ **Step 2.3.** Assumptions removal.

The detailed model for this first order reaction will include a purge stream (see Fig. 3.1) and the recycle of product B as well, although this recycle is not of interest in practice.

◆ **Steps 2.4. and 2.5.** Unit Operations and new phenomena addition.

The initial number of unit operations does not vary. Consequently, additional phenomena are not included for analysis.

◆ **Step 2.6.** Model development.

The complete process model for the system is given in Equation (3.8), thus

$$g = \left(\frac{kV_r \rho_m}{F_A} \right) - \frac{\sigma \alpha_{Y,S} (\sigma - \beta_{Y,S} (1 - x_A))}{(\sigma - \beta_{Y,S}) (1 - x_A) (\sigma - \alpha_{Y,S} (1 - x_A))} = 0 \quad (3.8)$$

For the sake of simplicity the definition for the Da number (Eq. (3.6)) will be retained.

◆ **Step 2.7.** Model solution.

Equation (3.8) adds two more variables (in comparison to Eq. (3.5)) that have to be specified in order to solve this non-linear equation, namely, the purge factor (σ) and the recovery of component B ($\beta_{Y,S}$). In Eq. (3.8), function g now comprises of $[Da, \sigma, \alpha_{Y,S}, \beta_{Y,S}]^T$ that have to be specified in order to calculate the conversion of A (x_A).

◆ **Step 2.8.** Model analysis.

In the framework of the bifurcation theory, in order to determine the location of a bifurcation point, the derivative of Eq. (3.8) with respect to the conversion of A is taken, which after rearranging, leads to the following critical condition (x_A^{cr}),

$$x_A^{cr} = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad (3.9)$$

where

$$\begin{aligned} a &= \sigma(\alpha_{Y,S} - \beta_{Y,S}) + \alpha_{Y,S}\beta_{Y,S} \\ b &= \beta_{Y,S}(\sigma - \alpha_{Y,S}) \\ c &= \sigma(\sigma - (\alpha_{Y,S} + \beta_{Y,S})) + \alpha_{Y,S}\beta_{Y,S} \end{aligned} \quad (3.10)$$

In Eq. (3.9) only the positive root has been taken since we are only interested in the feasible range of solution of x_A ($0 \leq x_A \leq 1$). In this context, examining Eq. (3.9), the conditions yielding to positive roots are

$$\alpha_{Y,S}^2 - \alpha_{Y,S}(\sigma + \beta_{Y,S}) + \beta_{Y,S}\sigma < 0 \quad (3.11)$$

To verify Eq. (3.11) set $\sigma = 1$ (no purge) and $\beta_{Y,S} = 0$ (no recovery of product B), the corresponding solutions are:

$$\begin{aligned} \alpha_{Y,S,1} &< 0 \\ \alpha_{Y,S,2} &< 1 \end{aligned} \quad (3.12)$$

the only feasible operation corresponds to a $\alpha_{Y,S} < 1$, which is then substituted into Eq. (3.9) leading to

$$x_A^{\text{cr}} = 0$$

therefore,

$$\lim_{\substack{\alpha_{Y,S} \rightarrow 1 \\ x_A \rightarrow x_A^{\text{cr}}}} g(x_A^{\text{cr}}, Da, \alpha_{Y,S}) = Da - 1 = 0 \quad (3.13)$$

Equation (3.11) states that if $\alpha_{Y,S} = 1$ (infinite recycle) a change of stability will occur at $Da = 1$ and $x_A^{\text{cr}} = 0$ and increasing the Da number, the (stable) feasible solution appears, while the infinite-recycle solution loses stability.

The results given in Tables 3.1 and 3.2 are obtained by solving Eq. (3.8) for different Da values (Table 3.1) and also for different values of the recovery of A ($\alpha_{Y,S}$) and B ($\beta_{Y,S}$)(Table 3.2). Tables 3.1 and 3.2 help also to select an operating point of the system since they comprise most of the information in terms of design and process variables.

Table 3.1: Effect of Da number on conversion of A and reactor outlet flowrate.

F_A	Da	$\alpha_{Y,S}$	Conversion of A, x_A			Reactor flow, S		
			1.0	0.85	0.5	1.0	0.85	0.5
20	172.893		0.9942	0.9942	0.9943	20.116	20.098	20.058
100	34.577		0.9712	0.9713	0.9716	102.966	102.499	101.441
1000	3.458		0.7118	0.7272	0.7524	1404.743	1301.923	1141.263
2000	1.729		0.4237	0.4989	0.5776	4719.784	3483.722	2535.481

F_A, S [=] kmol/h, $\beta_{Y,S} = 0$, $V_r = 10 \text{ m}^3$, $\rho_m = 40.62 \text{ kmol/h}$, $k = 8.51 \text{ h}^{-1}$

It can be observed in Table 3.1 that, the more reactant A is recycled, the lower conversion is achieved, and consequently, the reactor outlet flowrate (S) is increased. On the other hand, it is clear that the recycle of product B does not bring a positive impact in the system (see Table 3.2) since the more B is recovered, the product flowrate as well as the conversion of A decrease, which is not economically beneficial. Also, by recovering more B, the recycle flowrate (y_B) increases the possibility to end in a “snowball” effect. This effect can also be seen in Table 3.1.

Table 3.2: Effect of recovery of A and B on performance variables at $Da = 2$.

$\beta_{Y,S} \setminus \alpha_{Y,S}$	Conversion of A, x_A			Recycle flow of B, y_B			Product flow of B, p_B		
	1×10^{-6}	0.5	1.0	1×10^{-6}	0.5	1.0	1×10^{-6}	0.5	1.0
0	0.667	0.618	0.500	0	0	0	0.667	0.764	1.0
0.02	0.664	0.615	0.495	0.014	0.016	0.020	0.664	0.761	1.0
0.10	0.651	0.600	0.474	0.072	0.083	0.111	0.651	0.750	1.0
0.20	0.633	0.580	0.444	0.158	0.184	0.250	0.633	0.734	1.0

$F_A = 1728.93 \text{ kmol/h}$, $V_r = 10 \text{ m}^3$, $\rho_m = 40.62 \text{ kmol/h}$, $k = 8.51 \text{ h}^{-1}$

In this way, since the design target is an operation that achieves a conversion x_A of 75%, analysis of the results given in Table 3.1 point to three ways to achieve it, i.e.,

for $\alpha_{Y,S} = [0.5, 0.85, 1.0]$. However, the more A is recovered, the larger is the recycle stream. Consequently, a feasible selection could be a 50% of the recovery of A for a fresh flowrate $F_A = 1000$ kmol/h. Also, it can be argued that since this point is at $Da > 1$ a safe operation could be expected.

◆ **Step 2.9.** Results agreement.

There has not been found mismatches between the results from *Stage 1* and *2*. Table 3.1, for example, confirms that an operation close to a Da of 1 the system shows a high sensitivity (see the high reactor outlet), therefore, the likelihood of a “snowball” effect increases.

◆ **Step 2.10.** Storage of information.

In this stage the complete process model has been developed and analysed the interaction of the design and process variables that allowed the determination of a design matching the design target defined in this *Stage 2*.

It is possible now to proceed to the final stage of the analysis.

3.3.3 *Stage 3. Verification.*

The *Stage 3* is the verification through rigorous simulation (steady state and/or dynamic). The objective will not only be the verification of the results from the two previous stages, but also they will provide a better starting point for setting up the rigorous simulation problem. This is, with the information that has been generated from the two previous stages, it is meant that all the assumptions, limiting conditions, operational regions, etc., can be stated and identified when the problem is to be set into a process simulator, so that the simulation will be carried out more efficiently.

Hence, the subproblem for *Stage 3* defined as:

Resolve the RSR system by using more rigorous models (as in a process simulator) by either steady-state or dynamic simulations in order to verify the set of analysis carried out in Stages 1 and 2.

The use of process simulation tools where the use of more rigorous unit operation models as well as appropriate thermodynamic models provide a means for the validation of the results and design decisions made at *Stages 1* and *2*.

The analysis of the simulation results are expected to agree with respect to the findings from the previous steps. Otherwise, at this point a ‘recycle’ of information to either *Stage 1* or *2* will have to be made in order to analyse assumptions or considerations taken.

Finally, from the knowledge that has been extracted through the application of the model-based Methodology, it is possible to sketch a control structure that ensures the design targets that will be achieved during operation. The sketching of a control structure is performed by studying the degrees of freedom of the system such that, even though they may be different for the individual design and control problem, in an integrated approach the common sets of variables

may be considered both for design and control. *Stage 1* deals with a reduced process model lumping both design and process variables, like the Da number which considers the inlet flowrate of one of the main reactants being a typical design/manipulate variable and also V_r , which is a common process/control variable in terms of level of the reactor. Therefore, it makes sense to control such variable by manipulating the feed flowrate and, by doing that the impact on a related performance variable such as x_A or Y_P , etc. will be known. The remaining degrees of freedom that were not paired from such analysis could be made from the results of *Stage 2*. It is clear that several control structures could be proposed, nevertheless, from the knowledge obtained, a logical control structure could be synthesised as a first estimate.

In this context, the following steps are considered (the corresponding flow diagram is provided in Fig. 3.8):

- 3.1** Flowsheet set up in the process simulator.
- 3.2** Use the information obtained from *Stage 1* and *Stage 2* as initial estimates for the simulation (hold-ups, temperatures, flowrates, etc.).
- 3.3** Run the simulations (steady-state and/or dynamic) and verify the results. The results obtained from the simulations will be used for comparison against *Stage 1* and *Stage 2*.
- 3.4** If the simulation and the model results match then go to [3.5], else,
 - 3.4.1** Analyse the model in order to search for inconsistencies. Go to [1.2] to verify the validity of the assumptions.
 - 3.4.2** Analyse the simulation results in order to look for inappropriate set ups. Go to [3.1].
- 3.5** Store this information in order to complete the design.

After this analysis, the corresponding control structure outline can be performed based on the results of the model-based Methodology.

Illustrative example of Stage 3

We continue with the same RSR process used to illustrate *Stages 1* and *2*. The algorithm will be applied to the isomerization of *o*-xylene (A) to *p*-xylene (B). The reaction is assumed to take place in the liquid phase and follows a first order scheme approximately at 300 K (Zhorov 1987).

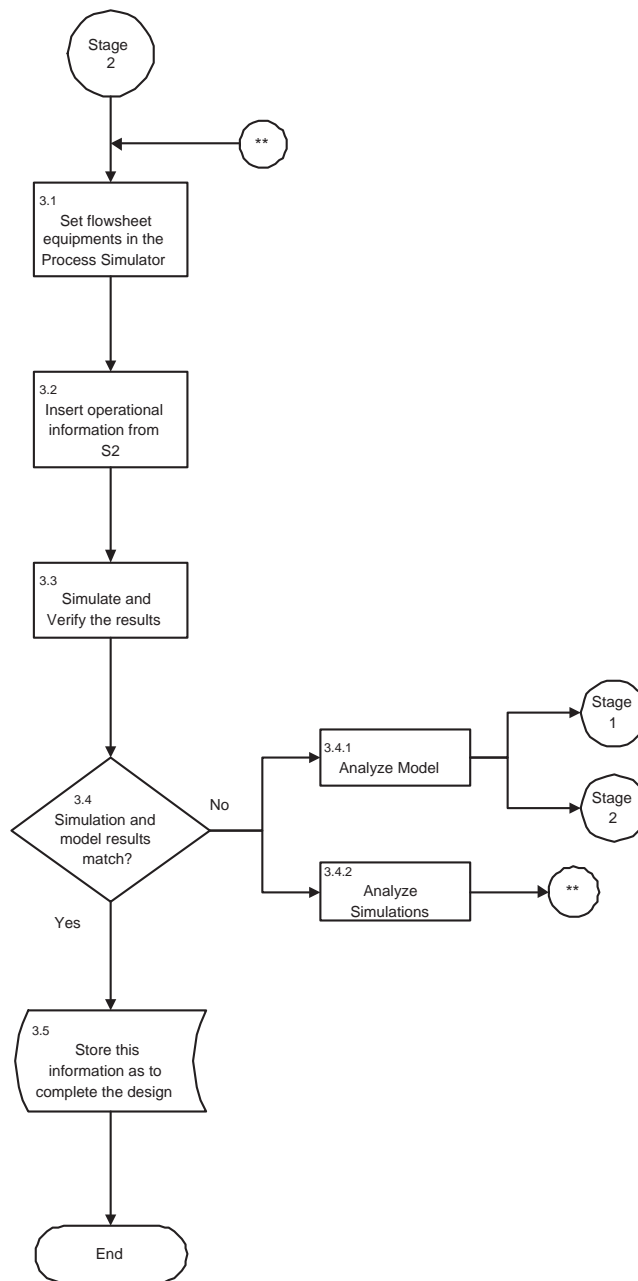


◆ **Step 3.1.** Flowsheet set up.

This flowsheet was built up in ICASSim (Gani 2002) using a *mixer* tank, a CSTR ($V_r = 5 \text{ m}^3$) and a sharp splitter.

◆ **Step 3.2.** Generated knowledge from previous stages.

From the analysis made in *Stages 1* and *2* the likelihood for obtaining a “snowball” effect at high recovery values and also for a $Da = 1$.

Figure 3.8: Flow Diagram for *Stage 3* algorithm.

◆ **Step 3.3.** Run of simulations.

The simulations carried out in MoT (Sales-Cruz 2003) (*Stage 1* and *Stage 2* models) show good agreement when compared against the results with ICASSim (see Fig. 3.9).

It is important to stress that when the feed to the system is increased the recycle stream increases up to a point where the system is not able to handle the amount of material recycled back to the reactor (“snowball” effect). For example, for a feed equal to 2,000 kmol/hr and a complete recovery of A ($\alpha_{Y,S} = 1.0$), the reactor outlet is twice as large in comparison with a recovery of $\alpha_{Y,S} = 0.5$. On the other hand, the conversion increases at lower $\alpha_{Y,S}$ values (see Fig. 3.5). This can be explained in terms of the residence time τ which is $\tau = 0.086$ hr for $\alpha_{Y,S} = 1.0$, and is 0.16 hr for $\alpha_{Y,S} = 0.5$. Therefore a higher conversion can be obtained since the reaction is allowed to proceed further within the reactor.

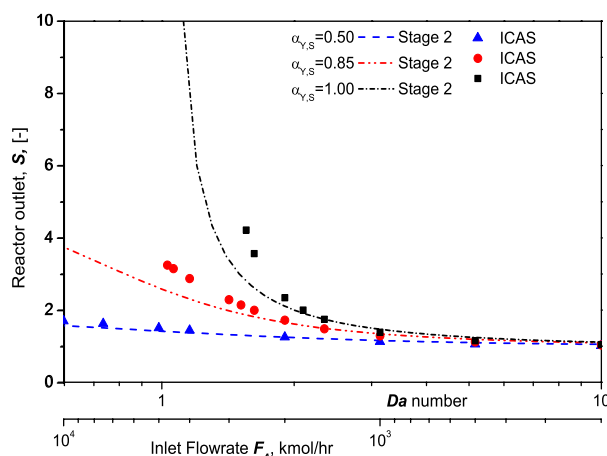


Figure 3.9: Reactor flowrate S as function of Da number and F_A . Results comparison between *Stages 2* and *3* ($\beta_{Y,S} = 0$).

◆ **Step 3.4.** Simulations agreement.

As it can be seen, the results obtained through the rigorous simulations (Fig. 3.9) confirmed the insights generated through *Stage 1* and *Stage 2* models (see also Fig. 3.6) with respect to the recovery factors ($\alpha_{Y,S}$, $\beta_{Y,S}$) as well as the sensitivity of the process to the fresh feed F_A (interpreted as Da number) in order to avoid the “snowball” effect (compare Table 3.1 and Fig. 3.9).

◆ **Step 3.5.** Storage of information.

The design and control implications of this kind of analysis have been considered in the work of Luyben (1993a), Bildea et al. (2000) among others. A plantwide control structure, where the reactor volume is kept constant, the separation section is on dual-composition control and the plant throughput is set by the reactant feed is equivalent to a set of specifications for the following process-control variables ($F_A, V_r, z_{A,Y}, z_{B,P}$). This control structure is shown in Fig. 3.10a. During the *Stage 1* analysis, the overall behaviour of the system is assessed through the Da and the recovery factors which involve the above-mentioned set of variables. In *Stage 2*, by

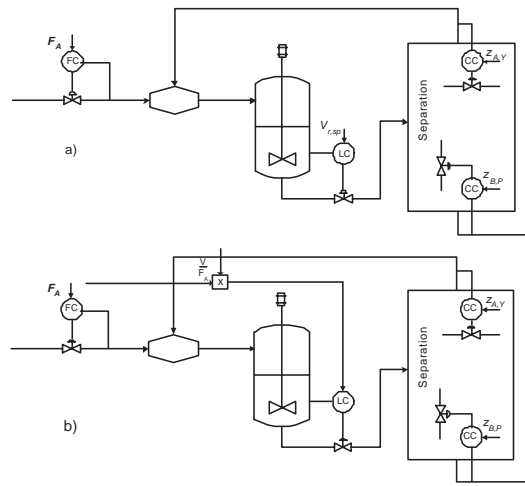


Figure 3.10: (a) Conventional control structure for illustrative example and (b) Balanced control structure.

delumping the Da number, the reactor volume V_r as well as the kinetic constant k were kept constant, while F_A was allowed to vary. In the separation section the compositions of A and B were still fixed through the recovery factors $\alpha_{Y,S}$ and $\beta_{Y,S}$, respectively. On the other hand, Bildea et al. (2000) show that small reactors or slow reaction rates ($Da < 2$) are better controlled by the control structure proposed by Luyben (1994). However, systems with large reactor or fast reaction rate ($Da > 3$) are better controlled by the conventional control structure (as in Fig. 3.10a). As the design moves towards a $Da = 1$ (see Fig. 3.6) the RSR system becomes more sensitive to this variable, which can be counted a disturbance in the feed flowrate for the conventional control structure. On the other hand, the analysis carried out at Stage 1 and 2 is also valid if another control strategy is intended to be used, as long as the dimensionless model parameters do not change. For example, the maintenance of a set of operational conditions, like stream compositions, can be achieved by changing the fresh feed flowrate and modifying the reaction conditions (V_r or k) in order to keep the Da number constant. Wu and Yu (1996) called this a ‘balanced control’ (see Fig. 3.10b) because the disturbances are rejected by changing both the reactor and the separation conditions.

The model-based Methodology for integrated design-analysis presented above, intends to follow a logical sequence in the design and analysis of a process, by providing a more fundamental basis of understanding since the design and analysis is based on the actual design model of each unit of the process. Also, instead of dealing with a highly complex process model incorporating all variables and phenomena, the problem is decomposed into sub-problems such that at every stage important information is attained (and within each stage, successive steps), so that the appropriate stage models can be generated and their results analysed for the specific integrated design-analysis (control) problem.

Case Studies

This chapter presents case studies that have been worked out in order to demonstrate the applicability of the model-based Methodology for design and analysis of RSR systems. The first two case studies deal with RSR systems that have also been studied extensively by other researchers but with a different perspective. These examples are presented with the aim of illustrating the advantages of the model-based analysis to identify process operability and feasibility issues. In a more complex RSR system, the process for Ethylbenzene production is considered and the application of the model-based analysis is highlighted for the design decisions that can be made corresponding to defining and matching design target values. The final case study is the Tennessee Eastman Problem, which is a very well-known plantwide control example through which the design and control structure issues are addressed through the application of the model-based Methodology.

4.1 Theoretical Case Studies

The following two simple case studies are presented as a motivation and starting point for the development of the present model-based Methodology. The examples to be considered are RSR systems involving i) a consecutive reaction $A \longrightarrow B \longrightarrow C$ and, ii) a second order reaction $A + B \longrightarrow C$.

The following assumptions for both examples are made:

- \mathcal{A}_0 . The reactions are considered to take place isothermally in a continuous stirred tank reactor (CSTR),
- \mathcal{A}_1 . The separation section will be modelled as a component sharp *splitter* unit,
- \mathcal{A}_2 . A fraction of the unreacted raw materials (mainly) is recycled back to the reactor through a *mixer* unit, the possibility of a *purge* stream is considered as well,
- \mathcal{A}_3 . The modelling steps will be performed on a steady-state basis.

Figure 4.1 shows the flowsheet for these systems (nomenclature is referred to this figure).

With the above-mentioned considerations, steps [1.1] and [1.3] of *Stage 1* are covered.

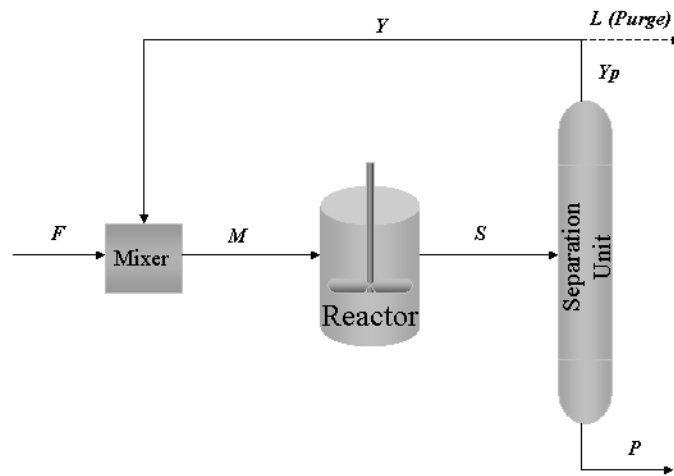
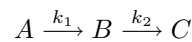


Figure 4.1: Flowsheet considered for a RSR system.

4.1.1 Consecutive Reactions (Case Study 1)

The reaction scheme for this system is



where both reactions are assumed to follow a forward direction and a first order kinetics.

4.1.1.1 Stage 1. Model-based analysis by Simple Models.

◆ **Step 1.1.** Process flowsheet simplification.

This step has been covered in assumptions $\mathcal{A}_1 - \mathcal{A}_2$ (see page 47).

◆ **Step 1.2.** Reaction Analysis.

▷ **Step 1.2.A.** The following assumptions are made: no recovery of products B and C ($\beta_{Y,S} = 0$, $\gamma_{P,S} = 1$, respectively), pure A feed to the system ($F_B = 0$), and no purge ($\sigma = 1$).

▷ **Step 1.2.B.** This case is developed in terms of conversions as one of the main performance variables.

◆ **Step 1.3.** Thermal considerations.

This step has been covered in assumption \mathcal{A}_0 (see page 47).

◆ **Step 1.4.** Model Development.

Given the above-mentioned assumptions, the mass balance equations in terms of dimensionless variables are:

Mixer:

$$m_A = \frac{1}{1 - \alpha_{Y,S}(1 - x_A)} \quad (4.1)$$

$$y_A = m_A \quad (4.2)$$

Splitter:

$$s_A = \frac{(1 - x_A)}{1 - \alpha_{Y,S}(1 - x_A)} \quad (4.3)$$

$$s_B = \frac{x_A(1 - x_A)}{(1 - \alpha_{Y,S}(1 - x_A))(1 - x_A(1 - k_2^*))} \quad (4.4)$$

Reactor:

$$Da - \frac{x_A}{(1 - x_A)(1 - \alpha_{Y,S}(1 - x_A))} = 0 \quad (4.5)$$

where $Da = k_1 V_r \rho_m / F_A$ and $k_2^* = k_2 / k_1$.

◆ **Step 1.4.1.** Model solution.

Equation (4.5) has two design variables, namely, the plant Da number and the recovery of pseudo-component A, $\alpha_{Y,S}$ and is solved for the conversion x_A of A.

◆ **Step 1.4.2.** Identification of limiting values and operational windows.

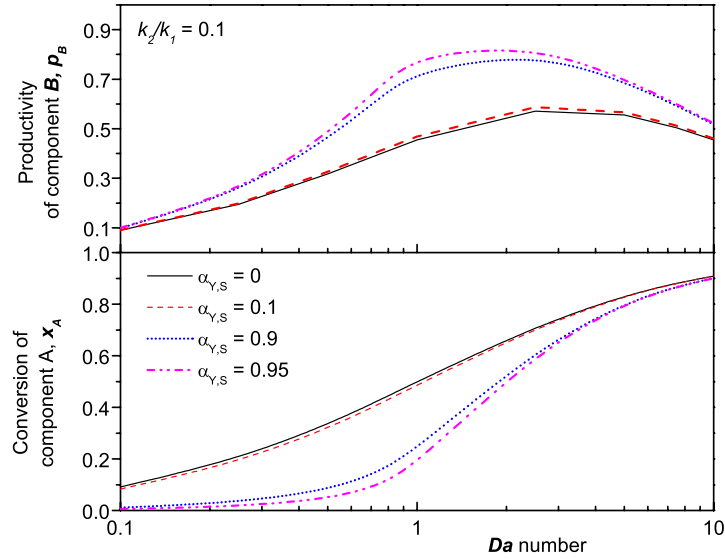


Figure 4.2: Productivity of B and conversion of A as function of Da number.

It is important to highlight that Eq. (4.5) follows the same form as Eq. (3.5) for a first order reaction given the assumptions stated initially, this is confirmed also by Fig. 4.2 (see the lower plot).

From Fig. 4.2 a maximum in the production of B is observed at high recoveries (and low values for the Da number), which can be explained in terms of the amount of reactant (in this case A) that has to be converted, thus the higher amount of A present, the higher the production of B is initially obtained until a point where the production of product C starts to get favoured. Consequently, the production of B decreases, which is a typical behaviour of a consecutive reaction system.

◆ **Step 1.9.** Storage of information.

From this simple analysis it can be suggested that, if the objective were to maximise the production of component B, it can be achieved by operating at high recoveries of A and at relatively low values for the Da number (as shown in Fig. 4.2).

4.1.1.2 **Stage 2. Model-based analysis by Detailed Models.**

◆ **Step 2.1.** Multiple reaction analysis.

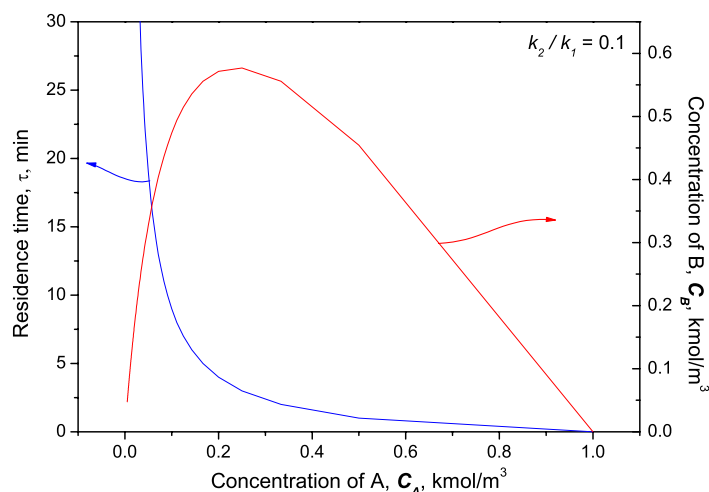


Figure 4.3: Candidate Attainable Region for a Consecutive Reaction system.

Two reactions in series occur in the RSR system being considered B as the product of interest. Therefore, one way to determine the maximum yield of B that this system can achieve, is to perform an Attainable Region (AR) analysis. In this respect, in Fig. 4.3 the CSTR-trajectory described by the concentration of B (C_B) as function of the concentration of A (C_A) for this reaction system is presented. The CSTR-trajectory is convex and no rate vectors point out of the region, thus the necessary conditions for an AR are satisfied. However, we cannot claim that this is the complete *attainable region* for the reaction system since the operation is confined to the CSTR and no modification to the process layout is considered. Thus no further improvement to this region could

be made. This is referred as *candidate* regions for the AR, i.e., regions that satisfy the necessary conditions (Glasser and Hildebrandt 1997).

◆ **Step 2.2.** Driving force analysis.

For this case-study the separation section is again assumed to operate as a sharp splitter, whereby a driving force analysis is not performed. Also for purposes of illustration, it is assumed that the separation does not represent a limiting step in the design and analysis of the process.

◆ **Step 2.3.** Assumptions removal.

The two main assumptions from *Stage 1* are relaxed in this modelling step: the recovery of product B is not 100% ($\beta_{Y,S} \neq 0$) and purge stream is not zero ($\sigma \neq 0$).

◆ **Step 2.4.** All-important phenomena.

The important phenomena in this case study are related mainly to the reaction, which has already been identified.

◆ **Step 2.5.** Process equipments.

The flowsheet is unchanged (see Fig. 4.1).

◆ **Step 2.6.** Model Development.

Equations (4.6) and (4.7) are obtained from the mass balances in the process for components A and B, respectively, where

For A:

$$\left(\frac{k_1 V_r \rho_m}{F_A} \right) = \frac{\sigma x_A}{(\sigma - \alpha_{Y,S}(1 - x_A))} \left[\frac{\sigma - \beta_{Y,S}(1 - (x_A + x_B))}{(1 - x_A)(\sigma - \beta_{Y,S}(1 - x_B))} \right] \quad (4.6)$$

For B:

$$\left(\frac{k_1 V_r \rho_m}{F_A} \right) = \left[\frac{\sigma x_A (\sigma - \beta_{Y,S})}{(\sigma - \alpha_{Y,S}(1 - x_A)) (\sigma - \beta_{Y,S}(1 - x_B))} \right] \times \left[\frac{\sigma - \beta_{Y,S}(1 - (x_A + x_B))}{(1 - x_A)(\sigma - \beta_{Y,S}(1 - x_B)) - \sigma k_2^* x_A} \right] \quad (4.7)$$

whence $k_2^* = k_2/k_1$.

◆ **Step 2.7.** Model Solution.

Equations (4.6) and (4.7) form a non-linear algebraic system of equations with respect to two unknown process variables: the conversion of A (x_A) and B (x_B). Therefore, when k_1 , V_r , ρ_m are specified, the system can be solved for different values of the recovery factors ($\alpha_{Y,S}$, $\beta_{Y,S}$), the reaction rate ratio (k_2^*) and the fresh feed of A (F_A). The advantage of using this model is that when F_A is set, the value of Da number is known. Therefore, the Da number is now a function of these variables and not a parameter to be varied ‘freely’.

◆ **Step 2.8.** Model Analysis.

There are two main effects to be examined: i) the effect of the kinetic ratio, k_2^* and, ii) the occurrence of the “snowball” effect in the system.

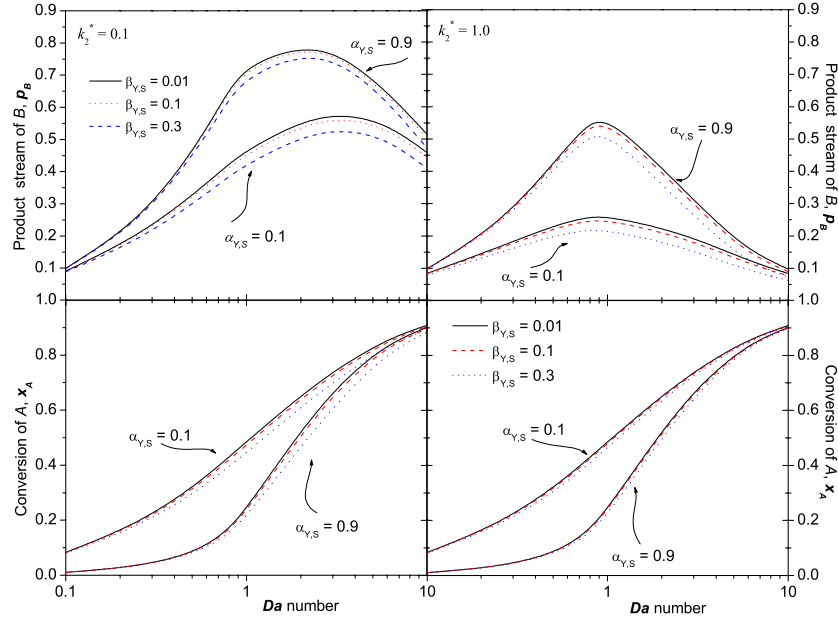


Figure 4.4: Effect of the kinetic ratio on the performance of the system.

The effect of the kinetics on the process performance is first analysed. Figure 4.4 shows the behaviour of the conversion of A and the productivity of B as function of the (calculated) Da number for different values in the recoveries of A and B at two different kinetic ratio values of k_2^* . Even though the conversion of A does not vary significantly with respect to k_2^* , the main effect is observed on the product flow rate (referred here as *productivity*) of B (p_B). In this regard, if it was desired to maximise the productivity of B while using high k_2^* values (see the upper right-hand panel in Fig. 4.4), higher recoveries of A would be required given that the second reaction is proceeding faster than the first one ($k_2 > k_1$). This increase in the recovery of A would have a ‘delaying’ effect on the production of C due to the higher amount of material to be processed within the same reactor volume. Similar observations can be made for a lower value of k_2^* . In this case, however, the range with respect to the Da number to obtain higher productivity values of B is enlarged (compare both top-panels in Fig. 4.4).

The analysis of “snowball” effect is also studied for this example. Figures 4.5 describes the effect of the outlet reactor flowrate S and productivity of B with

respect to the conversion of A at different recovery values $\alpha_{Y,S}$.

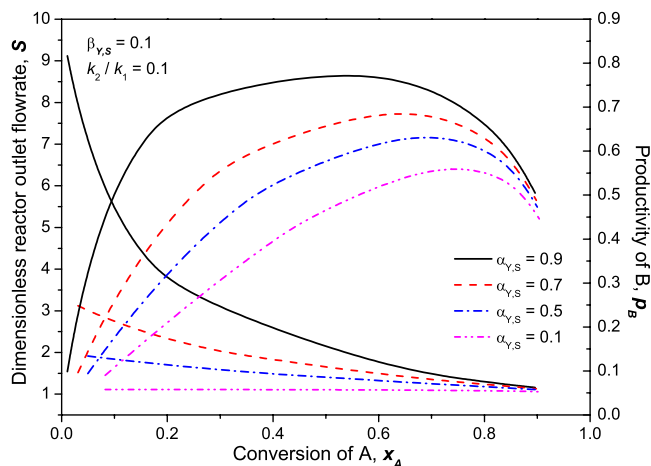


Figure 4.5: “Snowball” effect in Consecutive Reaction RSR system.

As it can be expected, higher conversions of A can achieve higher productivity values of B. The later is valid until a point where the production of C starts to get favoured, as previously mentioned (steps [1.4.2], [2.8]), thus decreasing the value of p_B . On the other hand, as the recovery of A is increased, the likelihood of a “snowball” effect increases as well (see the profiles of flowrate S in Fig. 4.5), in spite of the positive effect of higher recovery values on the productivity of B.

◆ **Step 2.9.** Results agreement.

Figure 4.4 confirms the trends observed in the conversion x_A and productivity p_B (compare the profiles at $\beta_{Y,S} = 0.01$) with respect to the simple model in *Stage 1* (Fig. 4.2) when the recovery of B is not included ($\beta_{Y,S} = 0$).

◆ **Step 2.10.** Storage of information.

From Fig. 4.3 information related to the design target for this system can be extracted. Say, for example, there is interest in obtaining the maximum yield that the CSTR can achieve, this is approximately at $p_B = 0.58$, corresponding to a conversion $x_A = 0.76$. This will be considered as the *design target*. This information together with the analysis carried out in this stage will be used in the subsequent stage.

4.1.1.3 Stage 3. Verification.

The isothermal consecutive reaction $A \rightarrow B \rightarrow C$ could be considered to represent,



◆ **Step 3.1.** Flowsheet set up.

The flowsheet consisting of a *mixer* tank, a CSTR ($V_r = 5 \text{ m}^3$ and $T_r = 300 \text{ K}$) and a sharp splitter (see Fig. 4.1) is considered also for this verification step. The simulation tool for this example was ICASSim (Gani 2002).

◆ **Step 3.2.** Generated knowledge from previous stages.

From *Stage 1* it has been obtained the sensitivity of the process, mainly, to the Da number and the recovery of the limiting reactant A ($\alpha_{Y,S}$), and from *Stage 2* the effect of the reaction rate ratio (k_2^*) and the recovery of product B ($\beta_{Y,S}$), as well as the analysis of the attainable region. The range where the maximum values of p_B with respect to the Da number are found at $0.1 < Da < 10$ with $0.1 < \alpha_{Y,S} < 0.9$. The conditions defining the design are: $\alpha_{Y,S} = 0.5$, $\beta_{Y,S} = 0.01$ and $k_2^* = 0.1$.

◆ **Step 3.3. and 3.4.** Simulations and Verification of Results.

The verification of the “snowball” effect was carried by means of rigorous simulations. In Fig. 4.6 the reactor outlet flowrate S is plotted as a function of

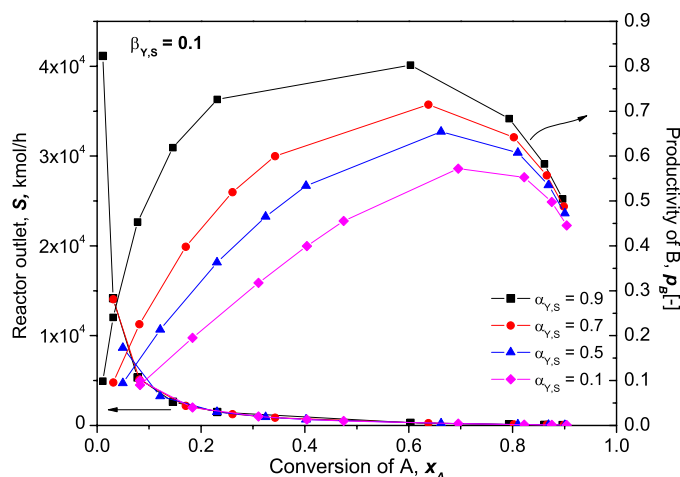


Figure 4.6: Reactor outlet S and productivity of B as function of x_A .

the conversion of component A together with the productivity of B (p_B), for different recovery factors $\alpha_{Y,S}$. Figure 4.6 verifies the results obtained in *Stage 2* in Fig. 4.5. As it has previously been established (steps [1.4.2], [2.8]), the increase in the reactant recycle improves the value of p_B but it also increases the “snowball” effect likelihood, especially at low conversion values. The later can also be verified through Eq. (4.3). As $\alpha_{Y,S} \rightarrow 1$ with a x_A relatively low the reactor outlet increases considerably. On the contrary, operating for high conversion values implies either low feeds to the system or the use of large equipments. Therefore a tradeoff might arise and an appropriate criteria should be established through the formulation and solution of an optimisation

problem.

Table 4.1 provides a comparison of the simulation results obtained by solving the *Stage 2* model through MoT and by using the simulation models available in ICASSim. It is observed that the results obtained by the two models are comparable and in agreement with respect to the design-process variables analysed.

Table 4.1: ICASSim and MoT results for a Consecutive Reaction RSR system.

F_A	Da	ICASSim		MoT	
		x_A	$p_B, [-]$	x_A	$p_B, [-]$
4511.60	0.10	0.04987	0.09450	0.04985	0.09447
1804.64	0.25	0.12308	0.21612	0.12296	0.21594
902.32	0.50	0.23599	0.37031	0.23558	0.36982
601.55	0.75	0.33319	0.47583	0.33248	0.47514
451.16	1.00	0.41403	0.54659	0.41308	0.54584
180.46	2.50	0.67680	0.66631	0.67562	0.66624
90.23	5.00	0.81966	0.61744	0.81889	0.61812
60.15	7.50	0.87542	0.54602	0.87492	0.54689
45.12	10.0	0.90492	0.48441	0.90457	0.48528

$F_A [=]$ kmol/h, $k_2^* = 0.1$, $\alpha_{Y,S} = 0.5$, $\beta_{Y,S} = 0.01$

◆ **Step 3.5.** Storage of information.

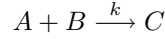
From Fig. 4.3 the location for the ‘optimal’ design was obtained, which was then combined with Fig. 4.5 (and/or Table 4.1 for *Stage 2* model results) to derive the corresponding operating policy. That is, a set of specifications for the process-control variables ($x_A = 0.76$, $p_B = 0.58$) corresponding to a recovery of component A of $\alpha_{Y,S} = 0.5$, recovery of B of $\beta_{Y,S} = 0.01$, kinetic ratio $k_2^* = 0.1$ and $Da = 3.61$ ($F_A = 125$ kmol/h). Based on this, an operation that achieves a maximum productivity (design target) of B is ensured.

4.1.1.4 Case Summary.

The analysis of this case study reveals the interactions between the design variables (Da , $\alpha_{Y,S}$, k_2^* , etc.) and process behaviour (with respect to x_A , p_B) when a given design target is searched for, as in this case the productivity of B, p_B . Large recycle streams, which imply high recoveries enhance the productivity of B but increase the energy and capital costs of the separation section (Luyben 1993b). Likewise, keeping kinetic considerations in mind, it was demonstrated that low kinetic ratios favour the productivity of B, due to a slower rate of reaction to produce C. This condition can be achieved, for example, by adjusting the reactor temperature. A low Da number might also favour such a situation. The later can be achieved either by using small reactor volumes or by controlling the fresh feed flowrate of reactant A. Nagiev (1964) makes a theoretical discussion from the design viewpoint on this kind of systems applied, mainly, to oil and gas processes, highlighting the potential of recycling methods for the development of refined and economically-efficient technological processes.

4.1.2 Second Order Reactions (Case Study 2)

In this example a second order reaction of the type,



where the rate of reaction is assumed to be of first order with respect to the concentrations of each component and second order overall is considered. The reaction rate is given by,

$$r_A = -kC_A C_B$$

The reaction also takes place in the presence of a solvent D.

4.1.2.1 Stage 1. Model-based analysis by Simple Models.

◆ **Step 1.1.** Process flowsheet simplification.

This step has been covered in assumptions $\mathcal{A}_1 - \mathcal{A}_2$ (see page 47).

◆ **Step 1.2.** Reaction Analysis.

The analysis starts by assuming a complete recovery of components A and B from the separation section, such that $\alpha_{Y,S} = \beta_{Y,S} = 1$. Also, it is assumed that all of product C is removed from the system ($\gamma_{P,S} = 1$) and that there is no purge ($\lambda = 0$) from the RSR system.

◆ **Step 1.3.** Thermal considerations.

This step has been covered in assumption \mathcal{A}_0 (see page 47).

◆ **Step 1.4.** Model Development.

Given the assumptions in step [1.2], the model describing the system is represented by Eq. (4.8).

$$Da - \frac{\left[\frac{(1 - x_A)}{x_A + v_B(y_B - 1) + v_C + v_D y_D} \right]^2}{\frac{(1 - x_A)}{x_A} v_B (y_B - 1)} = 0 \quad (4.8)$$

where

$$Da = \frac{kV_r \rho_m^2}{F_A} \quad (4.9)$$

is the plant Da number of second order.

◆ **Step 1.4.1.** Model solution.

Equation (4.8) is a non-linear algebraic equation in terms of conversion of A (x_A) as the unknown variable. The set of design variables, are therefore, the Damköhler number (Da) and the recycle flowrate (y_B). While, the recycle of solvent D (y_D) is considered as a parameter of the system as well as as the

dimensionless molar densities v_C and v_D .

◆ **Step 1.4.2.** Identification of limiting values and operational windows.

Given the nature of this reactive system with respect to the non-linearity in the reaction rate combined with the effect of the recycle, the possibility of encountering multiple steady-states is investigated. In this respect, the existence of bifurcation points, which relate the locus where only one solution can be obtained and also establishes the limiting operation conditions was examined. In this way, for the simplified model the critical Damköhler number, Da^{cr} , and critical conversion, x_A^{cr} , respectively are:

$$Da^{cr} = \frac{4[v_B(y_B - 1) + v_C + v_D y_D]}{v_B(y_B - 1)} \quad (4.10)$$

$$x_A^{cr} = \frac{1}{1 + v_B(y_B - 1) + v_C + v_D y_D} \quad (4.11)$$

In addition, by re-arranging Eq. (4.8), a quadratic expression results with respect to x_A , which leads also to the following condition:

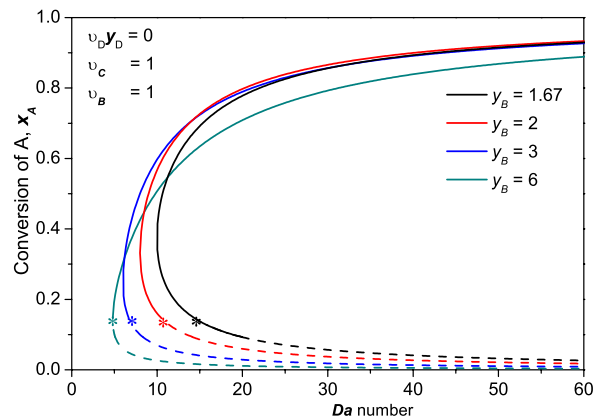
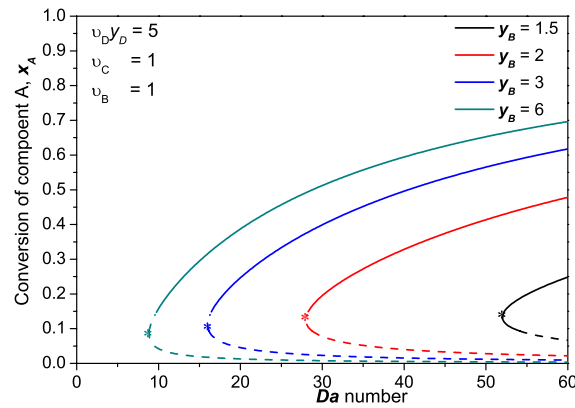
$$y_B^m > \frac{v_B(Da - 4) + 4(v_C + v_D y_D)}{v_B(Da - 4)} \quad (4.12)$$

Thus, non-equality (4.12) establishes the condition for the recycle of B where state-multiplicity (y_B^m) can be found at a given recycle value y_D and Damköhler number, Da .

Having obtained the limiting conditions (Da^{cr} , x_A^{cr} , y_B^m), Fig. 4.7 is drawn for different values of the recycle of component B. It is observed that an *output* multiplicity is found for this RSR system. That is, for one value of the Da number, two different conversions x_A can be obtained. As Bildea et al. (2000) pointed out, in general large B (y_B) and small D (y_D) recycles enlarge the region where feasible solutions exist. From non-linear analysis theory, it is expected that one stable and one unstable steady state can emerge from the fold (critical) point. The lower branch (low conversion values (dotted line in Fig. 4.7)) is unstable as an eigenvalue analysis demonstrated.

◆ **Step 1.9.** Storage of information.

The critical conditions for this reactive system have been identified, in terms of a critical Da number (Da^{cr}) and a critical conversion x_A^{cr} of A, as well as the condition where state-multiplicity can be obtained with respect to the recycle of component B (y_B^m). On the other hand, an *output* multiplicity has been found due to the nonlinearity in the reaction scheme when $Da > Da^{cr}$. Also, when $Da < 0$, the conversion is negative and has no physical significance; whereas $0 < Da < Da^{cr}$, the solutions for the conversion are complex.

(a) $v_D y_D = 0$ (* = critical point)(b) $v_D y_D = 5$ (* = critical point)Figure 4.7: Conversion of component A as function of Da number.

4.1.2.2 Stage 2. Model-based analysis by Detailed Models.

◆ Step 2.1. Multiple reactions analysis.

In this case study there is only one forward reaction, therefore an *Attainable Region* analysis is not applicable.

◆ Step 2.2. Driving force diagram.

As in Case Study 1, it is assumed that the separation takes place in a perfect separator and that separation of the reaction mixture is assumed to have a negligible effect.

◆ Step 2.3. Assumptions removal.

The detailed model from this stage should now allow the recovery of both components A and B in the recycle stream to be represented as design variables.

The recycle of C, however, is not considered since no effect on the reaction is expected.

◆ **Step 2.4. and 2.5.** Important phenomena and Process equipments.

No additional phenomena is included in the model to be developed and the separation section is again modelled as a sharp splitter.

◆ **Step 2.6.** Model Development.

The delumped model for *Stage 2* is given by,

$$\left(\frac{kV_r \rho_m^2}{F_A}\right) - \sigma m_A \cdot \left\{ \frac{\left\langle s_A + \left[\frac{f_B(\sigma - \alpha_{Y,S}(1 - x_A)) - \sigma x_A}{(\sigma - \beta_{Y,S})(\sigma - \alpha_{Y,S}(1 - x_A))} \right] v_B + m_A v_C + v_D y_D \right\rangle^2}{\left[m_B - \frac{\sigma x_A}{(\sigma - \alpha_{Y,S}(1 - x_A))} \right] s_A} \right\} = 0 \quad (4.13)$$

where

$$\begin{aligned} m_A &= \frac{x_A}{\sigma - \alpha_{Y,S}(1 - x_A)} \\ s_A &= \frac{(1 - x_A)}{\sigma - \alpha_{Y,S}(1 - x_A)} \\ m_B &= \sigma \cdot \frac{f_B [\sigma - \alpha_{Y,S}(1 - x_A)] - \beta_{Y,S} x_A}{(\sigma - \beta_{Y,S})(\sigma - \alpha_{Y,S}(1 - x_A))} \end{aligned}$$

For the sake of simplicity, the *Da* number definition (see Eq. (4.9)) will be retained.

◆ **Step 2.7.** Model Solution.

Equation (4.13) is a non-linear algebraic equation (NLAE) with respect to the conversion of A (x_A) as unknown variable and, where the main design variables are: *Da* number, inlet flow ratio (f_B), purge factor (σ), recovery factors ($\alpha_{Y,S}$, $\beta_{Y,S}$) and the recycle flowrate of solvent D (y_D).

◆ **Step 2.8.** Model Analysis.

Rearranging Eq. (4.13), the following cubic polynomial in X is obtained:

$$0 = X^3 + a_1 X^2 + a_2 X + a_3 \quad (4.14)$$

where $X = 1 - x_A$, and with coefficients

$$\begin{aligned} a_1 &= [\alpha_{Y,S} u - \sigma t] Da + (p - 2q) \sigma p / (\alpha_{Y,S} t Da - \sigma p^2) \\ a_2 &= [\sigma(2pq - uDa - q^2)] / (\alpha_{Y,S} t Da - \sigma p^2) \\ a_3 &= \sigma q^2 / (\alpha_{Y,S} t Da - \sigma p^2) \end{aligned}$$

with

$$\begin{aligned} p &= \sigma - \alpha_{Y,S}(f_B + y_D(\sigma - \beta_{Y,S})) \\ q &= \sigma(f_B + y_D(\sigma - \beta_{Y,S})) - \beta_{Y,S} \\ t &= (\sigma - \beta_{Y,S})(\sigma - \alpha_{Y,S}f_B) \\ u &= \sigma(\sigma - \beta_{Y,S})(f_B - 1) \end{aligned}$$

Using the model represented by Eq. (4.14), values of x_A are calculated for different sets of values of design variables. In Fig. 4.8 the conversion of component A, (x_A), and the recycle of component B (y_B), are plotted as function of the feed ratio of B (f_B). It is observed that up to three different values of f_B satisfy a given condition of y_B . Consequently, three resulting conversion values can be obtained. This behaviour is known as *input multiplicity*, i.e., different input values reproducing the same output. It is usually desired to operate in a high conversion region, which implies the use of feed ratios to be close to a stoichiometric feed ($f_B \rightarrow 1$). Nevertheless, it is also in this region where small changes on f_B lead to high sensitivity in the process, given that the recycle of component B increases significantly.

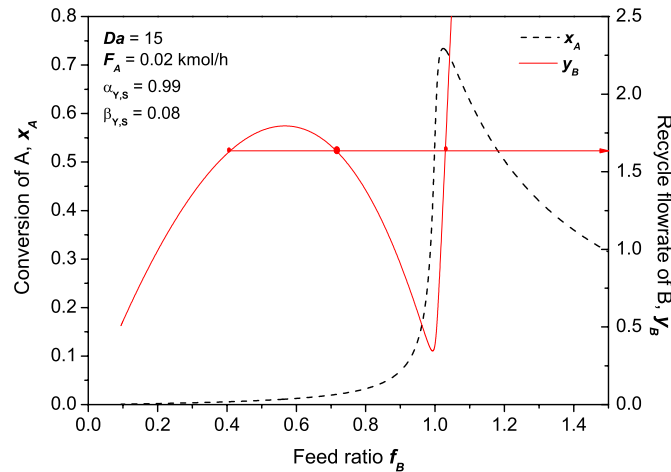


Figure 4.8: Conversion of A and recycle flowrate of B as function of f_B .

◆ **Step 2.9.** Results agreement.

Stage 1 model represents an operation extreme, i.e., complete recovery of unreacted A and B, and a stoichiometric feed ratio ($f_B = 1$). For comparison purposes, from Fig. 4.7(a) a design condition with $Da = 15$ and $y_B = 1.67$ is selected, and the corresponding conversion value obtained $x_A = 0.7$. Now, from Fig. 4.8 it can be observed that, in general, as $f_B \rightarrow 1$, higher conversions are achieved for a specific y_B value (e.g., $y_B = 1.67$). Therefore, given the above design condition, at $f_B = 1.03$ (see Fig. 4.8), the corresponding conversion value $x_A = 0.73$. In this regard, it is considered that the results between

Stages 1 and 2 are in good agreement. Further analysis is carried in Stage 3.

◆ **Step 2.10.** Storage of information.

An *input* multiplicity with respect to feed ratio f_B has been found by using the *Stage 2* model. High process sensitivity, i.e., a “snowball” effect likelihood is observed (see Fig. 4.8) as $f_B \rightarrow 1$. A design condition (see step [2.9]) has also been determined by combining the results from *Stages 1 and 2*, although it is a region of high sensitivity, but it is where the higher conversion values can be obtained.

4.1.2.3 *Stage 3. Verification.*

◆ **Step 3.1.** Flowsheet set up.

The same flowsheet as given in Fig. 4.1 is used again for rigorous simulations with ICASSim.

◆ **Step 3.2.** Generated knowledge from previous stages.

Two issues are verified through rigorous process simulation. The first is the possibility to reproduce the *output* or *input* multiplicity described by the *Stage 1 and 2* models. The second objective is to analyse the sensitivity of the process to the feed inlet ratio, f_B in order to verify the input multiplicity from the detailed model.

◆ **Step 3.3.** Simulation results analysis.

▷ *State-multiplicity analysis.* It was possible to obtain only the higher branch

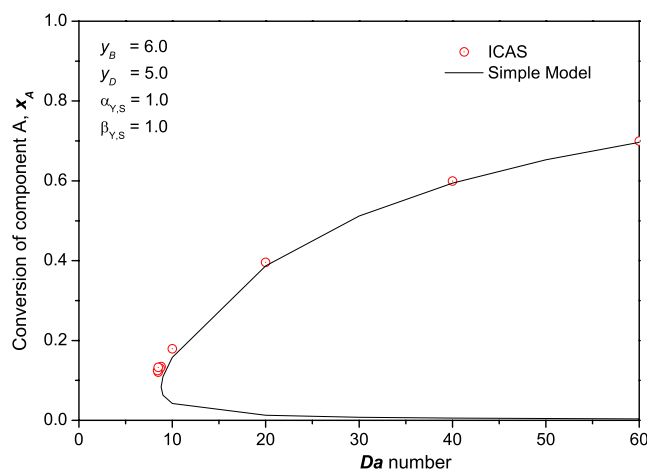


Figure 4.9: Conversion of A as function of Da number. Results comparison between *Stage 1* and *3* models.

of the x_A - Da curve (see Fig. 4.9) for a given set of specifications when using

rigorous process simulation. The procedure followed was: the Da number is fixed for a given F_A , while keeping V_r and k constant. Then, varying the feed of component B simulations were performed until a desired recycle value of y_B was found. The simulation exercise suggests that in the conversion range of interest ($0 < x_A \leq 1$) only one solution exists; this was also verified through a polynomial solver in MATLAB[®] for Eq. (4.14).

With the aim of finding the lower branch of the x_A - Da curve, it was necessary to change the set of specifications for the rigorous process simulation. Here, the key design variable is the feed ratio (f_B). It is important to remark that if $f_B < 1$, then lower conversions are found together with unrealistic values of feed flowrates. Table 4.2 highlights the simulation results obtained with ICASSim under the conditions discussed above.

Table 4.2: Simulation results from ICASSim at *Stage 3*.

Da	$k,$ (kmol/m ³) ² /hr	$F_A,$ kmol/hr	f_B	x_A	y_B
76.33	18.750	100	1.00000	0.82408	0.10438
	18.750	100	0.09098	0.00097	0.10438
20	4.913	100	1.00000	0.64232	0.27135
	9.826×10^{-4}	0.02	0.97980	0.27459	0.27136
15	3.685	100	1.03035	0.73104	1.66652
	3.685	100	0.70000	0.01955	1.66656
	3.685	100	0.42625	0.00641	1.66657
	7.369×10^{-4}	0.02	1.03035	0.73104	1.66652
	7.369×10^{-4}	0.02	0.70000	0.01955	1.66656
	7.369×10^{-4}	0.02	0.42625	0.00641	1.66657

Specifications: $\alpha_{Y,S} = 0.99$, $\beta_{Y,S} = 0.98$, $\lambda = 0$
 $V_r = 5 \text{ m}^3$, $\rho_m = 9.0232 \text{ kmol/m}^3$

The results given in Table 4.2 can be understood in light of the lower conversions that need to be achieved at low feed ratios, which makes component B the limiting reactant in the process. On the contrary, as $f_B \rightarrow 1$, higher conversions result. From Table 4.2 it can also be seen that a single set of specifications, namely, $[k, F_A, f_B]^T$ cannot lead to an *output* multiplicity, in comparison to *Stage 1* model (for one Da number value, two x_A values are obtained).

▷ *Inlet feed ratio analysis.* Figure 4.10 highlights the results obtained with ICASSim for $Da = 15$ and $F_A = 0.02 \text{ kmol/hr}$. These results verify the behavior predicted by the *Stage 2* detailed model (see Fig. 4.8): high feed flowrates of B correspond to higher conversions of A, although the recycle stream increases in such a way that the system may become unstable (resulting in a “snowball” effect). Conversely, decreasing the feed flowrate of B, lower conversions are obtained.

◆ **Step 3.4.** Simulation results agreement.

As it has been shown, the results from the modelling stages are in agreement

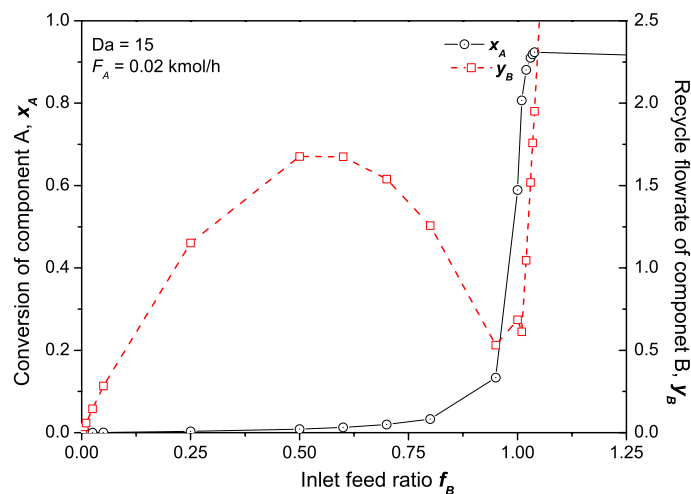


Figure 4.10: Simulation results for Conversion of A and Recycle flowrate of B as function of f_B .

with respect to the results in the verification stage regarding the *output* and *input* multiplicity analysis (see Fig. 4.7 for *Stage 1* model and Fig. 4.9 for *Stage 3*), as well as with respect to the feed ratio analysis (see Fig. 4.8 in *Stage 2* model and Table 4.2 and Fig.4.10 at *Stage 3*).

◆ **Step 3.5.** Storage of information.

A thorough analysis has been carried out for this reactive system. Critical conditions were derived with respect to the main design variables (i.e., Da^{cr} , y_B^m) as well as process variables (x_A^{cr}). Also, the incorporation of some other effects was carried out (e.g. f_B , $\beta_{Y,S}$), that led to find different process behaviour (from *output* multiplicity in *Stage 1* to an *input* multiplicity in *Stage 2* model). The rigorous simulations performed in this stage confirmed such insights.

4.1.2.4 Case Summary.

As Bildea et al. (2000) and Pushpavanam and Kienle (2001) pointed out, the behaviour of integrated plants differ from the stand-alone units when they are interconnected. Consequently, the design and control must be carried out systematically in order to achieve a set of design and control objectives.

This example highlights the differences in the process behaviour under various effects considered, i.e., reactants recovery and reactants feed ratio.

Simple models can be derived and used to identify the limiting or extreme conditions in the operation of a process. Thus, in *Stage 1* a complete recovery of unreacted A and B as well as solvent D was assumed. This resulted in a

model where an *output* multiplicity was observed. In addition, the corresponding critical expressions for the design-process variables (Da^{cr} , x_A^{cr}) were derived, relating the limiting conditions of operation where only one theoretical state can be found. However, in the verification stage (*Stage 3*), through rigorous simulations only one of such state could be obtained, suggesting the possibility that the second state (lower conversions) corresponds to an unstable state as Bildea et al. (2000) also pointed out. Now, regarding the control implications, the set of specifications employed for the design in *Stage 1* model, may correspond to a control structure where the feed of A is flow-controlled (see Eq. (4.9)), the recycles of B and D are on flow-control as well (y_B and y_D are fixed); the reactant B can be fed into the separation section in order to keep constant inventory. This structure is the same that Bildea et al. (2000) used.

On the other hand, the reason to develop more detailed models (Smith and Pantelides 1995, Luyben, Tyreus and Luyben 1996, Skogestad 2004) comes from the need to represent the behaviour of a process in a more realistic manner and where the most important phenomena involved within can be accounted for. In this respect, *Stage 2* model allows to study the effect of a variable recovery of unreacted A and B as well as the feed inlet ratio f_B . An *input multiplicity* was obtained with respect to the recycle of B (y_B) for different feed ratios, which is considered an important result since it gives a range ($f_B \rightarrow 1$) where a “snowball” effect can be observed. Also, it can be seen from *Stage 2* model that, if both reactants are specified the system cannot be solved due to an indetermination in the model equations. Therefore, when dealing with recycle systems, the ratio of reactants in the feed must reflect the reaction stoichiometry. On the other hand, it is important to mention that *Stage 2* model could only obtain the higher branch of the x_A - Da curve in *Stage 1* model (for a given set of specifications), such behavior was confirmed by the simulations performed in *Stage 3*. The verification step also confirmed the results from *Stage 2* with respect to the *input* multiplicity. Regarding the control implications, from the above discussion it follows that, a control structure where both reactants are in flow control results in an unfeasible performance and, on the other hand, that it is important to have a good control in the feed ratio in order to prevent a “snowball” effect.

Finally, Luyben (1994) and Luyben and Luyben (1997) did not find neither *output* nor *input* multiplicities in their studies. Bildea et al. (2000) stress that in Luyben and Luyben (1997) difficulties in control were not encountered as their design involved a $Da = 29.7 > Da^{cr} = 10.66$, which is far from the bifurcation point which has high sensitivity. On the other hand, in Luyben’s (1994) study for constant recycle flowrates, the solution procedure is somewhat similar to the one presented in this work. That is, for one set of operating conditions ($Da, y_B, \alpha_{Y,S}, \beta_{Y,S}, f_B$) only one solution can be found. This corresponds to a control structure where throughput changes are achieved by changing the set-point of the reactor temperature controller and reactor holdup is held constant.

4.2 Ethylbenzene Production (Case Study 3)

The Ethylbenzene production process has been selected as an illustrative example that highlights the applicability of the model-based Methodology for integrated design-analysis-control to more complex processes that incorporate not only real components but also typical process equipments such as flash drums and distillation columns. This case study will focus on addressing the issues related to the design perspective of this process.

4.2.1 Process Description

Ethylbenzene ($C_6H_5CH_2CH_3$) is an alkylaromatic compound, almost exclusively used (99% of its production) as an intermediate for the manufacture of styrene monomer, one of the most important bulk chemicals (Cavani and Trifirò 1995).

Nowadays the Friedel-Crafts reaction (Olah 1964) is the dominant source of Ethylbenzene from the two most commonly used routes either in the liquid or in the vapour phase.

The process is carried out over an alkaline earth metal halide catalyst which is usually $AlCl_3$ and an acid promoter (Chen 1997). The reactor is operated at atmospheric pressure and the raw materials are Benzene and Ethylene (see Fig. 4.11). The alkylation reaction is exothermic and it occurs between gaseous

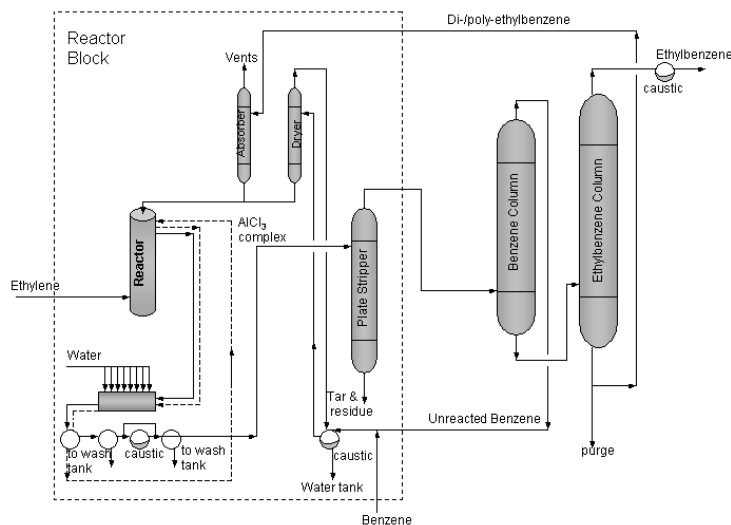


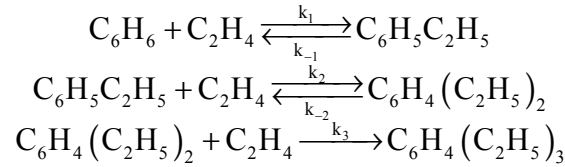
Figure 4.11: Industrial Ethylbenzene production flowsheet (Smith 1996).

Ethylene and liquid Benzene and its derivatives. Rates of reaction are governed by first-order kinetics in liquid-phase. Ethylene/Benzene molar ratios are adjusted to obtain an optimum yield of Ethylbenzene. As the Ethylene/Benzene

ratio increases, further alkylation of Ethylbenzene occurs, leading to polyalkylbenzenes.

For all reversible secondary reactions, deliberately feeding byproduct to the reactor inhibits their formation at the source by shifting the equilibrium of the secondary reactions. This is achieved in practice by separating and recycling the byproduct, rather than separating and disposing it directly. These byproducts are polyethylbenzenes (di-Ethylbenzene, tri-Ethylbenzene, etc.) which are formed through reversible sequential reactions of Ethylbenzene.

The reaction scheme in the process considered is:



The reactions occur between gaseous Ethylene (E) and liquid Benzene (B) at its boiling point and its derivatives also as liquid to obtain Ethylbenzene (EB) and higher order alkylated compounds (di-Ethylbenzene, DEB), from which only tri-Ethylbenzene (TEB) will be taken into account.

The governing reaction rates for the above reacting system are given by (Smith 1996):

$$\begin{aligned} -R_B &= k_1 C_B - k_{-1} C_{EB} \\ -R_{EB} &= (k_{-1} + k_2) C_{EB} - (k_1 C_B + k_{-2} C_{DEB}) \\ -R_{DEB} &= (k_{-2} + k_3) C_{DEB} - k_2 C_{DEB} \\ -R_{TEB} &= -k_3 C_{DEB} \end{aligned}$$

This is the starting information for application of the model-based Methodology.

4.2.1.1 Stage 1. Model-based analysis by Simple Models.

◆ Step 1.1. Flowsheet Simplification.

The three main operations identified in the process are: mixing, reaction and separation, represented by a simplified flowsheet as shown in Fig. 4.12. Stream subindices are referred to this figure.

◆ Step 1.2. Reaction Analysis.

The first scenario to be analysed is based on the following assumptions:

- \mathcal{A}_0 . Steady-state conditions using a CSTR,
- \mathcal{A}_1 . Complete recovery of Ethylene recycled back to the reactor ($\varepsilon_{Y,S} = 1$),
- \mathcal{A}_2 . No recycle of *EB*, *DEB* and *TEB* ($\alpha_{Y,S} = 0 = \delta_{Y,S} = \tau_{Y,S}$, respectively),
- \mathcal{A}_3 . No purge considered ($\lambda = 0$),
- \mathcal{A}_4 . Equimolar feed flowrate of reactants ($F_{B,F} = F_{E,F}$).

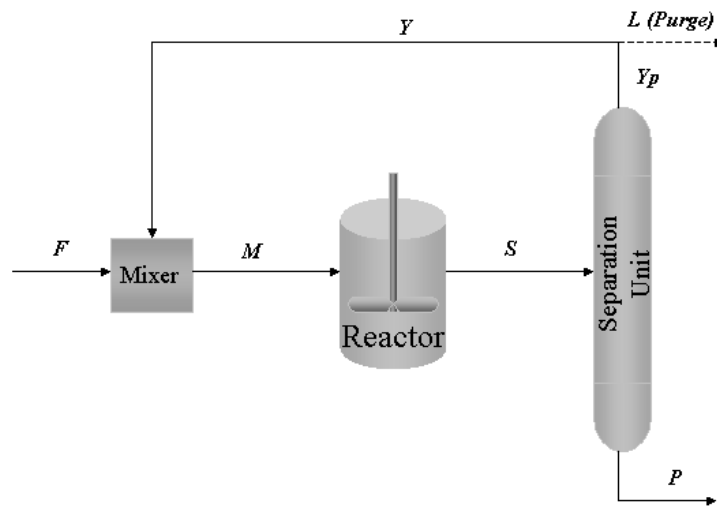


Figure 4.12: Simplified Flowsheet for the Ethylbenzene production.

The above assumptions are based on the idea that, even though the recycle of the secondary products (*DEB*, *TEB*) inhibits their production, it is known that the main effect on the formation of *EB* will come via the principal reaction. Therefore, the most important limiting conditions, in principle, can be found through the scenario defined above.

◆ **Step 1.3.** Thermal Effects.

The reactions will take place in an isothermal continuous stirred tank reactor (CSTR), therefore, the reaction rate constants assume a constant value: $k_1 = 0.4 \text{ h}^{-1} = k_{-1} = k_2 = k_{-2}$ and $k_3 = 0.02 \text{ h}^{-1}$ (Kokossis and Floudas 1991, Smith and Pantelides 1995). With these assumptions only mass balance effects need to be studied.

◆ **Step 1.4.** Model Development.

The mass balance equations are written for component i with respect the extent of reaction (ξ_k), which in the case of multiple reactions can be defined as:

$$F_{i,S} = F_{i,M} + \sum_{k=1}^{NR} \nu_{ik} \xi_k, \quad i = 1, \dots, NC \quad (4.15)$$

where subindex k refers to each reaction and $\nu_{i,k}$ is the stoichiometric coefficient of component i in the k th reaction.

Based on this, the model equations on a dimensionless basis representing the

entire flowsheet are:

$$\xi_{v,1} = \frac{\Omega}{(1 - \beta_{Y,S})} \{1 - \xi_{v,1}(1 + K_1^*(1 - \beta_{Y,S})) + K_1^*\xi_{v,2}(1 - \beta_{Y,S})\} \quad (4.16)$$

$$\xi_{v,2} = \xi_{v,1} + \Omega \left\{ \xi_{v,1} \left(K_1^* + K_2 + \frac{1}{(1 - \beta_{Y,S})} \right) - \xi_{v,2}(K_1^* + K_2 + K_2^*) + K_2^*\xi_{v,3} - \frac{1}{(1 - \beta_{Y,S})} \right\} \quad (4.17)$$

$$\xi_{v,3} = \xi_{v,2} + \Omega \{ \xi_{v,2}(K_2 + K_2^* + K_3) - K_2\xi_{v,1} - \xi_{v,3}(K_2^* + K_3) \} \quad (4.18)$$

where

$$\begin{aligned} K_k &= k_k/k_1; & K_k^* &= k_{-k}/k_1 \\ \Omega &= \frac{Da}{1 + y_E + (1 - \xi_{v,1})/(1 - \beta_{Y,S}) - (\xi_{v,2} + \xi_{v,3})} \end{aligned}$$

where the inlet flowrate of Benzene ($F_{B,F}$) and the kinetic constant k_1 have been taken as variables of reference; $\xi_{v,k}$ corresponds to the dimensionless extent of reaction. The details of the derivation of Eqs. (4.16)-(4.18) can be found in Appendix C. Once again, one of the most important design variables that appear is the Damköhler number, Da , which in this case is of first order in accordance with the order of the reactions in the system. The corresponding definition is:

$$Da = \frac{k_1 V_r C_{B,F}}{F_{B,F}} \quad (4.19)$$

▷ **Step 1.4.1A. Model Solution.**

Equations (4.16)–(4.18) represent a set of non-linear algebraic equations in terms of the dimensionless extent of reaction $\xi_{v,k}$, which can also be expressed in the following compact form at steady-state,

$$\mathbf{0} = \mathbf{f}[\xi_{\mathbf{v}}, \mathbf{u}, \mathbf{p}] \quad (4.20)$$

where

$$\mathbf{u} = [Da, \beta_{Y,S}, y_E]^T, \quad \mathbf{p} = [K_1^*, K_2, K_2^*, K_3]^T$$

vector \mathbf{u} contains the set of design variables, the parameters such as kinetic rate constants of the system, which remain constant in the following analysis ($K_1 = K_1^* = K_2 = K_2^* = 1$, $K_3 = 0.05$), are contained in vector \mathbf{p} . Once vector \mathbf{u} is specified the degrees of freedom of the system (for the design problem) are satisfied and Eqs. (4.20) can be solved for $\xi_{\mathbf{v}}$.

▷ **Step 1.4.1B. Model Analysis.**

The calculated profiles for the conversion of Benzene as a function of Da number at different recoveries of Benzene ($\beta_{Y,S}$) at $y_E = 2$, thereby, vector \mathbf{u} is defined, are shown in Fig. 4.13. As it has been demonstrated in the

previous case studies, the recycle enhances the conversion, a behaviour that is also verified with this example. It can be noted that the conversion of Benzene increases rapidly as more Benzene is recovered until approximately $Da = 5$. After this point, it can be assumed that the reaction reaches equilibrium.

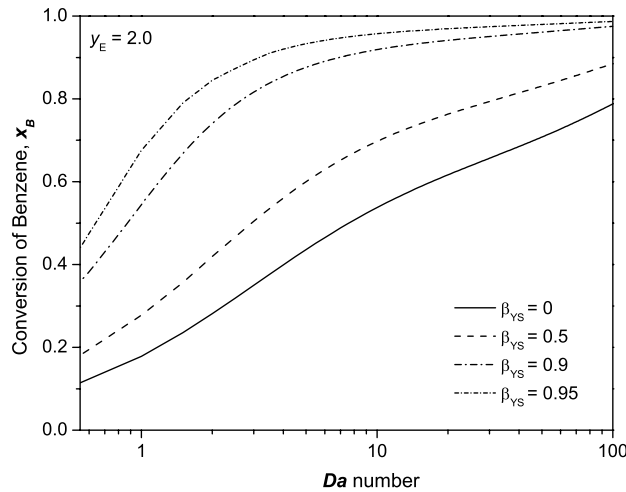


Figure 4.13: Conversion of Benzene as function of Da number.

In Fig. 4.14 it can be observed that higher $\beta_{y,s}$ values also favour the yield of EB (p_{EB}) and the maxima for this variable can be obtained within a range of $1 < Da < 10$. The behaviour displayed in Figs. 4.13-4.14 is not surprising since

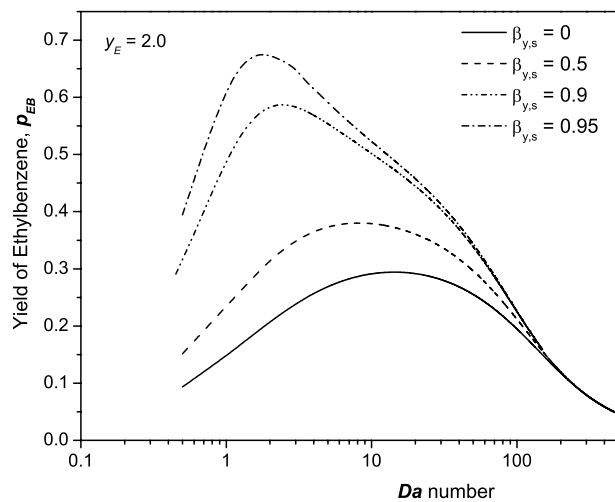


Figure 4.14: Yield of Ethylbenzene as function of Da number.

the reaction scheme follows a consecutive reaction system pattern (also seen in Case Study 1), even though this case study has one additional reaction. Therefore, the recycle of unreacted reactants will favour the production of *EB* until a point where the secondary reactions (production of *DEB* and *TEB*) become important and the yield of *EB* will start to decrease. The above trends are somewhat similar to Case Study 1 for a consecutive reaction system presented previously.

◆ **Step 1.4.2.** Identification of limiting values.

Another effect that should be considered is the size of the recycle stream of Ethylene (y_E) because it might lead to operational constraints such as the “snowball” effect and/or reaction limitations (e.g., becoming a limiting reactant). As Fig. 4.15 shows, even though low values of y_E can achieve higher concentrations of *EB*, one should be careful about such considerations due to a limited range of operation expressed in terms of the *Da* number. For instance, small y_E flowrates can lead to a higher concentration of *EB* (top of Fig. 4.15) but, on the other hand, it can exhaust more rapidly the amount of *E* in the reaction (bottom of Fig. 4.15) if the *Da* number is increased, thereby, turning-off the operation.

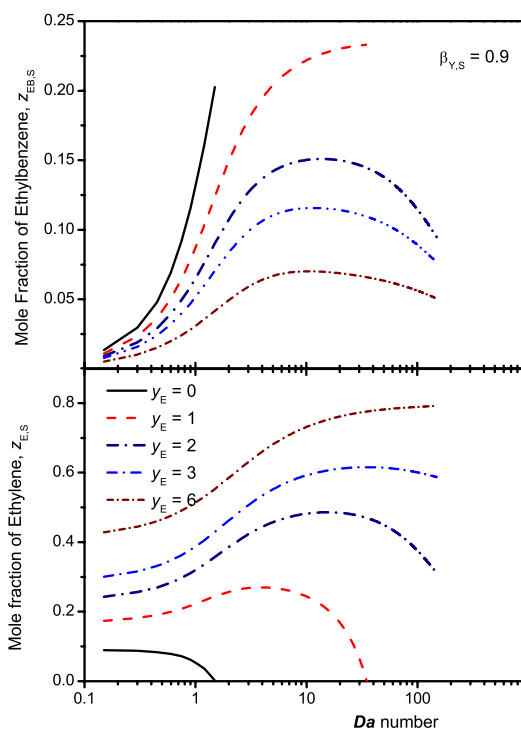


Figure 4.15: Mole fraction of E and EB as function of *Da* number.

In order to determine the condition where the Ethylene is exhausted in the reactor as a function of the Da number (denoted as Da^*) at a given recycle flowrate of E (y_E), the model equations (4.16)-(4.18) are rearranged for a mole fraction of Ethylene in the reactor $z_{E,S} = 0$. Based on this, Eq. (4.21) is obtained. The details in the derivation of this condition are given in Appendix C.

$$Da^* = \frac{[\xi_{v,1}^* + \xi_{v,2}^* - (1 + y_E)][(1 + y_E) + (1 - \xi_{v,1}^*)/(1 - \beta_{Y,S}) - (\xi_{v,2}^* + \xi_{v,3}^*)]}{K_3(\xi_{v,3}^* - \xi_{v,2}^*)} \quad (4.21)$$

thus, substituting Eq. (4.21) in Eqs. (4.16) to (4.18) yields

$$\xi_{v,1}^* = \Psi \{1 - \xi_{v,1}^*(K_1^*(1 - \beta_{Y,S}) + 1) + K_1^*\xi_{v,2}^*(1 - \beta_{Y,S})\} \quad (4.22)$$

$$\xi_{v,2}^* = \xi_{v,1}^* + \Psi \left\{ \xi_{v,1}^* \left(K_1^* + K_2 + \frac{1}{(1 - \beta_{Y,S})} \right) - \xi_{v,2}^*(K_1^* + K_2 + K_2^*) + K_2^*\xi_{v,3}^* - \frac{1}{(1 - \beta_{Y,S})} \right\} \quad (4.23)$$

$$\xi_{v,3}^* = \xi_{v,2}^* + \Psi \{ \xi_{v,2}^*(K_2 + K_2^* + K_3) - K_2\xi_{v,1}^* - \xi_{v,3}^*(K_2^* + K_3) \} \quad (4.24)$$

where

$$\Psi = \frac{[\xi_{v,1}^* + \xi_{v,2}^* - (1 + y_E)]}{K_3(1 - \beta_{Y,S})(\xi_{v,2}^* - \xi_{v,3}^*)}$$

◆ **Step 1.9.** Storage of information.

At this point of the Methodology operational windows with respect to the design variables (Da , $\beta_{Y,S}$, y_E) and process variables (x_B , p_{EB} , $z_{E,S}$) have been obtained (see Figs. 4.13–4.15), where the behaviour of the process can be assessed. The maximum values for the yield of EB can be found at $1 < Da < 10$ as well as by increasing $\beta_{Y,S}$. On the other hand, limiting operational conditions have been established, i.e., for a $z_{E,S}$ exhaustion (see Eqs. (4.22)–(4.24)), determining with that the limits of feasible operation of the process. There has not been found “snowball” effect, however, it is clear to see that (see Eqs. (4.16)–(4.17)) the process may show high sensitivity as $\beta_{Y,S} \rightarrow 1$. Also, steady-state multiplicities were not found in the range of design variables analysed, namely, y_E .

4.2.1.2 Stage 2. Model-based analysis by Detailed Models.

In this stage, an optimal design of the RSR system will be investigated in terms of a set of design “target” values, which will also be determined at this stage. Figure 4.16 shows the process flowsheet that will be used in *Stages 2* and *3* for modelling and simulation, respectively. The flowsheet consists of a CSTR tank, one isothermal flash drum whose main function is to recycle the unconverted Ethylene and two distillation columns. The first distillation column (Benzene column) serves to recover Benzene at the top and recycle it back to the reactor; the bottoms from the Benzene column are sent to the second distillation column

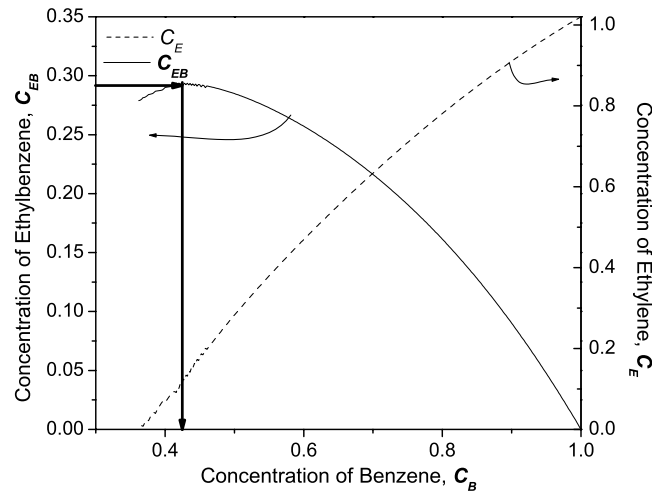


Figure 4.17: Candidate Attainable Region for the Ethylbenzene production.

compounds. This indicates that there will not exist problems to carry out the separation tasks by distillation. On the other hand, given that the design of the columns is already fixed (Smith and Pantelides 1995), no further modifications were carried out. However, if it was considered as an objective to improve the design of these units based on a given criteria, the *driving force* analysis (Bek-Pedersen 2003) will help to determine, e.g., the optimal feed tray location, reflux ratio, with respect to cost of operation.

◆ **Step 2.3.** Assumptions Removal.

The main assumption to be removed is that the separation section now it is modelled considering the actual process equipments, i.e., flash drum and distillation columns. Therefore, the recovery of byproducts (*DEB* and *TEB*) is also taken into account.

◆ **Step 2.4.** All-important phenomena consideration.

The main consideration at this point will be the addition of energy balances to the process model. The separation task in the distillation columns are modelled by determining the equilibrium conditions at the top and bottoms given P , T at each column. The flash drum is assumed to be isothermal. Ideal thermodynamics is considered significantly accurate for these purposes (Smith 1996).

◆ **Step 2.5.** Process Equipments.

It is clear from the process flowsheet given in Fig. 4.16 that the process model will increase in complexity once all the equipments are included.

◆ **Step 2.6.** Model Development.

The mass and energy balances for every unit operation are described (for a steady-state basis) below:

► Mixer.

Component mass balance for the Mixer:

$$x_{i,1}F_1 + y_{i,2}F_2 + y_{i,7}F_7 + x_{i,9}F_9 + x_{i,13}F_{13} - x_{i,3}F_3 = 0, \quad i = 1, \dots, NC \quad (4.27)$$

Note that only *B* and *E* are fed to the system. The corresponding energy balance is given by,

$$\sum_{j=1,2,7,9,13} F_j \left(\sum_{i=1}^{NC} x_{i,j} Cp_i \right) (T_j - T_3) = 0 \quad (4.28)$$

► Reactor.

Component mass balance:

$$x_{i,3}F_3 - z_{i,4}F_4 + R_k V_r = 0 \quad i = 1, \dots, NC \quad (4.29)$$

and the Energy Balance

$$F_4 \left(\sum_{i=1}^{NC} z_{i,4} Cp_i \right) (T_3 - T_4) - \sum_{k=1}^{NR} \Delta H_{r,k} R_k V_r - \dot{Q}_r = 0 \quad (4.30)$$

where

$$\Delta H_{r,k} = \sum_{i=1}^{NC} \nu_{i,k} Cp_i (T_4 - T_{ref}) + \Delta H_{f,i,k}^{\circ}$$

the heat exchanged through the jacket of the reactor is modelled as

$$\dot{Q}_r = m_{cw,r} Cp_{cw} (T_{cw,out} - T_{cw,in}) \quad (4.31)$$

$$\dot{Q}_r = UA_r \left(\frac{\Delta T_1 - \Delta T_2}{\ln(\Delta T_1 / \Delta T_2)} \right) \quad (4.32)$$

$$\Delta T_1 = T_4 - T_{cw,in}; \quad \Delta T_2 = T_4 - T_{cw,out} \quad (4.33)$$

► Purge 1 process model.

Total mass balance,

$$F_4 = F_5 + F_6 \quad (4.34)$$

with purge fraction defined as $\sigma_1 = F_6/F_4$. Note that the concentrations and temperatures on streams 4, 5 and 6 are the same, that is,

$$z_{i,4} = z_{i,5} = z_{i,6}; \quad i = 1, \dots, NC \quad (4.35)$$

$$T_4 = T_5 = T_6 \quad (4.36)$$

► Component (Phase) splitter.

This unit will be modelled as an isothermal flash drum. The overall mass balance is

$$F_6 = F_7^v + F_8^l \quad (4.37)$$

and the vapour-liquid equilibrium is described simply by

$$K_i = \frac{p_{i,F}^{sat}}{P_F}, \quad p_{i,F}^{sat} = \exp\left(A_i + \frac{B_i}{C_i + T_6 - T_{ref}}\right) \quad (4.38)$$

$$y_{i,7} = K_i x_{i,8}; \quad i = 1, \dots, NC \quad (4.39)$$

$$x_{i,8} = \frac{z_{i,6}}{1 - \beta_F(1 - K_i)} \quad (4.40)$$

$$\text{where } \beta_F = F_7^v / F_6 \quad (4.41)$$

where pressure is given in mmHg.

► Benzene Column.

For the sake of simplicity, the separation task in the distillation columns will be characterized by simply setting the amounts of light and heavy key components (LK_c and HK_c , respectively) to be recovered at column c . Therefore, flowrates, compositions and T at the top and bottom can be obtained. For this column, Benzene is selected as the light component and Ethylbenzene as the heavy key component. Thus,

Overall Mass Balance:

$$F_8 = F_9 + F_{10} \quad (4.42)$$

Balance per component:

$$x_{i,8}F_8 = y_{i,9}F_9 + x_{i,10}F_{10}; \quad i = 1, \dots, NC \quad (4.43)$$

Dew Point (top of the column):

$$1 = \sum_{i=E}^B x_{i,9} = \sum_{i=E}^B y_{i,9} P_{BC} / p_{i,BC}^{sat}(T_9) \quad (4.44)$$

Bubble point (bottom of the column):

$$1 = \sum_{i=B}^{NC} y_{i,10} = \sum_{i=B}^{NC} x_{i,10} p_{i,BC}^{sat}(T_{10}) / P_{BC} \quad (4.45)$$

► Ethylbenzene Column.

In this column the Ethylbenzene is assumed as the light-key component (LK_{EB}) while the heavy-key (HK_{EB}) is the di-Ethylbenzene. Hence,

Overall Mass Balance:

$$F_{10} = F_{11} + F_{12} \quad (4.46)$$

Balance per component:

$$x_{i,10}F_{10} = y_{i,11}F_{11} + x_{i,12}F_{12}; \quad i = 1, \dots, NC \quad (4.47)$$

Dew Point (top of the column):

$$1 = \sum_{i=E}^{EB} x_{i,11} = \sum_{i=E}^{EB} y_{i,11} P_{EBC} / p_{i,EBC}^{sat}(T_{11}) \quad (4.48)$$

Bubble point (bottom of the column):

$$1 = \sum_{i=EB}^{NC} y_{i,12} = \sum_{i=EB}^{NC} x_{i,12} p_{i,EBC}^{sat}(T_{12}) / P_{EBC} \quad (4.49)$$

► Purge 2 process model.

Total mass balance,

$$F_{12} = F_{13} + F_{14} \quad (4.50)$$

with purge fraction defined as $\sigma_2 = F_{13}/F_{12}$. Note that the concentrations and temperatures on streams 12, 13 and 14 are the same, that is,

$$x_{i,12} = x_{i,13} = x_{i,14}; \quad i = 1, \dots, NC \quad (4.51)$$

$$T_{12} = T_{13} = T_{14} \quad (4.52)$$

◆ **Step 2.7.** Model Solution.

Stage 2 model is presented in the following generic form:

$$\mathbf{0} = \mathbf{g}[\mathbf{x}, \mathbf{u}, \mathbf{p}] \quad (4.53)$$

$\mathbf{x} = [\mathbf{x}_s, \mathbf{x}_p]$ where

$$\mathbf{x}_s = [F_3, F_4, F_8, T_3, T_4, T_{cw,out}, T_9, T_{10}, T_{11}, T_{12}, \beta_F, z_{i,3}, z_{i,4}, x_{i,8}, y_{i,9}, x_{i,10}, y_{i,11}, x_{i,12}]^T; \quad i = 1, \dots, NC \quad (4.54a)$$

$$\mathbf{x}_p = [F_5, F_6, F_7, F_9, F_{10}, F_{11}, F_{12}, F_{13}, F_{14}, T_5, T_6, T_{cw,out}, \dot{Q}_r, x_B, x_E, p_{EB}, y_E, \beta_{Y,S}, \alpha_{Y,S}, \delta_{Y,S}, \tau_{Y,S}, \varepsilon_{Y,S}, R_k, z_{i,5}, z_{i,6}, y_{i,7}, x_{i,9}, y_{i,10}, x_{i,11}, y_{i,12}, x_{i,13}, x_{i,14}, K_i, p_{i,F}^{sat}, p_{i,BC}^{sat}, p_{i,EBC}^{sat}, \Delta H_{r,k}]^T; \quad i = 1, \dots, NC, k = 1, \dots, NR \quad (4.54b)$$

$$\mathbf{u} = [F_1, f_E, m_{cw,r}, LK_c, HK_c, x_{i,1}, y_{i,2}]^T; \quad c = BC, EBC \quad (4.55)$$

$$\mathbf{p} = [UA_r, V_r, Cp_{cw}, P_F, P_{BC}, P_{EBC}, T_1, T_2, T_{cw,in}, T_{ref}, \sigma_1, \sigma_2, A_i, B_i, C_i, \Delta H_{f,i}^\circ, Cp_i, k_k]^T; \quad i = 1, \dots, NC, k = 1, \dots, NR \quad (4.56)$$

where vector \mathbf{x} contains the 46 states (\mathbf{x}_s) and 81 process variables (\mathbf{x}_p) to be calculated for the entire flowsheet (performance variables definition such as conversions or recoveries are given in section C.3 in Appendix C). The system consists of 204 variables and 153 equations between state and algebraic equations. Therefore, $DOF N_{DOF} = 51$. The 9 known inputs (design variables) are contained in vector \mathbf{u} , and vector \mathbf{p} contains 42 parameters (Table D.1 in

Appendix D gives the values for the related physical properties of the system). Once specified vectors \mathbf{u} and \mathbf{p} for different process specifications, the system can be solved. The new model (Eqs. (4.53)) represents a set of non-linear algebraic equations where variables such as the feed flowrate of B (F_1), purge fractions, etc. are now included, compared to the *Stage 1* model, where, for example, F_1 was lumped into the Da number.

◆ **Step 2.8.** Model Analysis.

In *Stage 1* different operational windows were established and the overall behaviour of the process analysed under a set of assumptions (scenarios) imposed on the model. In the same way, a different scenario that includes the recycle of the byproducts to the reactor is considered so that the effect of this recycle on their production can be assessed. Solving *Stage 2* model (Eqs. (4.53)) for various values of \mathbf{u} with fixed \mathbf{p} , the corresponding values of \mathbf{x} are generated. For the sake of simplicity and with the aim of later comparison among stages, the results are presented as phase-planes in terms of recoveries or conversions. Figure 4.18 presents some of the simulated results obtained when the recovery of E ($\varepsilon_{Y,S}$) was analysed (main process specifications are given in Table D.2). The simulations were performed varying the purge factor σ_1 , given that it is from the Flash drum where most of the unreacted E is recycled back to the reactor. Therefore, the more E is sent to the Flash, the more E can be recovered. From Fig. 4.18 it can be observed that the sensitivity of the process increases

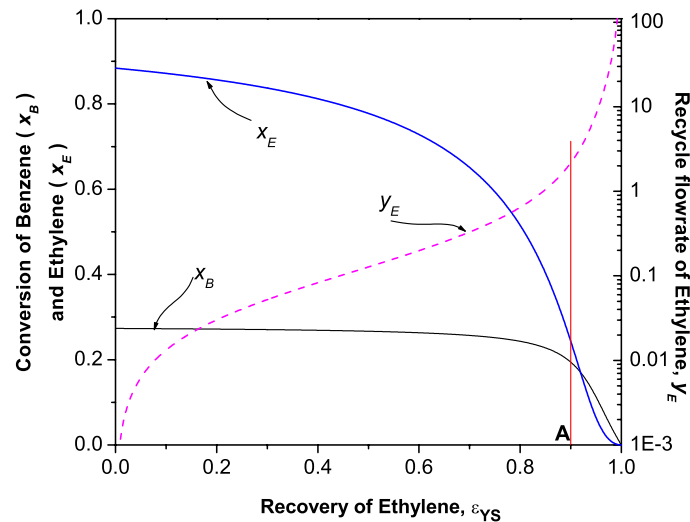


Figure 4.18: Calculated conversions of Benzene and Ethylene as function of Ethylene recovery using *Stage 2* model.

with increasing recovery of Ethylene, note the log scale in the recycle flowrate of Ethylene (y_E). As a consequence, the likelihood of a “snowball” effect increases

and a feasible performance cannot be ensured. It is important to remark that, even though operations at high recoveries (and corresponding low conversions) are not recommended, it is still important to study the conditions where the above-mentioned effects can be found such that the corresponding operational designs can avoid them.

Based on the above discussion, assume that there is the interest to find the operational conditions that achieve a yield of *EB* of $p_{EB} = 0.20$, this will be the *design* target (de Lera Alonso 2000). From Fig. 4.18 the calculated process variables (x_B, x_E, y_E) relating such *design* target (point A) can be seen. Table 4.3 summarises the conditions in terms of inlet temperatures and flowrates, reactor and separation column specifications and the resulting process variables (see also Tables D.2 and D.3 in Appendix D for a complete list of results) for the *design* target.

Table 4.3: Process specifications and conditions for the *design* target.

Inlet Conditions		Reactor Conditions	
$x_{B,1}F_1 =$	10.08 kmol/h	$V_r =$	4.74 m ³
$f_E =$	1.019	$m_{cw,r} =$	2500 kmol/h
$T_1 = T_2 =$	353.15 K	$T_{cw,in} =$	293.15 K
$\sigma_1 =$	0.90	$UA_r =$	4.594×10^5 kJ/K/h
$\sigma_2 =$	0.91	$P_F = P_{BC} = P_{EBC} =$	760 mmHg
Benzene Column		Ethylbenzene Column	
$LK_{BC} =$	0.9926	$LK_{EBC} =$	0.99994
$HK_{BC} =$	2.5303×10^{-2}	$HK_{EBC} =$	1.00×10^{-3}
Calculated Process Variables			
$Da = 1.97$	$\alpha_{Y,S} = 0.03$	$x_B = 0.1944$	$y_E = 2.18$
$F_{E,2} = 10.27$ kmol/h	$\delta_{Y,S} = 0.82$	$x_E = 0.2431$	$F_{11} = 5.77$ kmol/h
$\beta_{Y,S} = 0.90$	$\tau_{Y,S} = 0.82$	$p_{EB} = 0.2215$	$F_{14} = 0.34$ kmol/h
$\varepsilon_{Y,S} = 0.90$		$T_4 = 300.45$ K	

◆ **Step 2.9.** Results agreement.

Figure 4.19 is shown in order to compare the results between *Stages* 1 and 2 models. The simulations were performed for different values of the feed ratio f_E (with $\sigma_1 = 0.9$ and $\sigma_2 = 0.01$ as constants). In this regard, according to the process variables (calculated at point B) given in Fig. 4.19, which are comparable to the assumptions made in *Stage* 1 (assumptions $\mathcal{A}_1, \mathcal{A}_2$ and \mathcal{A}_4 in page 66), it can be seen that the mole fractions values of *E* and *EB* in Fig. 4.15 (that is, $z_{E,S} = 0.35, z_{EB,S} = 0.10$, respectively) are in conformity with the values read from Fig. 4.19.

◆ **Step 2.10.** Storage of information.

In this stage, a *design* target ($p_{EB} = 0.20$) was defined (de Lera Alonso 2000) and the corresponding operating conditions related to it, i.e., flowrates, T and P for the entire flowsheet were obtained (see Table 4.3). Also, the process behaviour was assessed (see Fig. 4.18) and compared with respect to the results derived from *Stage* 1 model (see Figs. 4.15 and 4.19). The sensitivity of the

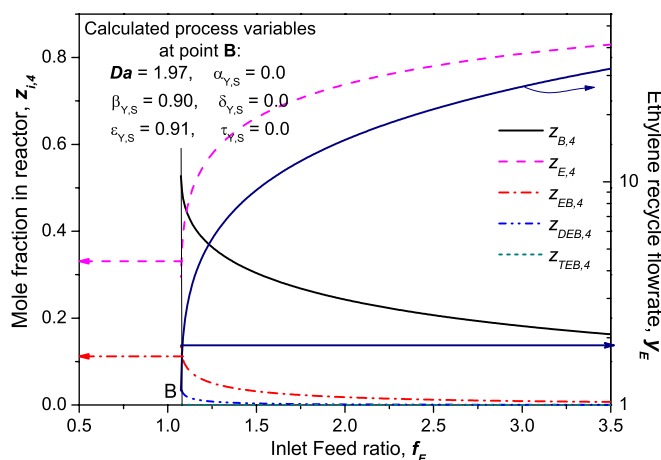


Figure 4.19: Reactor mole fractions and recycle flowrate of E as function of f_E .

process ($\varepsilon_{Y,S} \rightarrow 1$) in order to avoid the “snowball” effect was addressed as well.

4.2.1.3 Stage 3. Verification.

◆ Step 3.1. Flowsheet set up.

For this case study the rigorous simulations were carried out using ICASSim and Pro/II (Simulation Sciences Inc. 1994), the flowsheet follows essentially the layout given in Fig. 4.16.

◆ Step 3.2. Generated knowledge from previous stages.

The information about the likelihood of a “snowball” effect was considered at the moment of carrying out the simulations, e.g., as $\varepsilon_{Y,S} \rightarrow 1$. This condition can be interpreted, for example, as a high Ethylene flowrate from the Flash drum.

◆ Steps 3.3. and 3.4. Simulation and verification of the results.

Fig. 4.20 compares the results obtained with the process simulators and the Stage 2 model, when the recovery of Ethylene ($\varepsilon_{Y,S}$) was analysed. As it can be seen, the Stage 2 model (see also Fig. 4.18) reproduces the behaviour described by the rigorous simulations. Also, the high sensitivity of the process is confirmed when a complete recovery of E is attempted, which results either in a “snowball” effect or the process simulator is unable to obtain a solution.

Given the importance to have a good control of the feed inlet ratio in order to avoid the exhaustion of Ethylene, simulations using different f_E values were also performed, showing good agreement (see Fig. 4.21) with respect to Stage 2 model results. As Fig. 4.21(a) shows, the conversion of Ethylene increases (as well as the conversion of Benzene) as $f_E \rightarrow 1$. Therefore, higher concentrations

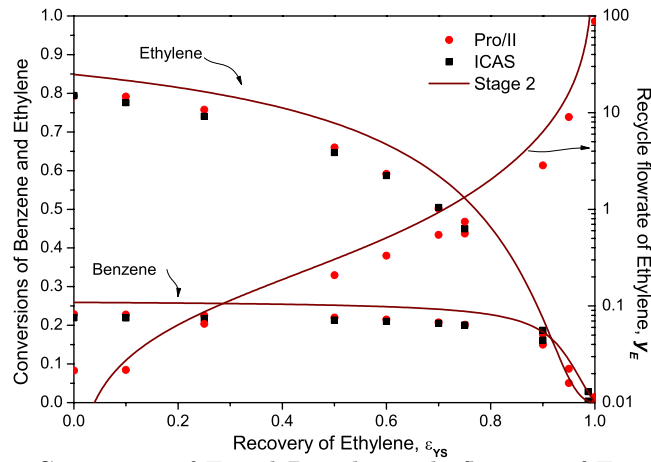


Figure 4.20: Conversion of E and B and recycle flowrate of E as function of Ethylene recovery. Comparison of results from *Stage 2* and process simulators.

of *EB* are obtained (see Fig 4.21(b)). However, the later leads to a quick exhaustion of *E*, therefore, turning off the operation.

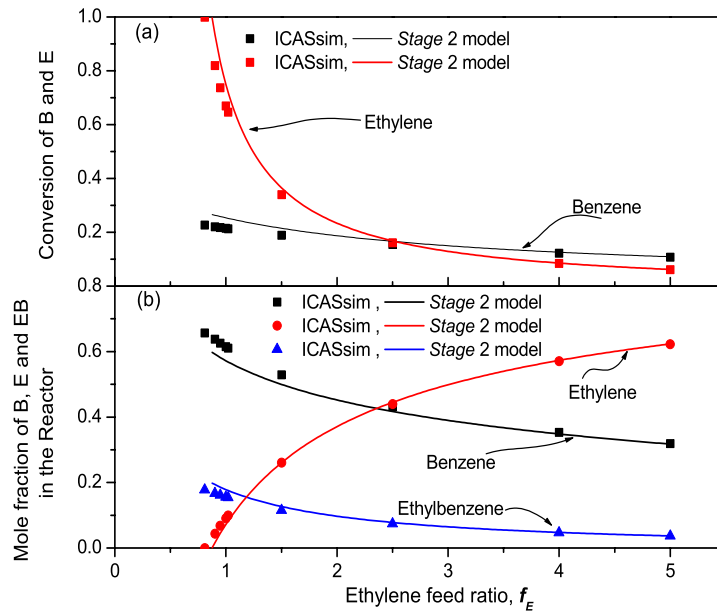


Figure 4.21: (a) Conversion of *E* and *B*, (b) Mole fractions in the Reactor of *E*, *B* and *EB* as function of f_E . Comparison of results from *Stages 2* and *3*.

◆ Steps 3.5. Storage of Information.

The rigorous simulations performed in Pro/II and ICASSim have confirmed the results obtained from the *Stage 2* model for various conditions of operation, e.g., at different recoveries of Ethylene and feed inlet ratio (see Fig. 4.20 and 4.21, respectively). From Fig. 4.20 it was assessed the sensitivity of the process when a complete recovery of E was attempted, which results in convergence problems in the process simulator failing to obtain a solution. Problems of convergence were encountered also when $f_E \rightarrow 1$, a condition that is confirmed from Fig. 4.21.

4.2.1.4 Case Summary.

Through *Stage 1* model where some ‘extreme’ operational conditions were assumed, e.g., $\varepsilon_{Y,S} = 1$, it was possible to open operating windows for the main process variables, e.g., $x_B, x_E, p_{EB}, z_{E,S}$ with respect to some of the most important design variables ($Da, \beta_{Y,S}, y_E$), helping to determine regions where the process can exhibit a feasible operation. In this context, analytical conditions (Eqs. (4.21)-(4.24)) were also derived in order to find the location where E gets exhausted from the system.

Consequently, with the information generated from *Stage 1*, more detailed models considering the actual unit operations in the process were derived in *Stage 2*. Note that, even though the complexity of the *Stage 2* model was increased, it does not incorporate rigorous unit operation models as in the case of the distillation columns. However, the *Stage 2* model is sufficiently accurate to characterize the overall process performance, as the calculated process behaviour was confirmed by rigorous simulations in the verification stage (*Stage 3*) and also when it was compared to the simple model in *Stage 1*. On the other hand, the operational conditions were obtained corresponding to a specific *design* target ($p_{EB} = 0.20$, design and process variables can be seen in Table 4.3), which in this case had been defined in advance (de Lera Alonso 2000).

The verification stage (*Stage 3*) utilises more rigorous models in an attempt to verify the design conditions and decisions made in *Stages 1* and *2*. In this regard, Pro/II (commercial process simulator) and ICAS (in-house Integrated Computer Aided System) were employed. It is important to highlight that, for those cases where a distillation column design is not available in advance, through the insights generated from the *Stage 2* results (P, T and recoveries at the top and bottoms), it is possible to use shortcut methods that can help later to complete the rigorous design of the column. On the other hand, the rigorous simulations performed validated the results obtained from *Stage 1* and *Stage 2* models.

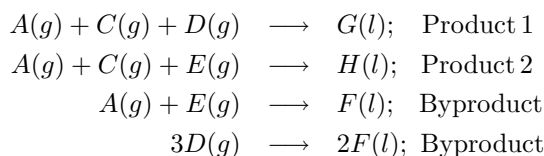
Given the results and information generated, it can be argued that a complete characterization of the process has been reached in terms of performance (sensitivity to design variables) and operating conditions (flowrates, P, T , etc.).

4.3 Tennessee Eastman Problem (Case Study 4)

The Tennessee Eastman Problem (TE) first appeared in an *AIChE* meeting (Downs and Vogel 1990) and at the Chemical Process Control Conference in 1991 since then it has led to a number of publications and research around it. This is a good example of what plantwide control involves including nonlinearities not only in the reaction section but also due to the interconnections. The perspective to be taken in this study is related to the analysis of its behaviour from a design viewpoint and from there attempt to sketch a proposal for the control structure. It is important to remark that the objective of this work is not to perform a control study of the process as such, but to provide sufficient information to outline an appropriate control structure for the problem.

4.3.1 Process Description

The process produces two products from four reactants. Also present are an inert and a byproduct making a total of eight components: A, B, C, D, E, F, G, and H. The original reaction scheme is:



All the reactions are irreversible and exothermic. The reaction rates are a function of temperature and represented through an Arrhenius expression. The reaction to produce G has a higher activation energy resulting in higher sensitivity to temperature. Also, the reactions are approximately first-order with respect to the reactant concentrations.

The process has five major unit operations: the reactor, the product condenser, a vapor-liquid separator, a recycle compressor and a product stripper. Figure 4.22 shows the flow diagram of the process.

The gaseous reactants are fed to the reactor where they react to form liquid products. The gas phase reactions are catalyzed by a nonvolatile catalyst dissolved in the liquid phase. A Continuous Stirred Tank Reactor (CSTR) has an internal cooling bundle for removing the heat of reaction. The products leave the reactor as vapours along with the unreacted reactants. The catalyst remains in the reactor.

The reactor product stream passes through a cooler for condensing the products and from there to a vapour-liquid separator. Noncondensed components are recycled back through a centrifugal compressor to the reactor feed. Condensed components move to a product stripping column to remove remaining reactants by stripping with feed stream number 4. Products G and H exit the

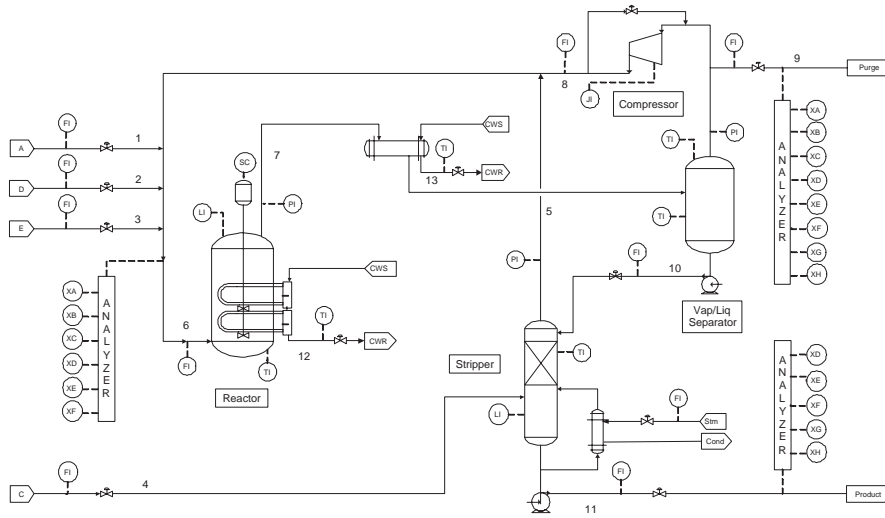


Figure 4.22: TE-Problem Flowsheet.

stripper base and are separated in a downstream refining section which is not included in the problem. The inert and byproduct are primarily purged from the system as a vapour from the vapour-liquid separator.

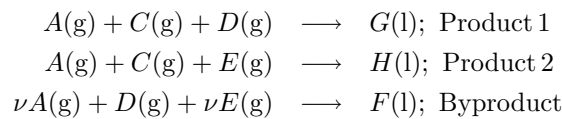
The reaction kinetics are as follows:

$$R_1 = \epsilon_1 V_{v,r} \exp \left[44.06 - \frac{42600}{R_g T_r} \right] p_{A,r}^{1.08} p_{C,r}^{0.311} p_{D,r}^{0.874} \quad (4.57)$$

$$R_2 = \epsilon_2 V_{v,r} \exp \left[10.27 - \frac{19500}{R_g T_r} \right] p_{A,r}^{1.15} p_{C,r}^{0.370} p_{E,r}^{1.00} \quad (4.58)$$

$$R_3 = \epsilon_3 V_{v,r} \exp \left[59.50 - \frac{59500}{R_g T_r} \right] p_{A,r} (0.77 p_{D,r} + p_{E,r}) \quad (4.59)$$

where the byproduct reactions have been added in order to produce Eq. (4.59). Therefore, the modified scheme of reaction is



where $\nu = 1/3$.

4.3.1.1 Stage 1. Model-based analysis by Simple Models.

◆ Step 1.1. Flowsheet simplification.

The first step requires to simplify the process flowsheet in terms of the main

operations, which are, mixing, reaction and separation, and which provide the basis for the mass and energy balance models (see Fig. 4.23, nomenclature will also be referred to this figure).

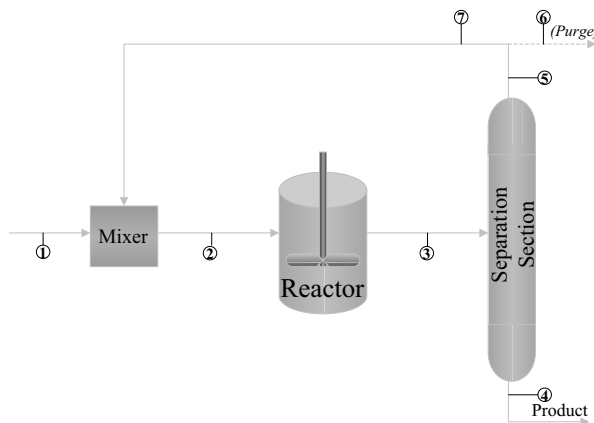


Figure 4.23: Simplified flowsheet for the TE-problem.

◆ **Step 1.2.** Reaction Analysis.

The following main assumptions are made:

- \mathcal{A}_0 . Constant pressure within the reactor, thus $p_{i,r} = y_{i,r}P_r$,
- \mathcal{A}_1 . Reaction 1 (Eq. (4.57)) is taken as reference since it has the highest sensitivity to temperature (Downs and Vogel 1993),
- \mathcal{A}_2 . The feed flowrate of component A ($F_{A,1}$) is taken as reference variable for the dimensionless model,
- \mathcal{A}_3 . No recycle back to the reactor of products or byproducts is considered,
- \mathcal{A}_4 . The important products are G and H, so their yields are followed as well as the selectivity of G with respect to H, $S_{G/H}$.

◆ **Step 1.3.** Thermal effects.

Since the thermal effects are particularly important, the model-based Methodology recommends to move to step [1.5].

◆ **Step 1.4.** Model Development based on Mass balances only.

Not necessary.

◆ **Step 1.5.** Isothermal assumption.

Even though the thermal effects are important, it has been considered useful to first do an analysis with only the mass balance model. This is done with the aim to determine the effect of, mainly, the recycle stream. This assumption would imply perfect control of temperature and pressure in the reactor.

◆ **Step 1.6.** Model Development.

Equations (4.60) describe the components mass balances at steady-state for the simplified system, thus

$$0 = 1 - \left(\frac{\sigma - \alpha_{A,7}}{\sigma} \right) y_{A,3} f_3 - Da(\widehat{R}_1 + \widehat{R}_2 + \nu \widehat{R}_3) \quad (4.60a)$$

$$0 = y_{B,1} f_1 - \left(\frac{\sigma - \alpha_{B,7}}{\sigma} \right) y_{B,3} f_3 \quad (4.60b)$$

$$0 = y_{C,1} f_1 - \left(\frac{\sigma - \alpha_{C,7}}{\sigma} \right) y_{C,3} f_3 - Da(\widehat{R}_1 + \widehat{R}_2) \quad (4.60c)$$

$$0 = y_{D,1} f_1 - \left(\frac{\sigma - \alpha_{D,7}}{\sigma} \right) y_{D,3} f_3 - Da(\widehat{R}_1 + \widehat{R}_3) \quad (4.60d)$$

$$0 = y_{E,1} f_1 - \left(\frac{\sigma - \alpha_{E,7}}{\sigma} \right) y_{E,3} f_3 - Da(\widehat{R}_2 + \nu \widehat{R}_3) \quad (4.60e)$$

$$0 = - y_{F,3} f_3 + Da(\widehat{R}_3) \quad (4.60f)$$

$$0 = - y_{G,3} f_3 + Da(\widehat{R}_1) \quad (4.60g)$$

$$0 = - y_{H,3} f_3 + Da(\widehat{R}_2) \quad (4.60h)$$

$$0 = \sum_{i=1}^{NC} y_{i,1} f_1 + \sum_{i=1}^{NC} \left(\frac{\alpha_{i,7}}{\sigma} - 1 \right) y_{i,3} f_3 + Da(\widehat{R}_1 + \widehat{R}_2 + \widehat{R}_3) \quad (4.60i)$$

where

$$\widehat{R}_1 = y_{A,3}^{1.08} y_{C,3}^{0.311} y_{D,3}^{0.874} \quad (4.61a)$$

$$\widehat{R}_2 = \frac{\epsilon_2 \exp(c_{1,2} - c_{2,2}/R_g T_r)}{\epsilon_1 \exp(c_{1,1} - c_{2,1}/R_g T_r)} P_r^{2.52} y_{A,3}^{1.15} y_{C,3}^{0.370} y_{E,3}^{1.00} \quad (4.61b)$$

$$\widehat{R}_3 = \frac{\epsilon_3 \exp(c_{1,3} - c_{2,3}/R_g T_r)}{\epsilon_1 \exp(c_{1,1} - c_{2,1}/R_g T_r)} P_r^2 y_{A,3} (0.77 y_{D,3} + y_{E,3}) \quad (4.61c)$$

and

$$Da = \frac{\epsilon_1 \exp(c_{1,1} - c_{2,1}/R_g T_r) P_r^{2.265} V_r}{F_{A,1}} \quad (4.62)$$

is the plant Damköhler number which represents the relationship between the rate of reaction with respect to the rate of fresh feed of A.

▷ **Step 1.6.1.** Solution and Analysis of the model equations.

Equations (4.63) (or alternatively Eqs. (4.60)) represent a system of 8 non-linear algebraic equations (NLAE) with respect to the mole fractions $y_{i,3}$ in the reactor plus the overall mass balance (f_3), together with the dimensionless rate of reaction \widehat{R}_k (Eqs. (4.61)), hence $N_e = 12$. In order to classify the variables used in the above mass balance model, a vectorial compact form of Eqs. (4.63) is given below:

$$\mathbf{0} = \mathbf{f}[\mathbf{x}, \mathbf{u}, \mathbf{p}] \quad (4.63)$$

where

$$\mathbf{x} = [f_3, y_{i,3}, \widehat{R}_k]^T; \quad i = A, \dots, H, k = 1, \dots, NR \quad (4.64)$$

$$\mathbf{u} = [Da, \sigma, \alpha_{i,7}]^T; \quad i = A, \dots, E \quad (4.65)$$

$$\mathbf{p} = [F_1, T_r, P_r, R_g, y_{i,1}, \epsilon_k, c_{1,k}, c_{2,k}]^T; \quad i = B, \dots, E, k = 1, \dots, NR \quad (4.66)$$

where, vector \mathbf{x} are the representative process variables to be solved; vector \mathbf{u} contains the main design variables, namely, the Damköhler number (Da), recovery ($\alpha_{i,7}$) and purge factors (σ); vector \mathbf{p} stands for the main reaction parameters, pressure and temperature in the reactor, mole fractions and flowrate at the inlet stream, as well as pre-exponential factors and activation energies. Based on this, $N_u = 36$. Therefore, the DOF $N_{DOF} = N_u - N_e = 24$. Hence, by specifying the parameters vector \mathbf{p} and the design variables vector \mathbf{u} for a specific set of conditions of operation the system can be solved.

The model-based process analysis is carried out considering a constant pressure within the reactor $P_r = 2.806$ MPa and $T_r = 393.55$ K (at the Base case scenario, see Table D.5 in Appendix D for process specifications). The sim-

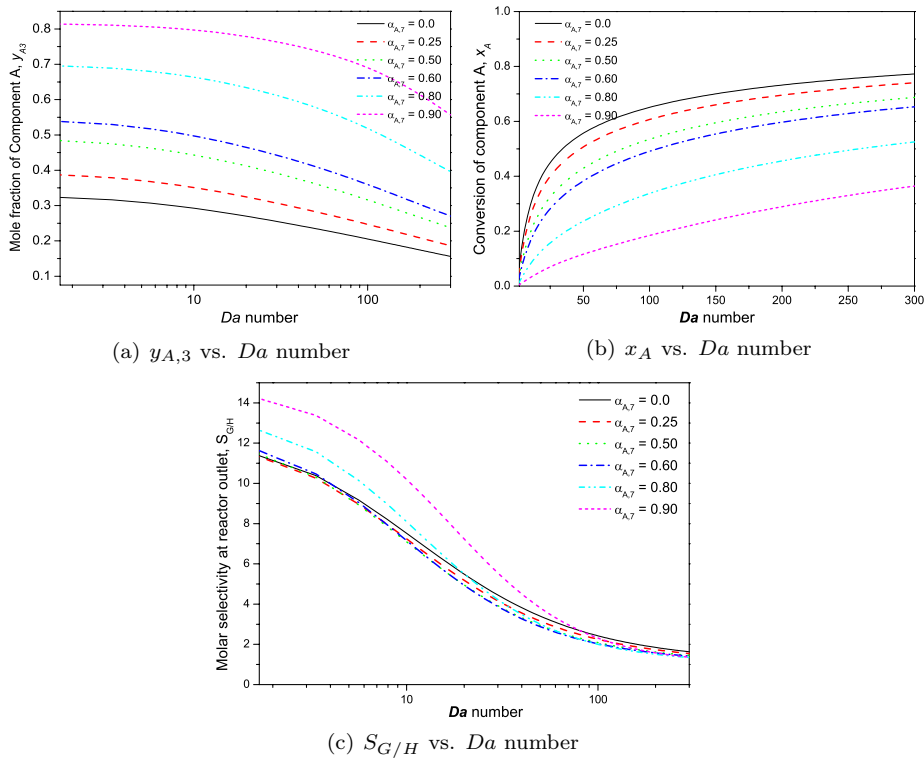


Figure 4.24: Mole fraction and conversion of A and Selectivity as function of Da number for various $\alpha_{A,7}$.

ulation results obtained by solving the mass balance model for different sets of values for the design variables (\mathbf{u}) are analysed through Figs. 4.24-4.26. In Figure 4.24(a) (where $\alpha_{i,7}=0, i \neq A; \sigma=1$) the sensitivity of the mole fraction of component A, $y_{A,3}$ with respect to the Da for different recovery values ($\alpha_{A,7}$) is shown.

As it can be expected, the more A is recycled, the higher its concentration within the reactor. Nevertheless, the conversion of A (x_A) decreases (see Fig. 4.24(b)) because of a larger amount of A that has to be reacted within the same reactor volume (assuming V_r is kept constant). On the other hand, it is important to highlight the combined effect of the Da number and the recovery factor $\alpha_{A,7}$. That is, in Fig. 4.24(b) a steeper slope is observed in the conversion profile as $\alpha_{A,7}$ decreases, especially at lower Da numbers ($Da < 50$). This effect indicates that a faster rate of reaction is most likely taking place due to the stoichiometric consumption of reactant A. Conversely, larger $\alpha_{A,7}$ values means that a higher residence time in the reactor is required for A. Now, in Fig. 4.24(c) the molar selectivity in the reactor, defined as $S_{G/H} = y_{G,3}/y_{H,3}$ is favoured also at low Da numbers ($Da < 10$) and high $\alpha_{A,7}$ values. A $Da > 200$ has no effect on the selectivity, since it can be assumed that the equilibrium has been reached. Thus, it can be argued that, 1) high selectivity values are obtained at low Da number because product G is produced faster than H, and 2) high recovery values increase the selectivity due to the higher concentration of A, which makes that the rates of reaction slower (see Eqs. (4.61a)-(4.61b)), causing thereby, the ratio G/H to increase.

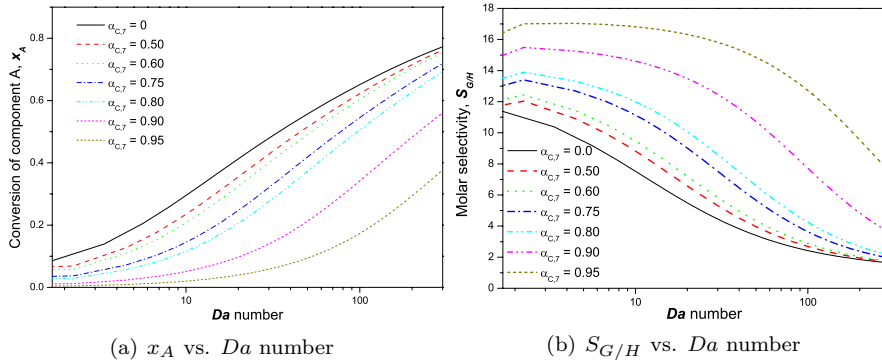


Figure 4.25: Conversion of A and Molar Selectivity as function of Da number.

Investigating now the effect of the recovery of component C, it can be seen through Figures 4.25(a) and 4.25(b) (where $\alpha_{i,7}=0, i \neq C; \sigma=1$) that the trend observed with respect to $\alpha_{A,7}$ is confirmed. However, even though it would be preferred to operate at high selectivity values, Fig. 4.26 shows that the recycle flowrate f_7 increases rapidly as $\alpha_{C,7} \rightarrow 1$, increasing thereby, the likelihood of a “snowball” effect to occur. This is, in fact, a characteristic of the TE-problem, which operates at high recovery values for the unreacted components, therefore

high process sensitivity can be expected if more reactants are recycled back to the reactor.

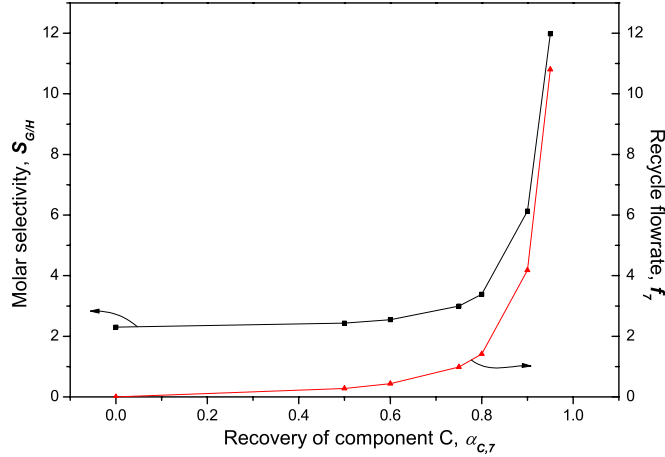


Figure 4.26: Molar selectivity and Recycle flowrate as function of $\alpha_{C,7}$.

From the above brief analysis, which assumed isothermal conditions, it was observed that i) the recycle of reactants enhances the selectivity of the product(s) of interest, but can also lead to operational restrictions (e.g., “snowball” effect), and ii) low Da numbers ($Da < 50$), which can be interpreted as high $F_{A,1}$ (see Eq. (4.62)) results in high selectivity values, since reactant A does not act as a limiting reactant, so that the overall effect is an increase in the rates of reaction.

◆ **Step 1.7.** Addition of Energy Balances.

When considering the energy balance, Eqs. (4.60) are not modified but extra equations are added to the mass balance model.

► *Mixing zone.* For the simplified flowsheet the mixing zone considers the feed stream F_1 and recycle stream F_7 as inlets and F_2 as outlet, thus giving the following equation for energy balance.

$$0 = \sum_{j=1,7} F_j \left(\sum_{i=A}^H y_{i,j} C p_i^v \right) (T_j - T_2) \quad (4.67)$$

► *Reactor.* The reactor operation assumes a non-adiabatic non-isothermal condition. Therefore, heat exchange with a cooling media (water) is included in the energy balance by considering a heat balance on the reactor side.

$$0 = F_3 \left(\sum_{i=A}^H y_{i,3} C p_i^v \right) (T_2 - T_3) - \sum_{k=1}^{NR} \Delta H_{r,k} R_k - \dot{Q}_r \quad (4.68)$$

where

$$\Delta H_{r,k} = \sum_{i=A}^H C p_i^v (T_3 - T_{ref}) + \Delta H_{f,k}^\circ \quad (4.69)$$

with heat balance on the cooling media side given by,

$$\dot{Q}_r = m_{cw} C p_{cw} (T_{cw,r,out} - T_{cw,r,in}) \quad (4.70)$$

$$\dot{Q}_r = U A_r \left(\frac{\Delta T_1 - \Delta T_2}{\ln(\Delta T_1 / \Delta T_2)} \right) \quad (4.71)$$

$$\Delta T_1 = T_3 - T_{cw,r,in}; \quad \Delta T_2 = T_3 - T_{cw,r,out} \quad (4.72)$$

► *Separation section and purge zone.* In this step, the reaction effects are mainly analysed. Therefore, it is assumed that there will be no change in the outlet stream temperatures from the splitter as well as the purge, that is,

$$T_4 = T_5 = T_3 \quad (4.73)$$

$$T_7 = T_6 = T_5 \quad (4.74)$$

The dimensionless energy balance equations take as a variables of reference the feed (inlet) to the process of component A ($F_{A,1}$), since component A is considered as the limiting reactant, and also its heat capacity in the vapour phase ($C p_A^v$). Likewise, the temperature of the inlet to the reactor, T_2 is taken as a reference value as in the definition of $\theta_j = (T_j - T_2) / T_2$, which is used in Eqs. (4.75)-(4.76).

Therefore, the dimensionless energy balance equations take the following form:

► *Mixing zone model.* Rearranging Eq. (4.67) for $T_7 = T_3$ and using the definition of θ_j , gives,

$$0 = \sum_{i=A}^E (f_{i,1} \tilde{C} p_i) \theta_1 + \sum_{i=A}^E \left(\frac{\alpha_{i,7}}{\sigma} f_{i,3} \tilde{C} p_i \right) \theta_3 \quad (4.75)$$

► *Reactor model.* Rearranging Eq. (4.68) in terms of dimensionless variables, gives,

$$0 = -f_3 \left(\sum_{i=A}^E \tilde{C} p_i \right) \theta_3 + Da \left[\sum_{k=1}^{NR} \tilde{C} p_{R_k} \exp \left(\frac{\gamma_k \theta_3}{1 + \theta_3} \right) K_k^* \hat{R}_k \right] (\theta_3 - \theta_{ref}) - \delta_c \left[\frac{\Delta \theta_1 - \Delta \theta_2}{\ln(\Delta \theta_1 / \Delta \theta_2)} \right] \quad (4.76)$$

where $\Delta \theta_1 = \theta_3 - \theta_{cw,r,in}$ and $\Delta \theta_2 = \theta_3 - \theta_{cw,r,out}$.

The following dimensionless variables have been used in Eqs. (4.75)-(4.76).

$$\begin{aligned}
 Da &= \frac{\epsilon_1 \exp(c_{1,1} - \gamma_1) P_r^{2.265} V_r}{F_{A,1}}; \\
 K_2^* &= \frac{\epsilon_2 \exp(c_{1,2} - \gamma_2) P_r^{2.52}}{\epsilon_1 \exp(c_{1,1} - \gamma_1) P_r^{2.265}}; & K_3^* &= \frac{\epsilon_3 \exp(c_{1,3} - \gamma_3) P_r^2}{\epsilon_1 \exp(c_{1,1} - \gamma_1) P_r^{2.265}} \\
 \gamma_1 &= \frac{c_{2,1}}{R_g T_2}; & \gamma_2 &= \frac{c_{2,2}}{R_g T_2}; & \gamma_3 &= \frac{c_{2,3}}{R_g T_2} \\
 \tilde{C}p_i &= \frac{Cp_i^v}{Cp_A^v}; & \delta_c &= \frac{UA_r}{F_{A,1} Cp_A^v}; & mcp_{cw} &= \frac{m_{cw,r} Cp_{cw}}{F_{A,1} Cp_A^v}
 \end{aligned}$$

▷ **Step 1.7.1.** Solution of the Equations.

Equations (4.75) and (4.76) together with Eqs. (4.60) form a NLAE system that have to be solved for the new set of process variables \mathbf{x} . In the same way as in step [1.6], the combined mass plus energy balance model is now represented in compact form,

$$\mathbf{0} = \mathbf{f}[\mathbf{x}, \mathbf{u}, \mathbf{p}] \quad (4.77)$$

where

$$\mathbf{x} = [\mathbf{x}_{\text{MBal}}, \theta_3, \theta_{cw,out}]^T \quad (4.78)$$

$$\mathbf{u} = [\mathbf{u}_{\text{MBal}}, \delta_c, mcp_{cw}]^T \quad (4.79)$$

$$\mathbf{p} = [\mathbf{p}_{\text{MBal}}, T_1, T_2, T_{cw,in}, P_r, \Delta H_{f,k}^\circ, Cp_i^v]^T; \quad i = A, \dots, H, \quad k = 1, 2, 3 \quad (4.80)$$

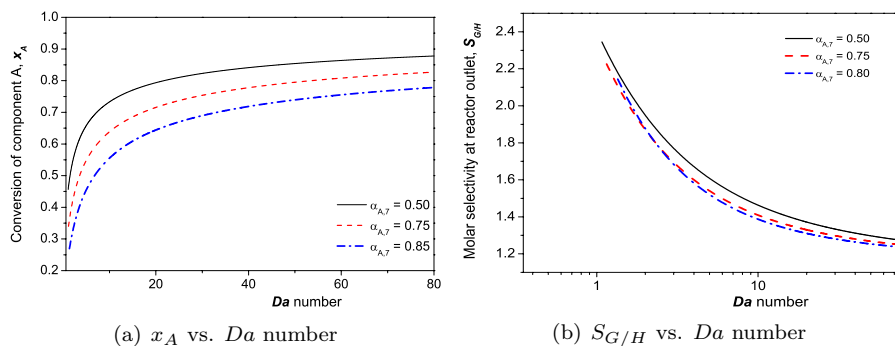
where the subscript “MBal” makes reference to the variables in step [1.6.1]. Therefore, vector \mathbf{x} now also includes the temperature in the reactor (θ_3) and the outlet temperature of the jacket ($\theta_{cw,out}$). Likewise, vector \mathbf{u} adds as design variables, a heat elimination capacity variable (δ_c) and cooling media variable (mcp_{cw}); vector \mathbf{p} stands for the reaction parameters, heat capacities, etc. The total model has now 59 variables, 19 equations between states and algebraic equations, thus $DOF = 40$. Therefore, by specifying the design variable vector \mathbf{u} plus the parameter vector \mathbf{p} the model can be solved. Table D.7 in Appendix D gives the values for some of these dimensionless variables that were kept constant in the following analysis.

▷ **Step 1.7.2.** Model Analysis.

The simulation results obtained by solving the mass balance model for different sets of values for the design variables (\mathbf{u}) are analysed through Figs. 4.27-4.31.

• ***Da number and Recovery factors analysis.***

The results from the mass and energy balance model highlighted in Fig. 4.27 ($\alpha_{i,7} = 0.98, i \neq A; \sigma = 1$) confirm the trends with respect to $\alpha_{A,7}$ seen previously with the mass balance model (see Fig. 4.24). Thereby, confirming that the insights from step [1.6] are correct. On the other hand, given that the energy balance of the reactor has been included, the profiles in Fig. 4.28 for the dimensionless variables θ_3 and $\theta_{cw,r,out}$ as function of Da number show that higher temperatures in the reactor, at low Da numbers, actually cause the rates of reaction to increase.



(a) x_A vs. Da number (b) $S_{G/H}$ vs. Da number
 Figure 4.27: Conversion of A and Selectivity as function of Da number.

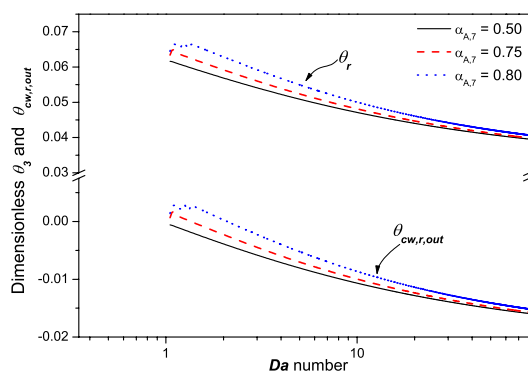


Figure 4.28: Dimensionless θ_3 and $\theta_{cw,r,out}$ as function of Da number and $\alpha_{A,7}$.

Fig. 4.29 shows the sensitivity of the process with respect to the recovery of C ($\alpha_{C,7}$). Note that component C is one of the main reactants in the process and, it also has the largest fresh feed. Therefore, as Fig. 4.29(a) shows, the recycle flowrate f_7 increases considerably as $\alpha_{C,7}$ approaches to a complete recovery. Now, if the yield of component i is defined as the amount of i produced with respect to the amount reacted of the limiting reactant A, we get

$$Y_i = \frac{f_{i,3}}{f_{A,2} - f_{A,3}} \quad (4.81)$$

The yields of components G and H, calculated through Eq. (4.81), are shown in Fig. 4.29(b). It can be noted that the production of component G (Y_G) is favoured when the recovery of C is increased, even though component C is present in the two main reactions (note that the second reaction involves the production of H).

It becomes clear from the above analysis that because of the policy of high reactant recovery in the TE-problem, high sensitivity can be expected in the main performance variables ($S_{G/H}$, x_A) with respect the recovery of the reactants, thereby leading to the possibility of the occurrence of the “snowball”

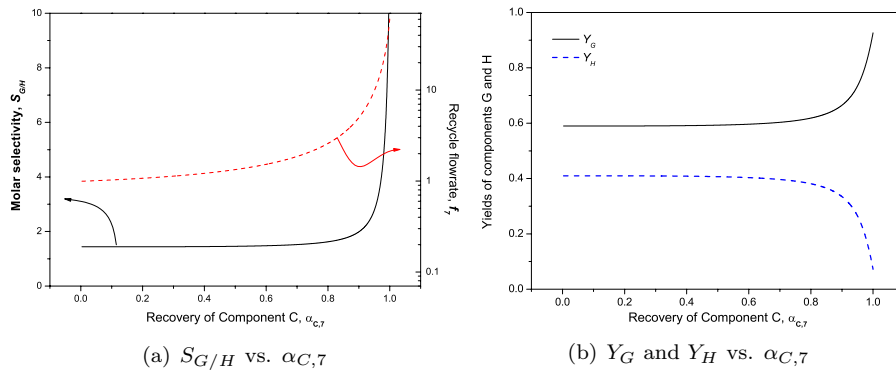


Figure 4.29: Selectivity and Yields of G and H as function of $\alpha_{C,7}$ ($Da = 1.049$).

effect. On the other hand, in the Da number analysis it has been shown that higher selectivity and conversions are found at low Da numbers as a result of higher rates of reaction.

• **Inlet flowrate-ratio analysis.**

Based on the simulation results from the mass and energy balance model, an inlet flowrate-ratio analysis was carried out in order to assess the sensitivity of the process due to changes in the inlet flowrate caused either by an increase in the throughput of the plant or a disturbance in the process. Figure 4.30

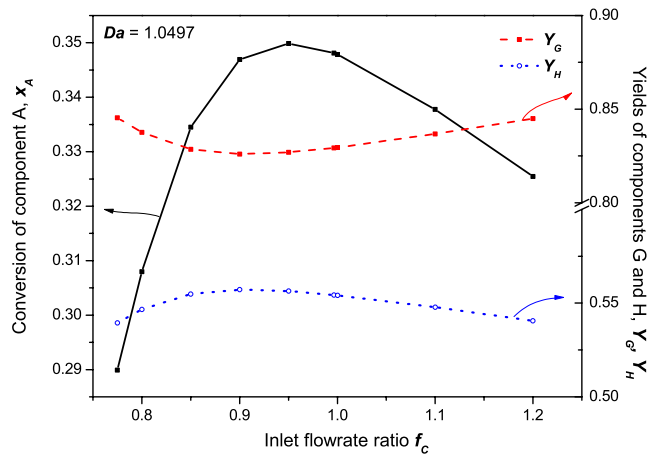
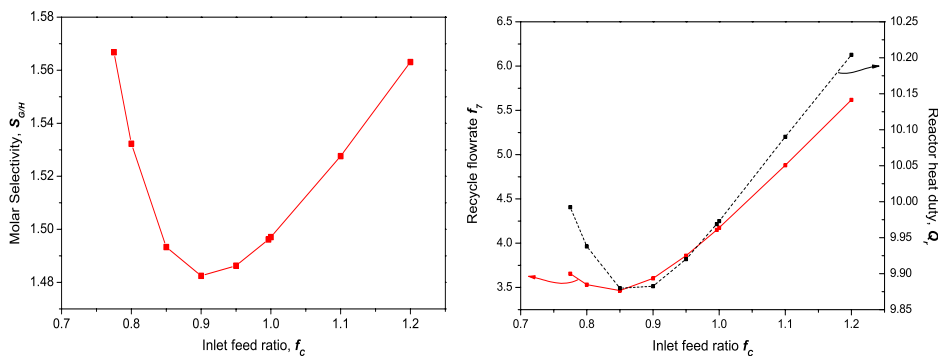


Figure 4.30: Conversion of A and yields of G and H as function of f_C .

presents the simulated responses of the conversion of A and the yields of G and H as function of feed ratio of component C, f_C ($F_{C,1}/F_{A,1}$). The Base-case scenario involves a $f_C = 0.99$ ($\alpha_{i,7} = 0.98$). Note that around $f_C = 0.99$ the highest conversions of A are achieved. By changing the feed ratio it is possible

to increase the selectivity, since more reactants are fed. However, an increase in \dot{Q}_r should be expected, given the exothermal nature of the reaction. This is confirmed through the plotted results in Fig. 4.31(b).



(a) Molar selectivity $S_{G/H}$ (b) Reactor heat duty and Recycle flowrate
Figure 4.31: Selectivity and Reactor heat duty as function of f_C ($Da = 1.049$).

On the other hand, an interesting effect is also observed: if the ratio f_C is reduced (from the Base-case scenario), the value of the selectivity increases (although leading to a lower throughput). In this way, for a given selectivity $S_{G/H}$, two different f_C ratios can be found, but, two different production rates as well.

◆ **Step 1.9.** Storage of information.

In this stage the effect that the size of the recycle stream on the performance of the RSR system (e.g., Fig. 4.29) has been verified. Also, how this effect is related to the Da number needed to achieve a given performance criteria (e.g., Figs. 4.24 and 4.29(a)-4.29(b)) has been verified. The feed ratio has been found to be an important (design) variable. The feed ratio can be used as an indicator of the behaviour of the process under disturbance or, under a shift in the operating policy (see operational window in Fig. 4.30 and 4.31).

4.3.1.2 Stage 2. Model-based analysis by Detailed Model Analysis.

◆ **Step 2.1.** Multiple reaction analysis.

There are three parallel reactions in this process. The candidate AR is presented (see Fig. 4.32) only for the CSTR as the operation involves only this equipment. The candidate AR has been constructed under the assumption of perfect temperature control (isothermal conditions). The CSTR trajectory with respect to $S_{G/H}$ is not convex, therefore, in order to make it convex, it would be required to add a bypass of the reactor. This modification, however, has been not attempted as the objective of the analysis is not to change the design of the TE-processs. The results do, however, provide directions to obtain an improved design that satisfies the criteria of the AR.

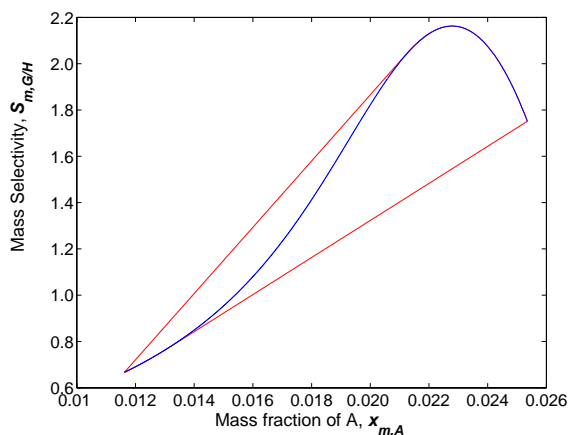


Figure 4.32: Candidate Attainable Region for CSTR for the TE-Problem.

◆ **Step 2.2.** Driving force analysis.

Due to the proprietary nature of the process, there is not sufficient information available about the thermodynamic properties of the components, or, the identities of the components. On the other hand, no distillation-based separation is employed in this system, therefore, *driving force* diagrams have not been developed.

◆ **Step 2.3.** Assumptions Removal.

All the assumptions considered in *Stage 1*, e.g., constant pressure in the reactor or the recovery of the reactants now are relaxed ($\mathcal{A}_0 - \mathcal{A}_3$).

◆ **Step 2.4.** All important phenomena.

► *Mixing zone.* All components are in the vapour phase, therefore the model includes the mass and energy balance equations plus two algebraic equations for mixing zone pressure and composition.

► *Reactor.* The reactor contains liquid and vapour phases, which are assumed to be in equilibrium. There is a significant holdup of liquid of G and H in the reactor, but there is no liquid effluent. To control liquid accumulation in the reactor, one must balance production (by reaction) against vaporization and removal in the gaseous effluent (stream 7) (Downs and Vogel 1993). The feed and the product streams of the reactor are in vapour phase.

► *Product separator.* The deviation from ideality in the vapour-liquid equilibrium is described by a constant activity coefficient for each (condensable) component. In general, where liquid and vapour co-exist, the accumulation of the less volatile components (D through H) in the vapour is neglected. In other words, these components have an equilibrium partial pressure, but the corresponding number of moles in the vapour is neglected when computing the molar holdups. Otherwise, an iterative flash calculation would be needed (Ricker and

Lee 1995b).

► *Compressor and purge.* Ricker and Lee (1995b) introduce the recycle stream as an independent variable. This avoids modelling the compressor in detail and the stream flowrate no longer depends on the valve position in the compressor recycle. Similar to the compressor simplification, the purge stream (F_9) is an algebraic variable.

► *Stripper.* There is little information available about the stripper. The unit is characterized by a split fraction model as in Ricker and Lee (1995b). Given that the energy balance is added, split fractions (Φ_i) are modelled as third-degree polynomials in temperature.

◆ **Step 2.5.** All process equipments.

The separation section includes, as above-mentioned, a stripper and a product separator, and a compressor.

◆ **Step 2.6.** Model development.

The model equations are based on the model by Jockenhövel et al. (2003), however, in this part of the analysis are presented in a steady-state basis.

► *Mixing zone.* Within the mixing zone all feed streams and the recycle stream are mixed and fed into the reactor.

Molar Balances for components A–H

$$0 = y_{i,1}F_1 + y_{i,2}F_2 + y_{i,3}F_3 + y_{i,5}F_5 + y_{i,8}F_8 - y_{i,6}F_6; \quad i = A, \dots, H \quad (4.82)$$

Energy balance for the mixing zone

$$0 = \sum_{j=1,2,3,5,8} F_j \left(\sum_{i=A}^H y_{i,j} C_{P_i}^v \right) (T_j - T_m) \quad (4.83)$$

Pressure and concentrations

$$y_{i,6} = \frac{N_{i,m}}{\sum_{j=A}^H N_{j,m}} \quad (4.84)$$

$$P_m = \sum_{i=A}^H N_{i,m} \frac{R_g T_m}{V_m} \quad (4.85)$$

► *Reactor.* In the reactor model the influence of the agitator is neglected and excess heat is removed by cooling water. Feed and product streams are in vapour phase.

Molar balances for components A–H

$$0 = y_{i,6}F_6 - y_{i,7}F_7 + \sum_{k=1}^3 \nu_{i,k} R_k; \quad i = A, \dots, H \quad (4.86)$$

Energy balance for the reactor

$$0 = F_6 \left(\sum_{i=A}^H y_{i,6} C p_i^v \right) (T_6 - T_r) - \dot{Q}_r - \sum_{k=1}^3 \Delta H_{r,k} R_k \quad (4.87)$$

$$\Delta H_{r,k} = \sum_{i=A}^H H_i \nu_{i,k} + H_o F_k, \quad \text{with } H_i = C p_i^v (T_r - T_{ref}) \quad (4.88)$$

Reaction kinetics

Eqs. (4.61a)–(4.61c) remain the same for this model.

Heat exchange with cooling water

$$\dot{Q}_r = m_{cw,r} C p_{cw} (T_{cw,r,out} - T_{cw,r,in}) \quad (4.89)$$

$$\dot{Q}_r = U A_r \left(\frac{\Delta T_{1,r} - \Delta T_{2,r}}{\ln(\Delta T_{1,r} / \Delta T_{2,r})} \right) \quad (4.90)$$

$$\Delta T_{1,r} = T_r - T_{cw,r,in}; \quad \Delta T_{2,r} = T_r - T_{cw,r,out} \quad (4.91)$$

Vapor-liquid equilibrium

$$p_{i,r} = \gamma_{i,r} x_{i,r} p_{i,r}^{sat}(T_r); \quad i = D, \dots H \quad (4.92)$$

$$p_{i,r} = \frac{N_{i,r}^v R_g T_r}{V_{v,r}}; \quad i = A, B, C \quad (4.93)$$

$$p_{i,r}^{sat}(T) = 10^{-3} \exp \left(A_i + \frac{B_i}{C_i + T_r - T_{ref}} \right); \quad i = D, \dots H \quad (4.94)$$

$$P_r = \sum_{i=A}^H p_{i,r} \quad (4.95)$$

$$y_{i,7} = \frac{p_{i,r}}{P_r}; \quad i = A, \dots H \quad (4.96)$$

$$x_{i,r} = \frac{N_{i,r}}{\sum_{i=D}^H N_{i,r}}; \quad i = D, \dots H \quad (4.97)$$

$$V_{l,r} = \frac{\sum_{i=D}^H N_{i,r}^l}{\rho_{l,r}}, \quad \text{with } V_{v,r} = V_r - V_{l,r} \quad (4.98)$$

Reactor input stream F_6 and reactor output stream F_7

$$F_6 = 0.8334 \frac{\text{kmol}}{\text{s}\sqrt{\text{MPa}}} \sqrt{P_m - P_r} \quad (4.99)$$

$$F_7 = 1.5355 \frac{\text{kmol}}{\text{s}\sqrt{\text{MPa}}} \sqrt{P_r - P_s} \quad (4.100)$$

The constants values in Eqs. (4.99) and (4.100) are given by Jockenhövel et al. (2003) to match the Base case. Note that the cooling water flux $m_{cw,r}$ is a control variable directly. Its dependence on a valve position is neglected. Note

that for components D-H the numbers of moles $N_{i,r}$ refer to the number of moles in the liquid phase only, due to the assumption that a buildup of these components in the vapor phase can be neglected.

► *Product Separator.* Molar balances for components A-H

$$0 = y_{i,7}F_7 - y_{i,8}(F_8 + F_9) - x_{i,10}F_{10}; \quad i = A, \dots, H \quad (4.101)$$

Energy balance for the separator

$$0 = F_7 \left(\sum_{i=A}^H y_{i,7} C p_i^v \right) (T_r - T_s) + HoV_s - \dot{Q}_s \quad (4.102)$$

$$HoV_s = \sum_{i=D}^H x_{i,10} F_{10} H_{vap,i} \quad (4.103)$$

Vapor-liquid equilibrium

$$p_{i,s} = \frac{N_{i,s}^v R_g T_s}{V_{v,s}}; \quad i = A, B, C \quad (4.104)$$

$$p_{i,s} = \gamma_{i,s} x_{i,10} p_{i,s}^{sat}(T_s); \quad i = D, \dots, H \quad (4.105)$$

$$P_s = \sum_{i=A}^H p_{i,s} \quad (4.106)$$

$$y_{i,8} = y_{i,9} = \frac{p_{i,s}}{P_s} \quad (4.107)$$

$$x_{i,10} = 0; \quad i = A, B, C; \quad x_{i,10} = \frac{N_{i,s}}{\sum_{i=D}^H N_{i,s}}; \quad i = D, \dots, H \quad (4.108)$$

$$V_{l,s} = \frac{\sum_{i=D}^H N_{i,s}^l}{\rho_{l,s}}; \quad V_{v,s} = V_s - V_{l,s} \quad (4.109)$$

Heat exchange with cooling water

$$\dot{Q}_s = m_{cw,s} C p_{cw} (T_{cw,s,out} - T_{cw,s,in}) \quad (4.110)$$

$$\dot{Q}_s = UA_s \left(\frac{\Delta T_{1,s} - \Delta T_{2,s}}{\ln \Delta T_{1,s} / \Delta T_{2,s}} \right) \quad (4.111)$$

$$\Delta T_{1,s} = T_s - T_{cw,s,in}; \quad \Delta T_{2,s} = T_s - T_{cw,s,out} \quad (4.112)$$

► *Compressor and purge.* The temperature changes due to the compressor work are taken into account by the Eq. (4.113).

$$T_8 = T_s \left(\frac{P_m}{P_s} \right)^{\frac{1-\kappa}{\kappa}} \quad (4.113)$$

► *Stripper.* This unit is modelled by a split fraction model as proposed in Ricker and Lee (1995b). An energy balance was added by Jockenhövel et al.

(2003) and the split fractions (Φ_i) are modelled as third-degree polynomials in temperature. The pressures in the stripper and the mixing zone are assumed to be the same. The heating medium is saturated steam, which condenses completely at a constant temperature. The enthalpy of the steam has been chosen to fit the steam flux with the heat duty of the stripper given in Downs and Vogel (1993) for the Base case.

Molar balances for components G-H

$$0 = (1 - \Phi_i)(x_{i,10}F_{10} + y_{i,4}F_4) - x_{i,11}F_{11}; \quad i = G, H \quad (4.114)$$

Energy balance for the stripper

$$0 = F_{10} \sum_{i=A}^H (x_{i,10} Cp_i^l)(T_s - T_{str}) + F_4 \sum_{i=A}^H (y_{i,4} Cp_i^v)(T_4 - T_{str}) - HoV_{str} + \dot{Q}_{str} \quad (4.115)$$

$$HoV_{str} = \sum_{i=D}^H H_{vap,i} (y_{i,5}F_5 - y_{i,4}F_4) \quad (4.116)$$

$$\dot{Q}_{str} = 2258.717 \frac{\text{kJ}}{\text{kg}} \dot{m}_{cw, str} \quad (4.117)$$

Vapor-liquid equilibrium

$$V_{l, str} = \sum_{i=D}^H \frac{N_{i, str}}{\rho_{str}} \quad (4.118)$$

$$\Phi_i = 1; \quad i = A, B, C; \quad (4.119)$$

$$\Phi_i = \sum_{j=0}^3 a_{i,j} (T_s - 273)^j; \quad i = D, \dots, H \quad (4.120)$$

$$F_5 = F_4 + F_{10} - F_{11} \quad (4.121)$$

$$y_{i,5} = \frac{\Phi_i (y_{i,4}F_4 + x_{i,10}F_{10})}{F_5}; \quad i = A, \dots, H \quad (4.122)$$

$$x_{i,11} = \frac{y_{i,4}F_4 + x_{i,10}F_{10} - y_{i,5}F_5}{F_{11}}; \quad i = D, \dots, F; \quad (4.123)$$

$$x_{i,11} = \left(1 - \sum_{j=D}^F x_{j,11} \right) \frac{N_{i, str}}{\sum_{j=D}^H N_{j, str}}; \quad i = G, H \quad (4.124)$$

◆ **Step 2.7.** Model Solution.

Due to the complexity of the system, the information generated from *Stage 1* will be helpful in order to guide/identify the solution's location of the system.

With the modifications made by Jockenhövel et al. (2003), there are 30 states, and 11 manipulated variables, compared with the model in Ricker and Lee (1995a, 1995b) which has 26 states and ten manipulated variables.

As it was done in steps [1.6] and [1.7], the model equations (4.82)–(4.124) are presented at steady state in a vectorial form, thus

$$\mathbf{0} = \mathbf{f}[\mathbf{x}, \mathbf{u}, \mathbf{p}] \quad (4.125)$$

$\mathbf{x} = [\mathbf{x}_s, \mathbf{x}_p]$ where

$$\mathbf{x}_s = [T_m, T_r, T_s, T_{str}, N_{i,m}, N_{i,r}, N_{i,s}, N_{G,str}, N_{H,str}]^T; i = A, \dots H \quad (4.126a)$$

$$\mathbf{x}_p = [F_5, F_6, F_7, P_m, P_r, P_s, T_8, T_{cw,r,out}, T_{cw,s,out}, V_{l,r}, V_{v,r}, V_{l,s}, V_{v,s}, V_{l,stri}, \\ H_i, HoV_s, HoV_{str}, \dot{Q}_r, \dot{Q}_s, \dot{Q}_{str}, \Delta T_{1,r}, \Delta T_{2,r}, \Delta T_{1,s}, \Delta T_{2,s}, \\ p_{i,r}, p_{i,r}^{sat}, p_{i,s}, p_{i,s}^{sat}, x_{i,r}, x_{i,10}, x_{i,11}, y_{i,5}, y_{i,6}, y_{i,7}, y_{i,8}, y_{i,9}, \\ R_k, \Delta H_{r,k}, \Phi_i]^T; i = A, \dots H, k = 1 \dots NR \quad (4.126b)$$

$$\mathbf{u} = [F_1, F_2, F_3, F_4, F_8, F_9, F_{10}, F_{11}, m_{cw,r}, m_{cw,s}, m_{cw,stri}]^T \quad (4.127)$$

$$\mathbf{p} = [T_1, T_2, T_3, T_4, T_{cw,r,in}, T_{cw,s,in}, V_m, V_r, V_s, UA_r, UA_s, R_g, \kappa, \rho_r, \rho_s, \rho_{stri}, \\ A_i, B_i, C_i, Cp_i^l, Cp_i^v, Cp_{cw}, HoF_k, H_{vap,i}, x_{i,1}, x_{i,2}, x_{i,3}, x_{i,4}, \gamma_{i,r}, \gamma_{i,s}, \\ \epsilon_k, a_{c,j}]^T; c = D, \dots H, i = A, \dots H, j = 0, \dots 3, k = 1, \dots NR \quad (4.128)$$

The state vector \mathbf{x} is comprised of 30 state variables (\mathbf{x}_s) and 129 process variables (\mathbf{x}_p); vector \mathbf{u} contains 11 design variables, and 100 properties and parameters of the system listed in vector \mathbf{p} (Tables D.4–D.8 in Appendix D provides the values for these variables). The system consists of 270 variables and 159 equations. Thus, $N_{DOF} = 111$. Therefore, by specifying vector \mathbf{u} and \mathbf{p} for different process specifications the system can be solved.

A *sequential modular* approach has been used to solve the steady-state model (Eqs. (4.125)). Here, the selection of dependent and independent variables becomes simpler (Wells and Rose 1986), if it is assumed that all equipment models are written as simulation models, i.e., the output flows are calculated from given input flows and conditions and for given dimensions of equipment. All input

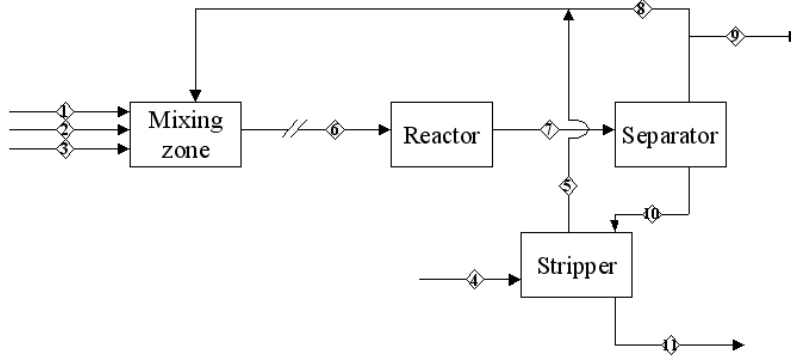


Figure 4.33: Modular flowsheet for TE-Problem.

flows and equipment dimensions are independent variables, specified by the “user”, and all equipment outlet streams are dependent variables. However, when recycle flows appear, it is necessary to apply *tearing* techniques (Sargent

and Westerberg 1964) in order to initialise appropriately the flowsheet, which leads to the use of iterative procedures until convergence is found in a “convergence block”. Figure 4.33 presents a scheme with the corresponding simulation modules that were used. Since a recycle process is dealt with, there is the need to select a tear stream in order to partition the flowsheet and give a sequence of solution. The common selection when only one loop is encountered is the stream entering the reactor, which in this case is stream 6.

Therefore, the corresponding module (unit) calculation sequence is: *Reactor* → *Separator* → *Stripper* → *Mixing zone*. After solution of each unit, the connectivity information, i.e., inlet flowrate, P and T becomes available for the following unit. Successive iterations are performed until the difference between iterations reaches a given tolerance value ε (1×10^{-4}) in stream 6.

◆ **Step 2.8.** Model Analysis.

▷ **Step 2.8.1.** Analysis.

Three different operation modes were analysed in this process. Table 4.4 lists the manipulated variables (vector \mathbf{u}) corresponding to these modes (Ricker and Lee 1995b).

Table 4.4: Manipulated variables for operation modes.

Input	Units	Base case	Mode 1 (50/50)	Mode 2 (10/90)
F_1	kmol/h	11.200	11.991	13.848
F_2	kmol/h	114.500	114.314	22.948
F_3	kmol/h	98.000	96.471	174.679
F_4	kmol/h	417.500	413.782	383.109
F_8	kmol/h	1201.500	1441.021	1419.501
F_9	kmol/h	15.100	9.497	16.164
F_{10}	kmol/h	259.500	253.563	243.825
F_{11}	kmol/h	211.885	210.885	194.638
$m_{cw,r}$	m ³ /h	93.70	75.40	62.95
$m_{cw,s}$	m ³ /h	49.37	52.02	47.40
$m_{cw,str}$	kg/h	230.31	4.74	4.90

In this respect, the results obtained from the *modular* approach for these operation modes in terms of streams compositions and flowrates are given in Tables 4.5–4.7.

On the other hand, the energy balances have been included with the aim to account with a model that is able to reproduce in a more realistic manner the behaviour of the process. Thereby, Table D.9 in Appendix D shows the solutions of the state vector \mathbf{x}_s obtained with the non-isothermal model (this work based on Jockenhövel et al. (2003)) and the reported values for the isothermal model (Ricker 1995) for the three operation modes analysed. As it can be seen, some of the major differences are in the product separator, where the vapour-liquid equilibrium is playing a key role as well as the amount of liquid that is vaporised. These differences can be assigned, mainly, due to the addition of energy balances to the process model.

Table 4.5: Base case results.

Component	Mole fraction $y_{i,j}$ in streams						
	5	6	7	8	9	10	11
A	0.45744	0.31928	0.27178	0.31724	0.31724	0.00000	0.00000
B	0.00448	0.07872	0.10765	0.12249	0.12249	0.00000	0.00000
C	0.43457	0.24844	0.18457	0.22363	0.22363	0.00000	0.00000
D	0.00124	0.07024	0.01030	0.01508	0.01508	0.00242	0.00024
E	0.07211	0.19793	0.18477	0.20286	0.20286	0.13427	0.00598
F	0.01197	0.02431	0.02702	0.03372	0.03372	0.02232	0.00104
G	0.02314	0.04659	0.13179	0.06456	0.06456	0.55138	0.54651
H	0.00630	0.01449	0.08212	0.02042	0.02042	0.28961	0.44623
Flow =	465.7	1892.102	1476.0	1201.5	15.1	259.5	211.3
mass $S_{G/H}$ =	0.999104						
Flowrate [=] kmol/h, mass $S_{G/H} = (y_{G,11}MW_G)/(y_{H,11}MW_H)$							

Table 4.6: Mode 1. 50/50 G/H mass ratio results.

Component	Mole fraction $y_{i,j}$ in streams						
	5	6	7	8	9	10	11
A	0.43965	0.32346	0.28053	0.32959	0.32959	0.00000	0.00000
B	0.00453	0.14777	0.18403	0.21655	0.21655	0.00000	0.00000
C	0.46232	0.18947	0.11387	0.13307	0.13307	0.00000	0.00000
D	0.00072	0.05933	0.00587	0.00798	0.00798	0.00140	0.00014
E	0.05666	0.16522	0.15097	0.15885	0.15885	0.10569	0.00443
F	0.01939	0.04123	0.05199	0.05467	0.05467	0.03622	0.00160
G	0.02067	0.04979	0.1291	0.0669	0.0669	0.48395	0.60702
H	0.00826	0.02373	0.08363	0.03239	0.03239	0.37273	0.38682
Flow =	456.46	2125.822	1707.081	1441.021	9.40888	253.563	210.885
mass $S_{G/H}$ =	1.280171						
Flowrate [=] kmol/h, mass $S_{G/H} = (y_{G,11}MW_G)/(y_{H,11}MW_H)$							

Table 4.7: Mode 2. 10/90 G/H mass ratio results.

Component	Mole fraction $y_{i,j}$ in streams						
	5	6	7	8	9	10	11
A	0.42958	0.34465	0.30864	0.36252	0.36252	0.00000	0.00000
B	0.00443	0.07869	0.09704	0.11352	0.11352	0.00000	0.00000
C	0.45172	0.19418	0.12464	0.14587	0.14587	0.00000	0.00000
D	0.00005	0.01153	0.00107	0.00059	0.00059	0.00010	0.00001
E	0.08549	0.26240	0.22146	0.23337	0.23337	0.15672	0.00726
F	0.02776	0.05793	0.07249	0.07610	0.07610	0.05097	0.00246
G	0.00399	0.00920	0.02492	0.01222	0.01222	0.09458	0.11842
H	0.01527	0.04142	0.14974	0.05581	0.05581	0.69763	0.87184
Flow =	430.4475	2062.893	1683.037	1413.116	16.09766	243.825	194.638
mass $S_{G/H}$ =	0.110807						
Flowrate [=] kmol/h, mass $S_{G/H} = (y_{G,11}MW_G)/(y_{H,11}MW_H)$							

▷ **Step 2.8.2.** Identification of operational targets.

Steps [2.1] and [2.2] identify the operating targets. However, for this problem the design targets are defined in advance (Table 1 in Downs and Vogel (1993)), i.e., a G/H mass ratio 50/50 (Base case scenario).

◆ **Step 2.9.** Simulations Agreement.

Figure 4.34 compares the results obtained with the simple (*Stage 1*) and de-

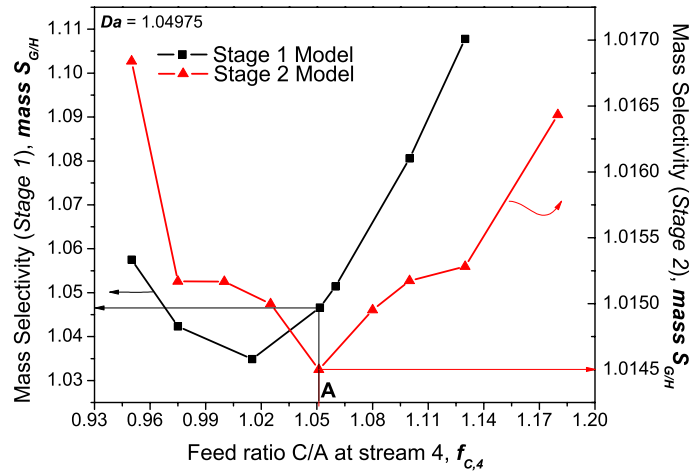


Figure 4.34: G/H Mass ratio as function of feed inlet ratio $f_{C,4}$.

tailed (*Stage 2*) models as function of the ratio of component C with respect to component A in stream 4, $f_{C,4}$ ($y_{C,4}/y_{A,4}$). As it can be seen, both curves follow the same trend, although the mass selectivity values ($mass S_{G/H}$) obtained from the two models do not match. This is not surprising as these differences are due to the simplifications made in *Stage 1* model, particularly, in the separation section, where the effects of the vapour/liquid separator and stripper are lumped into a ‘simple’ separation factor $\alpha_{i,7}$, thus thermodynamics effects and inherent nonlinearities were hidden.

Nevertheless, it is considered that *Stage 1* model is, to some extent, representative of the behaviour of the process and, therefore, it has been decided to proceed further with the analysis of the detailed model.

The flow ratio $f_{C,4}$ is considered a process disturbance (IDV(1)), therefore it is important to know its effect on the performance of the system. Point A in Fig. 4.34 is the nominal operating point (Base-case scenario) for the above-mentioned flow ratio. From Fig. 4.34 it can be seen that, if there was an interest to increase the selectivity of G to H, there exists the possibility to achieve such condition at two different $f_{C,4}$ values, although, two different production rates will also be achieved.

◆ **Step 2.10.** Storage of Information.

At this point of the model-based Methodology, it has been possible to determine the operating conditions at the Base case scenario from the *Stage 2* model but also, it has been possible to know the possible process behaviour under the actual variation in some of the variables of the process that were possible to acknowledge from the simple model, leading to reach a characterization of the process in terms of flowrates, P and T in all the streams of the process.

4.3.1.3 Stage 3. Verification.

The objective of this stage is that, from the development and analysis of simple and detailed models, it would become easier the validation of the actual process behaviour through the use of more rigorous models either by dynamic or steady state simulations. Another objective is that, from the information generated by *Stage 1* and *2* models, it would be possible to outline an appropriate control structure for a given design target(s), because of the static responses of the system are known from the analysis of sensitivity performed.

◆ **Step 3.1.** Flowsheet set up.

Figure 4.22 remains without change. For the TE-problem, due to proprietary reasons, the amount of information is limited, making the use of a commercial process simulator infeasible.

◆ **Step 3.2.** Generated knowledge from previous stages.

Given the above-mentioned reasons, the model implemented in *Stage 2* will be considered as the “rigorous” model, since it reproduces the data from the literature. On the other hand, from the analysis in *Stages 1* and *2*, the design decisions have also been verified by the use of static models.

◆ **Step 3.3. and 3.4.** Simulation and Verification of the Results.

This particular case study has the characteristic of its unstable performance in the open-loop. Consequently, it is important to analyse the dynamic behaviour of the system. In this respect, the nonlinear model represented by Eqs. (4.125) is presented now in its dynamic form,

$$\frac{d\mathbf{x}_s}{dt} = \dot{\mathbf{x}}_s = \mathbf{f}[\mathbf{x}, \mathbf{u}, \mathbf{p}] \quad (4.129)$$

$$\mathbf{y} = \mathbf{h}[\mathbf{x}, \mathbf{u}, \mathbf{p}] \quad (4.130)$$

where vectors \mathbf{x} , \mathbf{u} , \mathbf{p} remain without change in Eqs. (4.126a)–(4.128), respectively and vector \mathbf{y} stands for the output variables (variables to be measured) which is a function \mathbf{h} of the state variables \mathbf{x} , the manipulated variables vector \mathbf{u} and system parameters vector \mathbf{p} . Equation (4.131) lists the variables considered in the output vector \mathbf{y} .

$$\mathbf{y} = [F_{11}, P_r, T_r, T_{str}, V_{l,r}, V_{l,s}, V_{l,str}, y_{B,9}, y_{C,9}]^T \quad (4.131)$$

Consequently, the dynamic model has 30 ODEs (states) and 129 AEs with 11 control variables.

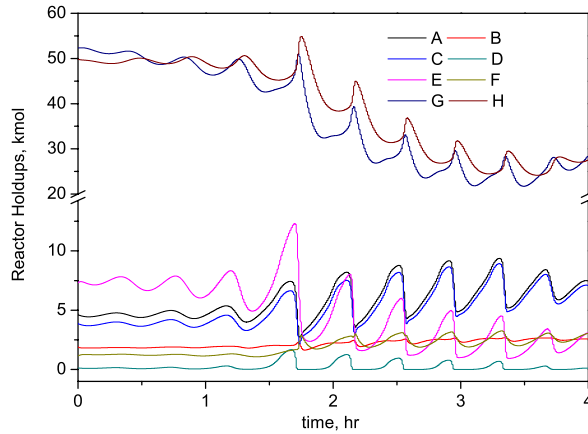


Figure 4.35: Reactor holdups profiles for the Base case.

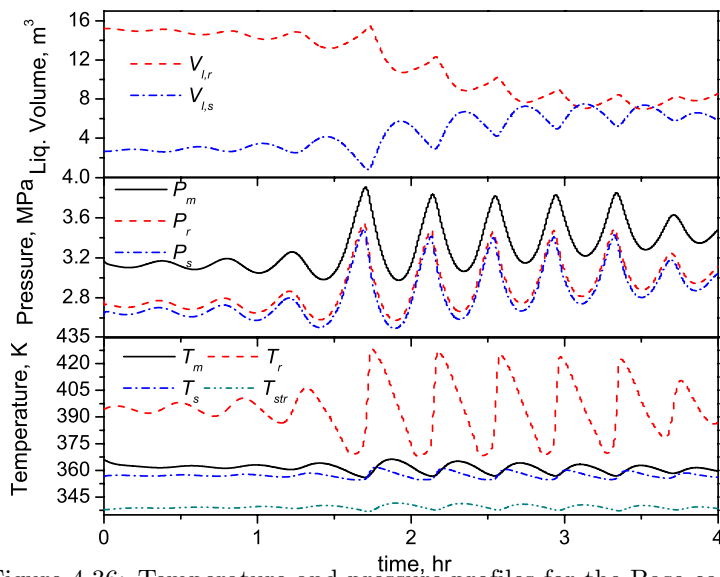


Figure 4.36: Temperature and pressure profiles for the Base case.

Figures 4.35 and 4.36 show the (open-loop) dynamic response for the reactor holdups, as well as the temperature, liquid volume and pressure profiles in the equipments, respectively. It is observed that there are small oscillations with increasing amplitude in the profiles during the first hour of operation. After this initial period, the amplitude of the oscillations increases substantially, mainly, in the reactor temperature. Hence, the instability of the process is confirmed

because the safety limits has been reached and therefore the operation has to be shut down.

In Fig. 4.37 the phase-planes of components A and G holdups with respect to the reactor temperature are presented. The limit-cycles found are a clear indication of the (open-loop) unstable nature of the process. Within the first

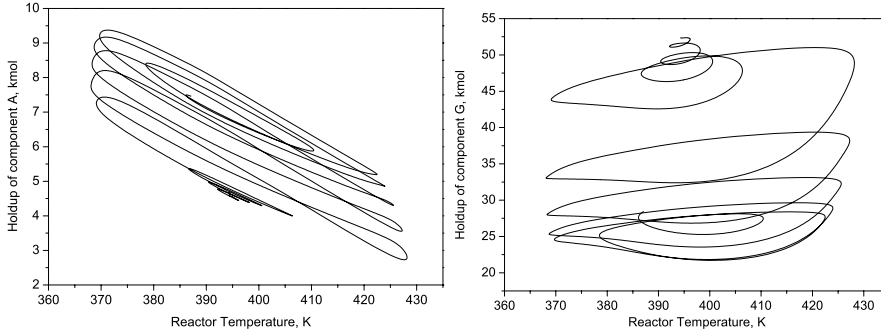
(a) $N_{A,r}$ vs. T_r (b) $N_{G,r}$ vs T_r

Figure 4.37: Limit cycles of the Base case scenario.

hour of operation, the system oscillates around a point relatively close to the steady-state value but as the time proceeds the cycles increase considerably.

Now, if Eqs. (4.129)-(4.130) are linearized around a given operating point (ss), thus

$$\begin{aligned}\frac{dx}{dt} &= \left. \frac{\partial f}{\partial x} \right|_{ss} (x - x_{ss}) + \left. \frac{\partial f}{\partial u} \right|_{ss} (u - u_{ss}) \\ y &= \left. \frac{\partial h}{\partial x} \right|_{ss} (x - x_{ss})\end{aligned}$$

therefore,

$$\begin{aligned}\frac{dx}{dt} &= \mathbf{A}(x - x_{ss}) + \mathbf{B}(u - u_{ss}) \\ y &= \mathbf{C}(x - x_{ss})\end{aligned}$$

where \mathbf{A} is an $n \times n$ state matrix, \mathbf{B} is an $n \times r$ input matrix, and \mathbf{C} is an $m \times n$ output matrix, all of them evaluated at a given steady-state for n states, r inputs and m outputs. Therefore, another test to verify the stability of a process is the analysis of the eigenvalues (λ_i) of the Jacobian of the plant (matrix \mathbf{A}) evaluated at the steady-state. In Table 4.8 the eigenvalues for matrix \mathbf{A} at the Base case scenario are listed. In this case, five positive values appear: the pair-conjugate $\lambda_{14}-\lambda_{15}$, λ_{23} , λ_{24} and λ_{26} . These results are an indication of the instability of the process, which it has been shown also through the dynamic simulations.

With respect to the operability of the system, it is necessary that all unstable states are observable, i.e. that plant is *detectable* and that these states also are

Table 4.8: Eigenvalues of \mathbf{A} for the Base case.

$\lambda_1 = -0.42525$	$\lambda_{11} = -0.01625 - 0.001685i$	$\lambda_{21} = -0.00176$
$\lambda_2 = -0.20689$	$\lambda_{12} = -0.00807$	$\lambda_{22} = -0.00065$
$\lambda_3 = -0.09266$	$\lambda_{13} = -0.00806$	$\lambda_{23} = 0.00044$
$\lambda_4 = -0.04290$	$\lambda_{14} = 0.00106 + 0.00369i$	$\lambda_{24} = 0.00041$
$\lambda_5 = -0.03216 + 0.00011i$	$\lambda_{15} = 0.00106 - 0.00369i$	$\lambda_{25} = -5.382 \times 10^{-5}$
$\lambda_6 = -0.03216 - 0.00011i$	$\lambda_{16} = -0.00396 + 0.00128i$	$\lambda_{26} = 6.125 \times 10^{-6}$
$\lambda_7 = -0.02236$	$\lambda_{17} = -0.00396 - 0.00128i$	$\lambda_{27} = -3.753 \times 10^{-6}$
$\lambda_8 = -0.01941 + 0.00671i$	$\lambda_{18} = -0.00404$	$\lambda_{28} = -3.845 \times 10^{-5}$
$\lambda_9 = -0.01941 - 0.00671i$	$\lambda_{19} = -0.00371$	$\lambda_{29} = -2.227 \times 10^{-5}$
$\lambda_{10} = -0.01625 + 0.00169i$	$\lambda_{20} = -0.00299$	$\lambda_{30} = -2.164 \times 10^{-5}$

controllable, i.e. that plant is *stabilizable*. However, such analysis has not been carried out within this work.

◆ **Step 3.5.** Storage of Information.

Several tests have been performed (open-loop simulations, eigenvalues analysis, controllability matrix analysis) validating the unstable nature of the TE-Problem. It has been verified as well that, as Downs and Vogel (1993) and Ricker and Lee (1995b) point out, after the first hour of operation the process starts to become unstable reaching the safety limits, therefore the operation has to be shut down.

From the previous analysis it is possible now to relate the different effects encountered in order to outline a control structure which leads to a feasible control strategy. This is done in the following.

4.3.1.4 Control Structure Implications.

The purpose of this section is to try to relate the insights obtained from the models developed in *Stage* 1 and 2 and their corresponding analysis with a sketch of a control structure. While the following description relies on the procedure developed by Luyben et al. (1998) for the synthesis of a control structure, it will become more clear that the selection of the manipulated and controlled variables can be facilitated through the information (insights) generated through the model-based Methodology. It is also intended to show how the degrees of freedom in the control problem can be fulfilled with the knowledge obtained through the model-based Methodology.

The plant Da number (Eq. (4.62)) assesses the ratio of the rate of reaction with respect to the feed to the process of one of the limiting reactants. In the analysis carried out, the Da number assumed P_r and V_r were kept constants, as well as the temperature at the inlet of the reactor (T_m). Therefore, a variation in the Da number can be interpreted, mainly, as a change in the feed of A to the plant. Ricker and Lee (1995b) assumed that T_m remained constant through the calculations and scenarios analysed. In this context, for this di-

mensionless group, the manipulated variables would be $F_{A,1}$ and the variables to be controlled would be P_r .

The mcp_{cw} variable relates the feed of cooling water to the reactor with respect to the feed of component A to the process. The analysis in this dimensionless variable reveals that the heat removal of the reactor (\dot{Q}_r) is affected due to changes on $T_{cw,r,out}$. Lyman et al. (1996) proposed to control $T_{cw,r,out}$ via $m_{cw,r}$ in an inner loop and in the master loop T_r would be controlled by the manipulation of $T_{cw,r,out,sp}$. It is logic to expect that, the more heat removed from the reactor, the lower selectivity obtained.

In *Stage 1*, the separation was modelled through the recovery factors $\alpha_{i,7}$, which help to determine the process conditions in order to achieve a given set of specifications. Note that the recovery factors are defined as the ratio of component i 's flowrate in the recycle stream with respect to component i 's flowrate from the reactor. Therefore, their control implications can be understood as to control the inventories through the plant in order to satisfy the product specifications. For example, in the control structure proposed by Luyben et al. (1998) the gas recycle (F_8) is used to control the yields; Lyman et al. (1996) use a temperature controller to manipulate the steam flowrate in order to control the composition of E at the bottom of the stripper. Both Luyben and Lyman use the purge flowrate (F_9) in order to maintain the composition of B, the former in the purge stream and the later in the recycle stream. On the other hand, since the recycle stream is in gas phase, the possibility to control either pressure or temperature through the cooling water in the separator or through the steam in the stripper are considered.

The flow ratio analysis helps to evaluate the process response under different feeds of reactants (disturbance) to the system. It can also help to determine appropriate set points in order to maintain a given operating condition, such as compositions or flowrates. In step 6 of Luyben et al.'s (1998) procedure it is required to fix a flow in every recycle loop, then to select the best manipulated variables to control inventories (pressures and levels). Based on this, Luyben et al.'s (1998) select the ratio $F_{D,2}/F_{E,3}$ ($(y_{D,2}F_2)/(y_{E,3}F_3)$) to control the liquid level in the reactor, as well as to maintain the desired product distribution G and H. In the analysis carried out in this case study, the flow ratio considered was mainly with respect to component A. This analysis revealed that, in the case of f_C , as the ratio was increased, the selectivity also increased. This is not surprising, since the more C fed, the larger the production of G. Consequently, the heat duty increases since the first reaction is the most exothermic. In this respect, the heat duty in the reactor can be seen as an indirect indication of changes in the level of the reactor.

Given the above considerations, in Table 4.9 is shown the control structure proposed for the TE-problem. It can be seen from Table 4.9 that most of the degrees of freedom for the control problem are covered through the model-based analysis of the process. However, the remaining degrees of freedom to be fulfilled follow a logical sequence. For instance, the flowrate product (F_{11})

Table 4.9: Control Structure proposal for TE-Problem.

u_{S1}	Meaning		u_{S2}	y_{S2}	y^*
Da	Reaction rate w.r.t. feed rate (process)	$k(f(P_r))$ w.r.t. $F_{A,1}$	$F_{A,1}$	P_r	$y_{A,9}$
mcp_{cw}	Reactor Heat removal	$m_{cw,r}$ w.r.t. $F_{A,1}$	$m_{cw,r}$	T_r	T_r
$\alpha_{i,7}$	Recovery of i from sep. section	$F_{i,rec}$ w.r.t. $F_{i,r}$	$m_{cw,s}$ $m_{cw,str}$	$V_{l,s}$ T_{str}	$V_{l,s}^\dagger$ T_{str}
f_i	Feed flow ratio	$F_{i,in}$ w.r.t. $F_{A,1}$	$F_{D,2}/F_{E,3}$	$V_{l,r}$	$V_{l,r}$
σ	Purge factor	F_9 w.r.t. $F_{top,s}$	F_9 F_{11} F_{10} F_8 $F_{C,4}$	$y_{B,9}$ F_{11} $V_{l,str}$ $yields$ $y_{C,9}$	$y_{B,9}$ F_{11} $V_{l,str}$ $yields$ P_r

S1 = Stage 1; S2 = Stage 2

† = Luyben uses the cooling water flow to the condenser

* = Luyben et al. (1998)

is actually the control objective, then this is set on flow control. The control of the level of the stripper ($V_{l,str}$) can be paired with the bottom flow from the separator (F_{10}), since the steam flow to the stripper has already been used to control the temperature (T_{str}). Douglas (1988) recommends to keep the valve wide open (maximising the flow) in gas recycle processes, in order to improve the yields. Therefore, one degree of freedom is removed. The remaining variable $F_{C,4}$, given that it is the largest gas feed, it will be used to control the inventory of C through the system. In Fig. 4.38 is shown the control structure applied to this system.

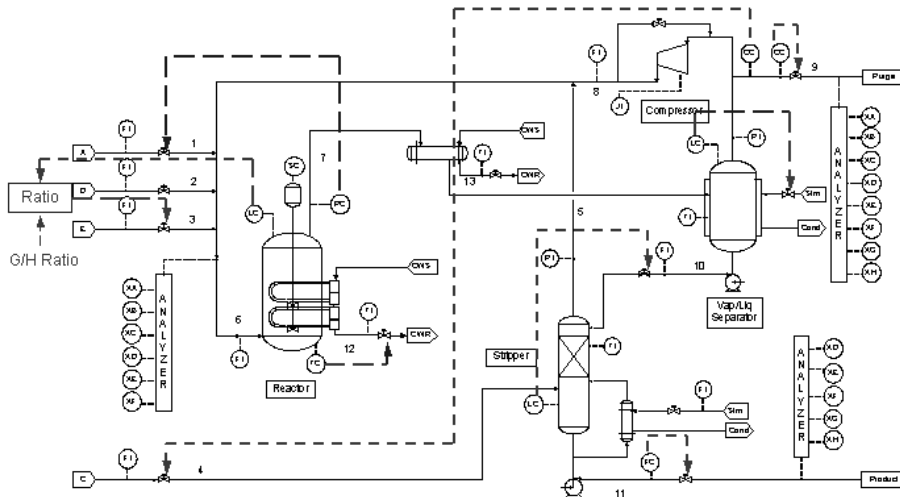


Figure 4.38: Control structure proposed for the TE-Problem.

Based on this control structure proposal (see Table 4.9), in Fig. 4.39 are shown the dynamic trajectories in the closed-loop for the (controlled) output variables (\mathbf{y}). The simulations were performed only for the Base case scenario.

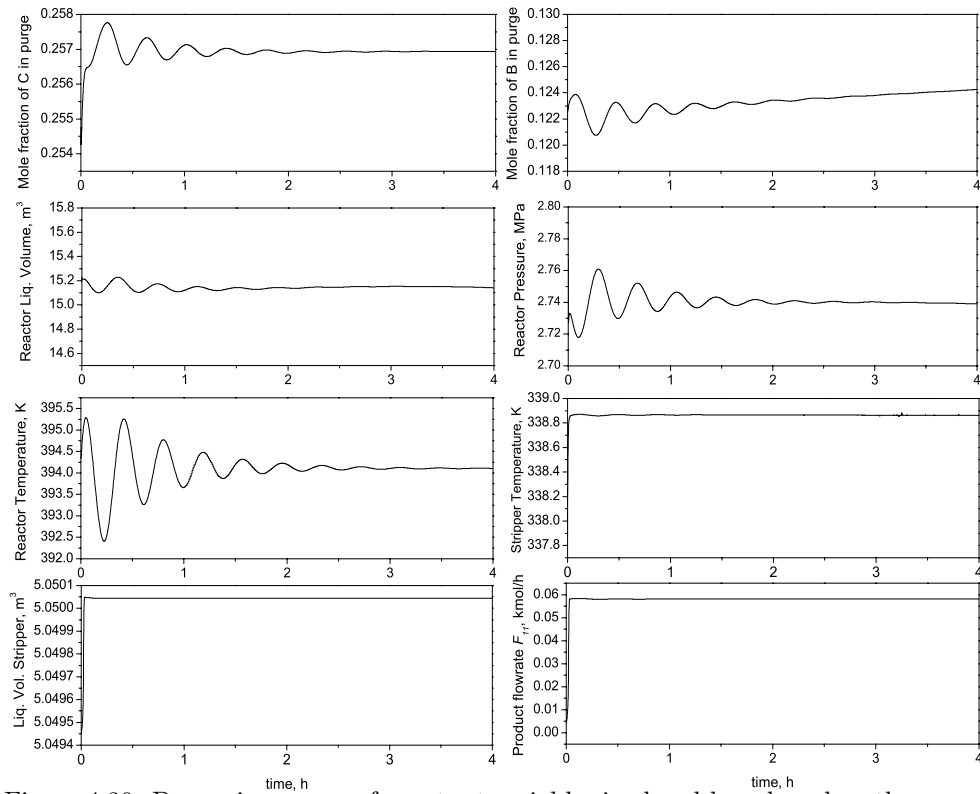


Figure 4.39: Dynamic response for output variables in closed-loop based on the control structure proposal at the Base case.

It is important to remark that only *proportional* controllers have been used to control the system. As it can be seen, the output variables (\mathbf{y}) result adequately controlled based on this implementation, thereby, verifying the insights generated from the model-based Methodology.

4.3.1.5 Case Summary.

In the present case study it has been demonstrated how through the model-based analysis it is possible to start from a conceptual design to the point where the implementation of a control strategy is devised in order to achieve (or maintain) a given set of design targets.

The TE-problem represents a quite interesting problem of integration in that, through the mode-based Methodology, it was possible to identify some of the

underlying phenomena involved. Most of the research conducted for the TE-problem addresses, mainly, the control problem. However, little attention has been paid to design related issues, which are a necessary step in order to carry out successive control studies. On the other hand, even though the control structure proposed turned out to be similar to Luyben et al.'s (1998), it was intended that the synthesis of the control structure followed a more fundamental basis, as it was done through the model-based analysis instead of from *a priori* knowledge.

With this example it was also demonstrated how the model-based analysis helps to verify the design decisions that have to be made in the modelling stages, but also, to relate (integrate) the design and control problems simultaneously as an ultimate objective of this work.

Conclusions

5.1 Main achievements

A model-based Methodology for the design and analysis for Reaction-Separation with Recycle systems has been developed. The Methodology consists of a systematic model-based analysis of a specified process flowsheet, at three levels (stages) of complexity to identify operational limits (through lumped variables) as well as feasible “near” optimal conditions of operation (via delumped variables).

The integrated design-analysis/control problem is not trivial and the strategy of its solution can be defined in different ways. Mathematical approaches trying to integrate simultaneously the design and control problem, while powerful, require good estimates of the solution, which makes it difficult to obtain the optimal solution (a global optimum) without insights to guide the solver towards the solution path. On the other hand, heuristics-based approaches rely on researcher’s experience, rules of thumb or similar worked-out problems. It is important to stress that it is not the intention in this Ph.D.-thesis to disregard any of the two solution approaches and/or the advantages that can be obtained from them. In this Ph.D.-thesis, emphasis is given to the development of (first-principles) models and their corresponding analysis that can, in principle, achieve similar goals.

Simple, yet appropriate models, in terms of dimensionless variables, that were developed in case studies 1 and 2, helped to highlight the potential of lumped variables-based models in identifying operability and feasibility issues of the process, as well as determining the limiting operational conditions that can be derived from them (i.e., operational windows). However, with the aim to determine an ‘optimal’ (or near-optimal) operation based on a *design* target for the RSR system, more detailed models were developed through *Stage 2*, which incorporated not only the actual unit operation models, but also, the most important phenomena characterizing the process operation. Despite the complexity of these models from *Stage 2*, their solution space has been found to be bounded through analysis of *Stage 1* model, establishing thereby, the importance of the operational windows and their effect when used as a guide for

a new design (or when the process faces a disturbance). The combined results from *Stage 1* and *Stage 2* models led to the development of operating policies ensuring the achievement of the *design* target. These features were highlighted through case studies 1-3. In particular, the Ethylbenzene production (Case study 3) turned out to be an interesting design exercise, where, first conceptual design issues (*Stage 1*) were investigated, followed by the implementation of more detailed models and the determination of an operating point (*Stage 2*). A final verification (*Stage 3*) of the design decisions by using rigorous models available in process simulation tools (*Stage 3*).

The objective of the TE-problem (Case Study 4) was to highlight the ability of the model-based Methodology to handle the integration of the design and control problems. It can be argued that the *knowledge* generated from the model-based analysis is one of the main ‘results’ of this Ph.D.-thesis, which performs a systematic model-based analysis for the integration of the design and control. Thereby, from the analysis of lumped variables, their physical implication and their impact on the behaviour of the process, the pairing between manipulated (design) variables and controlled (process) variables available become feasible. On the other hand, by developing detailed models in *Stage 2* together with the information generated in *Stage 1*, the fulfillment of the degrees of freedom with respect to the definition of the control problem (design of the control structure) become possible. It is not, however, claimed to have developed a *procedure* for the synthesis of the control structure (see Fisher, et al. (1988c) and Skogestad (2004)), but to sketch their design through the insights generated from the Methodology. The implications of the design decisions on the control problem (and operability) were also demonstrated.

It is important to remark that the model-based Methodology developed, although hierarchical, has its foundations on the development and analysis of the actual process models of the RSR system. Consequently, the interaction between design and process variables can be obtained in an *easier* way. Therefore, the model-based Methodology represents a balance between different available approaches, given that it is neither a pure heuristic-based method nor is it a control-oriented approach and, it is not even a trial-and-error procedure but a Method where the design and control problem issues are addressed systematically and simultaneously helping, as well, to reach a complete characterization and understanding of the process design and operation.

As it has been mentioned in section [3.2.1], the model-based Methodology aims to be an integrating tool because of the use of a series of techniques that help to resolve the integrated design-control problem. That is, by using techniques such as bifurcation analysis or non-linear analysis, it is possible to determine whether a region is stable or not; the use of the AR technique helps to define an optimal operating point in a reactor network; the driving force method helps to select the optimal operation in a separation section. This set

of tools, however, are used *systematically*: step-by-step, stage-by-stage, within the model-based Methodology.

5.2 Challenges and Future work

Several aspects need to be addressed in more detail in the model-based Methodology that, due to the large and complex nature of the problem were not fully treated. For example, even though it was highlighted the use of the AR technique to identify optimal design targets, few attempts have been done when dealing with RSR systems, given its multidimensional nature and interaction of variables that had to be considered within the characteristic and process vectors. Appendix B serves as a case study highlighting the application of the AR technique to a RSR problem from the perspectives of *Stage 1* analysis. In the same context, the driving force method was mentioned but not applied, since the separation scheme in all the case studies was pre-determined and no attempts were made to improve them.

In this Ph.D. thesis the recycle was considered to take place directly from the separation section to the reactor (via a mixing section). However, other chemical processes might present much more complex layouts. Therefore, the interaction between design-process variables and between unit operations may increase considerably due to such connectivity. Also, the case studies presented considered the recycle of mass only, but not energy, which is a very important issue in chemical plants. It can be noted, however, that this issue can be included in steps [1.3] and [1.5] of *Stage 1*, where the ‘thermal effects’ are addressed. Therefore, if a process consists of an energy recycle stream the isothermal assumption should no longer be used and the corresponding model should be developed.

Economic aspects remain untreated within the model-based Methodology. From an operational perspective, the selected (near) ‘optimal’ point could be achieved in more than one way. Therefore, the corresponding economic analysis should differentiate among alternatives, in order to obtain an ‘optimal’ design not only from an operational point of view, but also from an economic perspective. This analysis could be performed after the AR and driving force analyses, because more realistic design targets would then be identified together the operational windows. Note, however, that for the case studies presented, the design targets identified, would not be expected to be different as the mixture to be separated behaved ideally.

The derivation of a procedure for the synthesis of the control structure is a challenging issue. From the dimensionless variables analysis and the insights generated, it was possible to make a proposal, although the procedure was guided by Luyben et al.’s (1998) methodology. However, it can be argued that some guidelines have been established in order carry out further development.

Appendices

A

Application of the AR Technique within the Methodology

As it has been established (see section [3.2]), the objective of *Stage 1* is to identify the design variables through which the limiting and critical conditions in the system can be determined (e.g., critical conversions or operational constraints), opening with this operating windows able to show feasible regions of operation. This is done through the specification of recovery and purge factors, dimensionless variables, etc.

In this sense, *Stage 1* will provide the minimum set of (design and process) variables through which the system can be described, but also show the main interactions that are taking place leading to an initial idea about the control structure required on it.

On the other hand, in *Stage 2*, the objective is to find the design variables that can match the process behaviour (defined by the process variables) and the target values of the *Stage 1* design variables. Thereby, the overall design targets are set, and the values for a minimum set of design and process variables that matches these targets are found. This means that all the design-control structure related decisions needed to make in the early stages of the design has been made. The process can be described in terms of the performance it will give, the values of the design variables that can achieve it, and values of the process variables that will be attained by the process. From a control structure point of view, these process variables will need to be controlled by manipulating the identified design variables. Also, these calculated values correspond to the set-points for the manipulated and controlled variables.

In the Attainable Region (AR) technique (Horn 1964, Glasser and Hildebrandt 1987) the problem proposed is that given a system of reactions with given reaction kinetics, to find all possible concentrations that can be achieved by using any system of steady-flow chemical reactors, by using (mainly) the processes of mixing and reaction only, through the use of a geometric approach; once the region is found, the solution of concentration optimisation problems

is relatively straightforward. Therefore, the optimisation problem to find the optimum reactor network is changed to a “geometric” problem but with the advantage of once the AR is constructed, it is possible to find the reactor network that satisfies the required process specifications instead of solving a new optimisation problem.

Therefore, given the objectives of *Stage 2* and the results that can be obtained from the AR technique, their combination should provide, in principle, an appropriate way to complement the analysis and characterization of a process system.

The following example intends to illustrate the link between the model-based Methodology’s results and the AR analysis.

Let us consider a theoretical first order reaction $A \rightleftharpoons B$ (Glasser, Hildebrandt and Glasser 1992) taking place in a CSTR and may show a flowsheet as in Fig. A.1

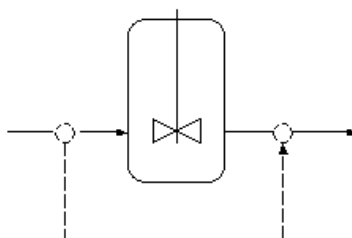


Figure A.1: Reaction system flowsheet

For the construction of the AR the only structure considered will be the CSTR due to the fact that the operation is restricted to this unit. Therefore, in Fig. A.2 a candidate attainable region for the reaction system under consideration is presented.

A desired design objective for this reactive system can be the *productivity*, as defined in Eq. (A.1)

$$P = Q \cdot x_A \quad (\text{A.1})$$

where P = Productivity,
 Q = Volumetric flowrate,
 x_A = Conversion of component A

In particular, there might be the interest to operate at a given productivity value P , the way to achieve this is showed following.

The residence time τ is the relationship between the reactor volume V_r and the volumetric flowrate Q , namely

$$\tau = \frac{V_r}{Q} \quad (\text{A.2})$$

therefore, substituting the value of Q from Eq. (A.1) in Eq. (A.2) and defining

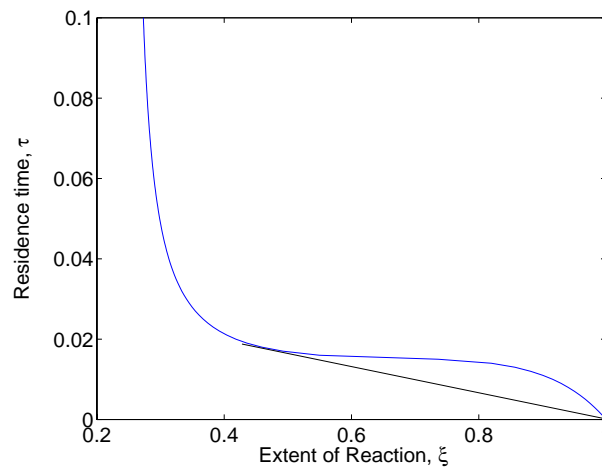


Figure A.2: Candidate Attainable Region for the reaction system.

the extent of reaction ξ as $\xi = 1 - x_A$, yields to

$$\tau = \frac{V_r}{P} - \frac{V_r}{P}\xi \quad (\text{A.3})$$

From Eq. (A.3) there are two variables that can be manipulated, namely the residence time τ and the volume of the reactor V_r . However, V_r is already fixed since the flowsheet has been defined in advance. Therefore, the only degree of freedom in order to achieve a specific value of P is τ , i.e., through the manipulation of the inlet flowrate to the reactor. Figure A.3 illustrates such relation.

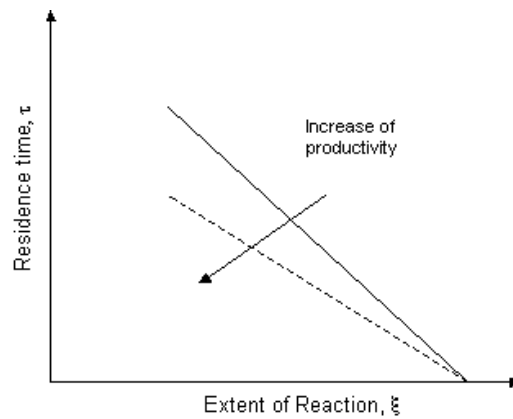


Figure A.3: Relationship of variables to increase productivity.

In this sense, combining the results from Figs. A.2 and A.3, Fig. A.4 is ob-

tained. From Fig. A.4 it can be seen that the line at constant productivity (P) intersects the boundary of the AR at point **A**, thus establishing the operating conditions for the system.

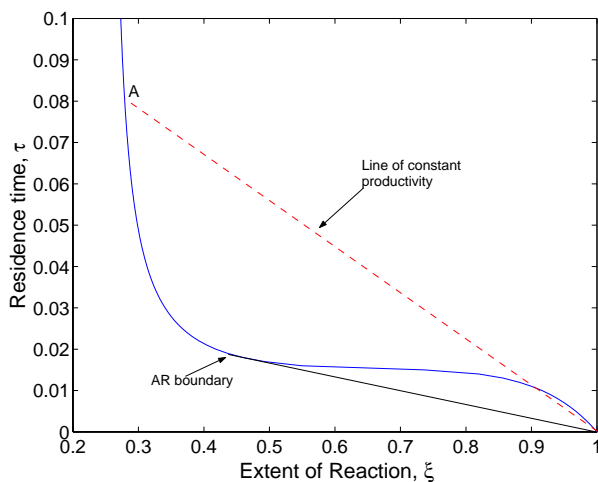


Figure A.4: Combined AR and productivity diagram.

Finally, having found the actual operating conditions at which the system should be operated it will be possible to perform the corresponding simulations in order to characterize completely the system in terms of its design and process variables. Moreover, when these results are mapped onto the operational windows, obtained at *Stage 1*, the feasibility of this particular operating point can be assessed to changes in the design variables.

It is worth to stress that the illustration made in this Appendix follows from an actual analysis carried out on a real system in the Center for Optimisation and Modelling Synthesis at the School for Process and Materials Engineering in the University of Witwatersrand, South Africa.

B

Attainable Region analysis for RSR systems

This Appendix will highlight some results of the AR analysis in RSR systems but from the perspective worked out within the Methodology, this is, by using perfect separators as a means to find delimiting values for the main design as well as process variables. The example to be shown has been previously studied but a sharp splitter is going to be used instead of a phase splitter as in Hildebrandt, McGregor and Glasser's (1998) work.

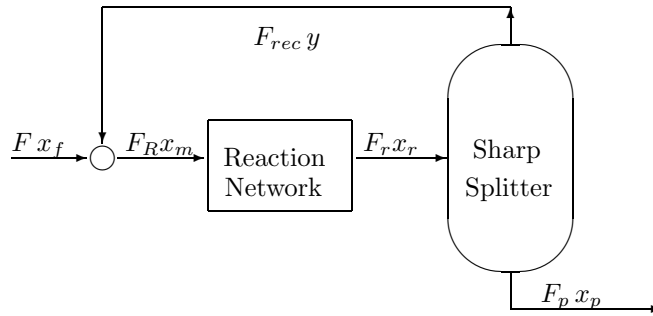


Figure B.1: RSR process layout

The following single exothermic, reversible reaction scheme is employed (Glasser et al. 1992):



with kinetics

$$-r_A = k_1 x_{A,r} - k_{-1}(1 - x_{A,r}) \quad (\text{B.1})$$

the kinetic constants follow Arrhenius expressions with parameters listed in Table B.1.

An overall mass balance on the system shown on Fig. B.1 gives

$$F x_f + \mathbf{r}V_T = F_p x_p \quad (\text{B.2})$$

where x_f and x_p are the molar fractions of component A at the inlet and

Table B.1: Kinetic constants for reversible reaction.

	$A,$ min^{-1}	$E/R_g,$ K
Forward	5×10^9	4000
Backward	5×10^8	8000

product stream, respectively. It is also possible to express Eq. (B.2) as

$$Fx_f + \sum_j r_j \Delta V_j = Fx_p \quad (\text{B.3})$$

for the j th reactor in the reactor network.

If it is assumed that the number of moles does not change and the density remains constant, thus

$$F = F_p \quad (\text{B.4})$$

therefore

$$\begin{aligned} x_f + \tau \mathbf{r} &= x_p \\ \tau \mathbf{r} &= x_p - x_f \end{aligned} \quad (\text{B.5})$$

where τ is the total residence time for the reactor network.

The mass balance around the separator leads to

$$F_r = F_p + F_{rec} \quad (\text{B.6})$$

and by components,

$$F_r x_r = F_p x_p + F_{rec} y \quad (\text{B.7})$$

then, substituting Eq. (B.6) in (B.7)

$$F_r x_r = F_p x_p + (F_r - F_p) y \quad (\text{B.8})$$

Introducing now the definitions of recovery factors for A and B and the split extent change, respectively,

$$\alpha_A = \frac{f_{p,A}}{f_{r,A}} = \frac{F}{F_r} \frac{x_{A,p}}{x_{A,r}} \quad (\text{B.9})$$

$$\alpha_B = \frac{f_{p,B}}{f_{r,B}} = \frac{F}{F_r} \frac{x_{B,p}}{x_{B,r}} \quad (\text{B.10})$$

$$\psi = \frac{F}{F_r} \quad (\text{B.11})$$

it can be seen that

$$\begin{aligned} Fx_{P,A} &= \alpha_A F_r x_{A,r} \\ \sum Fx_{i,p} &= \sum \alpha_i F_r x_{i,r} \\ \therefore \psi = \frac{F}{F_r} &= \sum \alpha_i x_{i,r} \end{aligned} \quad (\text{B.12})$$

Conversely, ψ can also be obtained by

$$\begin{aligned}
 \alpha_A &= \frac{F}{F_R} \frac{x_{A,p}}{x_{A,r}} \\
 x_{A,p} &= \alpha_A \frac{F_r}{F} x_{A,r} = \frac{\alpha_A}{\psi} x_{A,r} \\
 x_{A,r} &= \frac{\psi}{\alpha_A} x_{A,p} \\
 \sum x_{i,r} &= \sum \frac{\psi}{\alpha_i} x_{i,p} = \psi \sum \frac{x_{i,p}}{\alpha_i} \\
 \therefore \psi &= \sum \frac{\alpha_i}{x_{i,p}} \tag{B.13}
 \end{aligned}$$

if Eq. (B.13) is substituted into Eq. (B.8), an expression for the molar fraction of A in the recycle stream can be obtained, this is

$$\begin{aligned}
 x_r &= (F_p/F_r)x_p + [(F_r - F)/F_r] y \\
 x_r &= \psi x_p + (1 - \psi)y \\
 x_r &= \psi \left(\frac{\alpha_A x_r}{\psi} \right) + (1 - \psi)y \\
 y &= x_r \frac{(1 - \alpha_A)}{(1 - \psi)} \tag{B.14}
 \end{aligned}$$

The balance around the mixing point shows that,

$$\begin{aligned}
 (F_r - F)y + Fx_f &= F_r x_m \\
 (1 - \psi)y + \psi x_f &= x_m
 \end{aligned}$$

and by substituting Eq. (B.14) we obtain

$$x_m = \psi x_f + (1 - \alpha_A)x_r \tag{B.15}$$

A mass balance around the reactor network leads now to

$$\begin{aligned}
 F_r(x_m - x_r) &= V_T \mathbf{r} \\
 x_m - x_r &= \tau_T \mathbf{r} \tag{B.16}
 \end{aligned}$$

where τ_T is the total residence time for the reactor network.

Say now that there is the interest to operate a CSTR at its maximum rate of reaction in order to minimise the volume, thus

$$F_r(x_m - x_{max}) = r_{max} V_{\text{CSTR}} \tag{B.17}$$

therefore, substituting Eq. (B.1) yields

$$x_{max} = \frac{(x_m/\tau) + k_{-1}}{(k_1 + k_{-1}) + (1/\tau)} \quad (\text{B.18})$$

If adiabatic operation is assumed, and if the heat of mixing is small compared to the enthalpy of reaction, then the reaction temperature can be related to x_r by:

$$T_r = T_m + T_{ad}(x_m - x_r) \quad (\text{B.19})$$

where T_m is the temperature of the feed to the reactor, T_{ad} is the adiabatic temperature rise if pure A reacts completely to form B and x_m is the mole fraction in the feed to the reactor. Now, the reactor feed fraction x_m and the reactor feed temperature T_m will vary as the recycle ratio and separation products are changed. In order to fix the reactor feed temperature, a heat exchanger could be placed before the reactor. This heat exchanger heats the reactor feed to the temperature that would be obtained if the process feed was adiabatically reacted to form a stream of mole fraction x_m , that is (McGregor 1998):

$$T_m = T_b^\circ + T_{ad}(x_f - x_m) \quad (\text{B.20})$$

where T_b° is the basis temperature, the temperature of the feed to the process. Therefore, the reactor operates on the *adiabat* which originates at the process feed.

Based on the above discussion, the attainable region can now be constructed. Only one mole fraction needs to be included in the characteristic vector since their sum must be unity. The split extent ψ is not included in the characteristic vector since is not part of the objective function given the assumption that the cost of separators is small in comparison to the cost of reactors. The vectors then needed to describe the system are $\mathbf{c} = [x_{A,p}, \tau]$ and $\mathbf{r} = [r_x, 1]$. The fundamental processes allowed to occur are limited to reaction, split change and mixing, reaction occurs in a CSTR and separation in a sharp splitter.

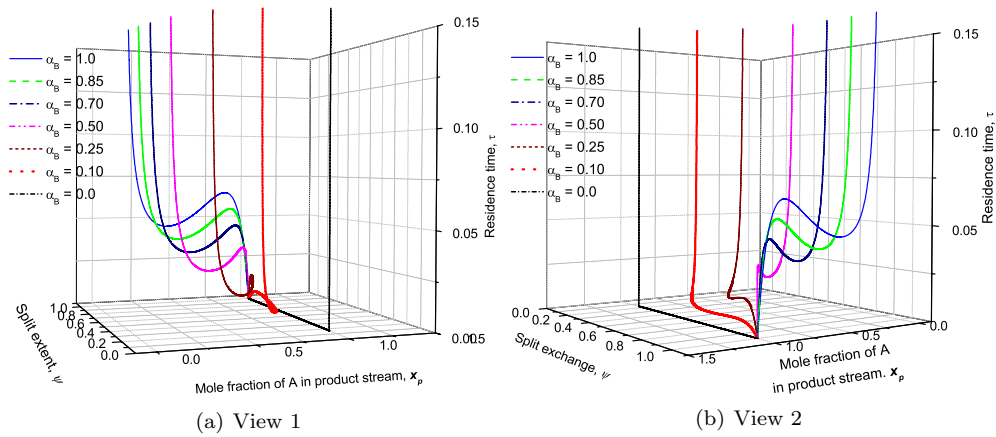
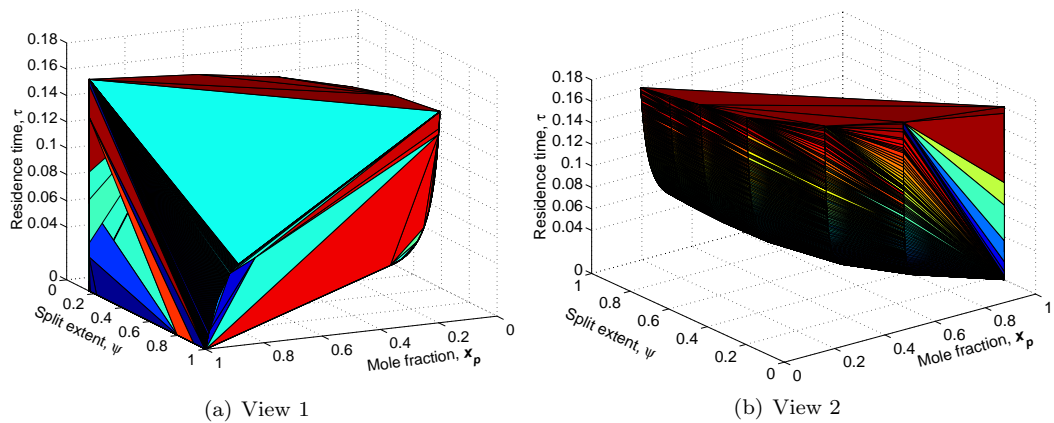
The main objective here will be to maximise the reaction rate as this will minimise the space-time, thus

$$\tau = \frac{x_{A,p}}{r_x(x_{A,r})} \quad (\text{B.21})$$

therefore, the separation should be chosen so as to achieve the above objective, even if this requires an infinite recycle ratio.

In this respect, Fig. B.2 shows a family of CSTR profiles as function of the split extent ψ for a constant recovery of A ($\alpha_A = 1$, i.e., no recycle of A). The corresponding convex hull is shown in Fig. B.3.

However, in order to get a complete description of the system, Fig. B.4 describes the profile of the mole fraction of A in the product stream as function


 Figure B.2: CSTR profiles as a function of ψ ($\alpha_A = 1$).

 Figure B.3: Convex hull considering an $\alpha_A = 1$.

of the recovery factors for A and B. As it can be expected, the more reactant A is recycled back to the reactor ($\alpha_A \rightarrow 0$) the higher the conversion to product B is obtained (for this kind of reactive system).

As a matter of interest, in Fig. B.5 and B.6 are shown the inverse of the reaction rate as a function of the mole fraction of A in the product stream and as function of the split extent, respectively.

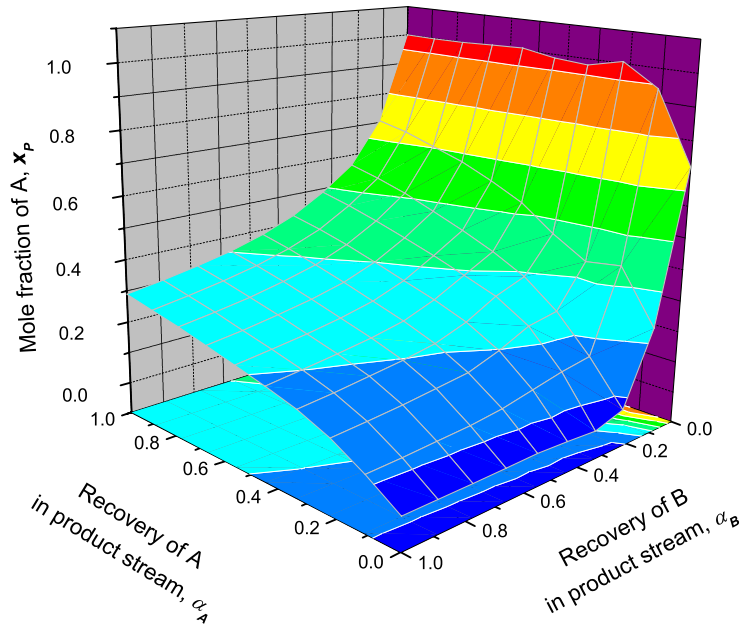


Figure B.4: Mole fraction of A in product stream.

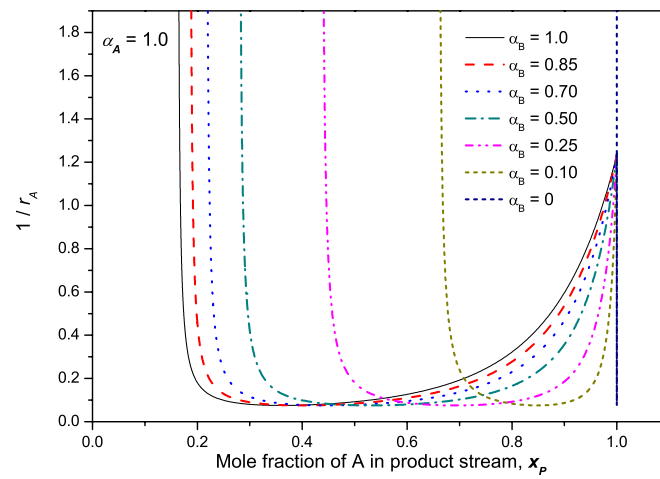


Figure B.5: Rate of reaction as function of Mole fraction in product stream.

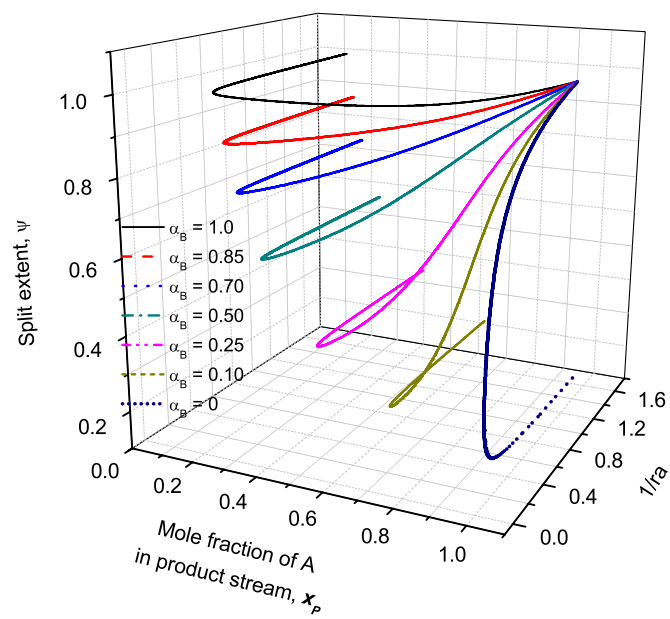


Figure B.6: Rate of reaction as function of Mole fraction and split extent.

C

Derivation details in Equations for Case Study 3

C.1 Derivation of Eqs. (4.16)–(4.18)

Based on the simplified flowsheet described in Fig. 4.12 for the Ethylbenzene production and the assumptions given in step [1.2], the corresponding mass balances are:

► *Mixer.*

$$F_{B,F} + F_{B,Y} = F_{B,M} \quad (\text{C.1})$$

$$0 = F_{EB,M} \quad (\text{C.2})$$

$$0 = F_{DEB,M} \quad (\text{C.3})$$

$$0 = F_{TEB,M} \quad (\text{C.4})$$

$$F_{E,F} + F_{E,Y} = F_{E,M} \quad (\text{C.5})$$

► *Splitter.*

$$F_{B,S} = \beta_{Y,S} F_{B,S} + (1 - \beta_{Y,S}) F_{B,S} \quad (\text{C.6})$$

$$F_{EB,S} = F_{EB,P} \quad (\text{C.7})$$

$$F_{DEB,S} = F_{DEB,P} \quad (\text{C.8})$$

$$F_{TEB,S} = F_{TEB,P} \quad (\text{C.9})$$

$$F_{E,S} = F_{E,Y} \quad (\text{C.10})$$

► *Reactor.*

$$0 = F_{B,M} - F_{B,S} - [k_1 C_{B,S} - k_{-1} C_{EB,S}] V_r \quad (\text{C.11})$$

$$0 = -F_{EB,S} - [(k_{-1} + k_2) C_{EB,S} - (k_1 C_{B,S} + k_{-2} C_{DEB,S})] V_r \quad (\text{C.12})$$

$$0 = -F_{DEB,S} - [(k_{-2} + k_3) C_{DEB,S} - k_{-2} C_{EB,S}] V_r \quad (\text{C.13})$$

$$0 = -F_{TEB,S} - [-k_3 C_{DEB,S}] V_r \quad (\text{C.14})$$

If $F_{B,F}$, k_1 and $C_{B,F}$ are taken as variables of reference, the corresponding mass balance (Eqs (C.1)–(C.14)) in terms of dimensionless variables are:

► *Mixer.*

$$1 + y_B = m_B \quad (\text{C.15})$$

$$0 = m_{EB} \quad (\text{C.16})$$

$$0 = m_{DEB} \quad (\text{C.17})$$

$$0 = m_{TEB} \quad (\text{C.18})$$

$$f_E + y_E = m_E \quad (\text{C.19})$$

► *Splitter.*

$$s_B = \beta_{Y,S} s_B + (1 - \beta_{Y,S}) s_B = y_B + (1 - \beta_{Y,S}) s_B \quad (\text{C.20})$$

$$s_{EB} = p_{EB} \quad (\text{C.21})$$

$$s_{DEB} = p_{DEB} \quad (\text{C.22})$$

$$s_{TEB} = p_{TEB} \quad (\text{C.23})$$

$$s_E = y_E \quad (\text{C.24})$$

► *Reactor.*

$$0 = m_B - s_B - Da [z_{B,S} - K_1^* z_{EB,S}] \quad (\text{C.25})$$

$$0 = s_{EB} + Da [z_{EB,S}(K_1^* + K_2) - (z_{B,S} + K_2^* z_{DEB,S})] \quad (\text{C.26})$$

$$0 = s_{DEB} + Da [z_{DEB,S}(K_2^* + K_3) - K_2 z_{EB,S}] \quad (\text{C.27})$$

$$0 = s_{TEB} - Da [K_3 z_{DEB,S}] \quad (\text{C.28})$$

In multiple reaction systems, the extent of reaction (see Eq. (4.15)) is an appropriate means to take into account the change in the number moles due to reaction. In this respect, Table C.1 summarizes the corresponding mole fractions $z_{i,S}$ for this reactive system.

Table C.1: Table of Moles for Case Study 3

Component	Initial	Final (at stream S)	Mole fraction, $z_{i,S}$	
B	$F_{B,M}$	$F_{B,M} - \xi_1$	$(F_{B,M} - \xi_1)$	$/(F_M - (\xi_1 + \xi_2 + \xi_3))$
EB	0	$0 + \xi_1 - \xi_2$	$(\xi_1 - \xi_2)$	$/(F_M - (\xi_1 + \xi_2 + \xi_3))$
DEB	0	$0 + \xi_2 - \xi_3$	$(\xi_2 - \xi_3)$	$/(F_M - (\xi_1 + \xi_2 + \xi_3))$
TEB	0	$0 + \xi_3$	ξ_3	$/(F_M - (\xi_1 + \xi_2 + \xi_3))$
E	$F_{E,M}$	$F_{E,M} - \xi_1 - \xi_2 - \xi_3$	$(F_{E,M} - \xi_1 - \xi_2 - \xi_3)$	$/(F_M - (\xi_1 + \xi_2 + \xi_3))$
Total	F_M	$F_M - (\xi_1 + \xi_2 + \xi_3)$	1	

Note that ξ_k has units of flow (kmol/h). Therefore, given that the fresh flowrate of B has been taken as a variable of reference, thus

$$\xi_{v,k} = \frac{\xi_k}{F_{B,F}}, \quad k = 1 \dots NR \quad (\text{C.29})$$

Equation (C.29) represents the dimensionless extent of reaction for the k th reaction.

From Table C.1 it can also be seen that the flowrate of B leaving the reactor, in terms of dimensionless variables, is

$$s_B = m_B - \xi_{v,1}$$

but, from (C.20) $y_B = \beta_{Y,S} s_B$, hence

$$s_B = (1 - \xi_{v,1}) / (1 - \beta_{Y,S}) \quad (\text{C.30})$$

Similarly, the flowrate of B into the reactor is

$$\begin{aligned} m_B &= 1 + y_B = 1 + \beta_{Y,S} s_B \\ &= (1 - \beta_{Y,S} \xi_{v,1}) / (1 - \beta_{Y,S}) \end{aligned} \quad (\text{C.31})$$

The reactor outlet flowrate can also be obtained from Table C.1, hence

$$\begin{aligned} s &= m - (\xi_{v,1} + \xi_{v,2} + \xi_{v,3}) \\ &= m_B + m_E - (\xi_{v,1} + \xi_{v,2} + \xi_{v,3}) \end{aligned} \quad (\text{C.32})$$

Note that only Benzene and Ethylene are fed to the reactor, since these are the only components recycled. The reactor outlet flowrate s , based on Eqs. (C.19) (where $f_E = 1$) and (C.30)–(C.31), after rearranging leads to

$$s = 1 + y_E + \left(\frac{1 - \xi_{v,1}}{1 - \beta_{Y,S}} \right) - (\xi_{v,2} + \xi_{v,3}) \quad (\text{C.33})$$

It is possible now to substitute Eq. (C.33) in the corresponding mole fraction expressions in the reactor $z_{i,S}$, thus

$$z_{B,S} = \frac{(1 - \xi_{v,1}) / (1 - \beta_{Y,S})}{1 + y_E + (1 - \xi_{v,1}) / (1 - \beta_{Y,S}) - (\xi_{v,2} + \xi_{v,3})} \quad (\text{C.34})$$

$$z_{EB,S} = \frac{\xi_{v,1} - \xi_{v,2}}{1 + y_E + (1 - \xi_{v,1}) / (1 - \beta_{Y,S}) - (\xi_{v,2} + \xi_{v,3})} \quad (\text{C.35})$$

$$z_{DEB,S} = \frac{\xi_{v,2} - \xi_{v,3}}{1 + y_E + (1 - \xi_{v,1}) / (1 - \beta_{Y,S}) - (\xi_{v,2} + \xi_{v,3})} \quad (\text{C.36})$$

$$z_{TEB,S} = \frac{\xi_{v,3}}{1 + y_E + (1 - \xi_{v,1}) / (1 - \beta_{Y,S}) - (\xi_{v,2} + \xi_{v,3})} \quad (\text{C.37})$$

By substituting Eqs. (C.34)–(C.37) into Eqs. (C.25)–(C.28) and after rearranging yields

$$\xi_{v,1} = \frac{\Omega}{(1 - \beta_{Y,S})} \{1 - \xi_{v,1}(1 + K_1^*(1 - \beta_{Y,S})) + K_1^*\xi_{v,2}(1 - \beta_{Y,S})\} \quad (\text{C.38})$$

$$\xi_{v,2} = \xi_{v,1} + \Omega \left\{ \xi_{v,1} \left(K_1^* + K_2 + \frac{1}{(1 - \beta_{Y,S})} \right) - \xi_{v,2}(K_1^* + K_2 + K_2^*) + K_2^*\xi_{v,3} - \frac{1}{(1 - \beta_{Y,S})} \right\} \quad (\text{C.39})$$

$$\xi_{v,3} = \xi_{v,2} + \Omega \{ \xi_{v,2}(K_2 + K_2^* + K_3) - K_2\xi_{v,1} - \xi_{v,3}(K_2^* + K_3) \} \quad (\text{C.40})$$

where

$$\Omega = \frac{Da}{1 + y_E + (1 - \xi_{v,1})/(1 - \beta_{Y,S}) - (\xi_{v,2} + \xi_{v,3})}$$

Therefore, Eqs. (C.38)–(C.40) are the dimensionless extent of reaction which are shown in Eqs. (4.16)–(4.18) in Case Study 3.

C.2 Derivation of Eqs. (4.21)–(4.24)

In order to determine the location where the concentration of Ethylene is exhausted, the mole fraction $z_{E,S}$ is set to 0, thus

$$z_{E,S} = \frac{m_E - (\xi_{v,1} + \xi_{v,2} + \xi_{v,3})}{s - (\xi_{v,1} + \xi_{v,2} + \xi_{v,3})} = 0 \quad (\text{C.41})$$

since, $m_E = 1 + y_E$, therefore

$$y_E = (\xi_{v,1} + \xi_{v,2} + \xi_{v,3}) - 1 \quad (\text{C.42})$$

Equation (C.42) indicates the recycle flowrate of E at which the Ethylene will be exhausted from the system.

In this sense, by substituting Eqs. (C.38)–(C.40) (or alternatively Eqs. (4.16)–(4.18)) into Eq. (C.42), after rearranging gives

$$y_E = \Omega K_3(\xi_{v,2} - \xi_{v,3}) + \xi_{v,1} + \xi_{v,2} - 1 \quad (\text{C.43})$$

From Eq. (C.43), it can be found the Da number (Da^*) for this operating condition, thus

$$Da^* = \frac{[\xi_{v,1}^* + \xi_{v,2} - (1 + y_E)] [1 + y_E + (1 - \xi_{v,1}^*)/(1 - \beta_{Y,S}) - (\xi_{v,2}^* + \xi_{v,3}^*)]}{K_3(\xi_{v,3}^* - \xi_{v,2}^*)} \quad (\text{C.44})$$

Eq. (C.44) is substituted into Eqs. (C.38)–(C.40), leading to

$$\xi_{v,1}^* = \frac{[\xi_{v,1}^* + \xi_{v,2}^* - (1 + y_E)]}{K_3(1 - \beta_{Y,S})(\xi_{v,2}^* - \xi_{v,3}^*)} [1 - \xi_{v,1}(K_1^*(1 - \beta_{Y,S}) + 1) + K_1^* \xi_{v,2}(1 - \beta_{Y,S})] \quad (\text{C.45})$$

$$\xi_{v,2}^* = \xi_{v,1}^* + \frac{[\xi_{v,1}^* + \xi_{v,2}^* - (1 + y_E)]}{K_3(1 - \beta_{Y,S})(\xi_{v,2}^* - \xi_{v,3}^*)} \left[\xi_{v,1} \left(K_1^* + K_2 + \frac{1}{(1 - \beta_{Y,S})} \right) - \xi_{v,2}(K_1^* + K_2 + K_2^*) + K_2^* \xi_{v,3} - \frac{1}{(1 - \beta_{Y,S})} \right] \quad (\text{C.46})$$

$$\xi_{v,3}^* = \xi_{v,2}^* + \frac{[\xi_{v,1}^* + \xi_{v,2}^* - (1 + y_E)]}{K_3(1 - \beta_{Y,S})(\xi_{v,2}^* - \xi_{v,3}^*)} [\xi_{v,2}^*(K_2 + K_2^* + K_3) - K_2 \xi_{v,1}^* - \xi_{v,3}^*(K_2^* + K_3)] \quad (\text{C.47})$$

In this way, Eqs. (C.44)–(C.47) relate the point at which the Ethylene runs out of the system, therefore turning off the operation.

C.3 Process variables listed in Equations (4.54b)

In this section the definition for some of the process variables listed in vector \mathbf{x}_p (page 76), namely, recovery factors, conversions and yield are presented.

$$x_B = (x_{B,3}F_3 - x_{B,4}F_4)/(x_{B,3}F_3) \quad (\text{C.48})$$

$$x_E = (x_{E,3}F_3 - x_{E,4}F_4)/(x_{E,3}F_3) \quad (\text{C.49})$$

$$p_{EB} = z_{EB,4}/z_{B,4} \quad (\text{C.50})$$

$$y_E = (y_{E,7}F_7 + y_{E,9}F_9)/(x_{B,1}F_1) \quad (\text{C.51})$$

$$\beta_{Y,S} = (y_{B,7}F_7 + y_{B,9}F_9)/(x_{B,4}F_4) \quad (\text{C.52})$$

$$\alpha_{Y,S} = (y_{EB,7}F_7 + y_{EB,9}F_9)/(z_{EB,4}F_4) \quad (\text{C.53})$$

$$\delta_{Y,S} = (y_{DEB,7}F_7 + y_{DEB,9}F_9 + x_{DEB,13}F_{13})/(z_{DEB,4}F_4) \quad (\text{C.54})$$

$$\tau_{Y,S} = (y_{TEB,7}F_7 + y_{TEB,9}F_9 + x_{TEB,13}F_{13})/(z_{TEB,4}F_4) \quad (\text{C.55})$$

$$\varepsilon_{Y,S} = (y_{E,7}F_7 + y_{E,9}F_9)/(z_{E,4}F_4) \quad (\text{C.56})$$

$$(\text{C.57})$$

The feed inlet ratio f_E is defined as

$$f_E = (x_{E,2}F_2)/(x_{B,1}F_1) \quad (\text{C.58})$$

D

Physical Data and Process Specifications for Case Studies 3 and 4

In this Appendix are shown the physical properties and selected process specifications employed in Case Studies 3 and 4 for the simulations performed with *Stage 2* model.

D.1 Ethylbenzene Production (Case Study 3)

Table D.1 lists the physical properties of the components for Case study 3.

Table D.1: Components physical properties.

Component	Heat Capacity (kJ/kmol/K)	Heat of formation (kJ/kmol)
B	137.000	82966.520
EB	182.312	29804.320
DEB	239.061	-21855.001
TEB	310.687	-70613.998
E	43.170	52308.256

Vapour Pressure (Antoine equation):
 $P = \exp [A_i + B_i / (C_i + T(^{\circ}C) + T_{ref})]$

Component	Constant A	Constant B	Constant C
B	15.84	-2755.64	219.16
EB	16.04	-3291.66	213.77
DEB	16.80	-4170.18	226.41
TEB	16.39	-4214.88	213.92
E	15.80	-1420.40	258.69

Table D.2 shows the process specifications utilised for the simulations at the *design* target (de Lera Alonso 2000).

Table D.2: Process specifications for the *design* target.

Inlet Conditions		Reactor Conditions	
$x_{B,1}F_1$	= 10.08 kmol/h	V_r	= 4.74 m^3
$y_{E,2}F_2$	= 10.27 kmol/h	$m_{cw,r}$	= 2500 kmol/h
$T_1 = T_2$	= 353.15 K	$T_{cw,in}$	= 293.15K
σ_1	= 0.90	UA_r	= $4.594 \times 10^5 \text{ kJ/K/h}$
σ_2	= 0.91	$k_1 = k_{-1} = k_2 = k_{-2} = 0.4 \text{ h}^{-1}$,	$k_3 = 0.02 \text{ h}^{-1}$
Benzene Column		Ethylbenzene Column	
LK_{BC}	= 0.9926	LK_{EBC}	= 0.99994
HK_{BC}	= 2.5303×10^{-2}	HK_{EBC}	= 1.00×10^{-3}
P_{BC}	= 760 mmHg	P_{EBC}	= 760 mmHg

In Table D.3 are given the results in terms of mole fractions, flowrates and temperatures for all the calculated streams in Case Study 3 for the *design* target value ($p_{EB} = 0.20$) based on the specifications of Table D.2.

Table D.3: Results obtained for the *design* target.

		Mole fraction in stream				
Component		3	4	5	6	7
B		0.500593	0.452591	0.452591	0.452591	0.097702
EB		0.002823	0.1002676	0.100268	0.100268	0.002423
DEB		0.04468	0.0612747	0.061275	0.061275	0.000198
TEB		0.003829	0.0052462	0.005246	0.005246	0.000004
E		0.448074	0.3806204	0.380620	0.380620	0.899673
Flow (kmol/h) =		71.90734	64.076214	6.407621	57.66859	23.89108
T (K) =		359.8394	300.44796	300.448	300.448	300.448

		Mole fraction in stream				
Component		8	9	10	11	12
B		0.703606	0.9751674	0.019172	0.031898	0.000000
EB		0.169474	0.0059894	0.581516	0.967490	0.000088
DEB		0.104475	0.0000000	0.367791	0.000612	0.920907
TEB		0.008954	0.0000000	0.031522	0.000000	0.079006
E		0.013491	0.0188432	0.000000	0.000000	0.000000
Flow (kmol/h) =		33.77751	24.182638	9.594874	5.766716	3.828159
T (K) =		300.448	353.66019	419.5957	408.4545	458.7692

		Mole fraction in stream	
Component		13	14
B		0.000000	0.0000000
EB		0.000088	0.0000088
DEB		0.920907	0.9209067
TEB		0.079006	0.0790058
E		0.000000	0.0000000
Flow (kmol/h) =		3.483624	0.3445343
T (K) =		458.7692	458.76919

D.2 TE-Problem (Case Study 4)

Table D.4 lists the physical properties for the components in the TE-problem.

Table D.4: Components physical properties (Downs and Vogel 1993).

Component	Molecular weight	Liquid density (kg/m ³)	Liquid heat capacity (kJ/kg/°C)	Vapour heat capacity (kJ/kg/°C)	Heat of vaporization (kJ/kg)
A	2.0	–	–	14.6	–
B	25.4	–	–	2.04	–
C	28.0	–	–	1.05	–
D	32.0	299.0	7.66	1.85	202
E	46.0	365.0	4.17	1.87	372
F	48.0	328.0	4.45	2.02	372
G	62.0	612.0	2.55	0.712	523
H	76.0	617.0	2.45	0.628	486

Vapour Pressure (Antoine equation):
 $P = \exp [A_i + B_i / (C_i + T(^{\circ}C))]$

Component	Constant A	Constant B	Constant C
D	20.81	–1444.0	259
E	21.24	–2114.0	266
F	21.24	–2144.0	266
G	21.32	–2748.0	233
H	22.10	–3318.0	250

Parameters values for components A, B and C are not listed because they are effectively noncondensable

In Table D.5 are listed the stream conditions utilised at the Base case scenario (Downs and Vogel 1993). Molar compositions and temperature do not change between operations modes. Streams 1-4 are combined to produce stream 1 in the simplified flowsheet (Fig. 4.23).

Table D.5: Stream conditions at Base case (Downs and Vogel 1993).

Component	Mole fraction $y_{i,j}$ in streams			
	1	2	3	4
A	0.99990	0.00000	0.00000	0.48500
B	0.00010	0.00010	0.00000	0.00500
C	0.00000	0.00000	0.00000	0.51000
D	0.00000	0.99990	0.00000	0.00000
E	0.00000	0.00000	0.99990	0.00000
F	0.00000	0.00000	0.00010	0.00000
G	0.00000	0.00000	0.00000	0.00000
H	0.00000	0.00000	0.00000	0.00000
Flow (kmol/h)=	11.2	114.5	98.0	417.5
$T (^{\circ}C) =$	45.0	45.0	45.0	45.0

Table D.6 gives the parameter values used in Eqns. (4.61a)–(4.61c).

Table D.6: Kinetic values in rate expressions.

$c_{1,1} =$	44.06	$c_{2,1} =$	42600
$c_{1,2} =$	10.27	$c_{2,2} =$	19500
$c_{1,3} =$	59.50	$c_{2,3} =$	59500

In Table D.7 are given the values for the dimensionless variables employed in *Stage 1* when the energy balance is added to the model, based on the Base case scenario and the definitions given in step [1.7].

Table D.7: Dimensionless variables.

$\gamma_1 =$	59.67809		
$\gamma_2 =$	27.37744	$K_2^* =$	1.763731
$\gamma_3 =$	83.35321	$K_3^* =$	3.11015×10^{-5}
$\delta_c =$	74.45931	$mcp_{cw} =$	62.62184
$T_2 =$	359.25 K		

The parameter specifications (vector \mathbf{p}) are given in Table D.8.

Table D.8: Parameters specifications for TE-Problem (Jockenhövel et al. 2003).

Mixing section		Reactor	
$V_m =$	141.53 m ³	$V_r =$	36.8117791 m ³
$R_g =$	8.31451 kPa m ³ /kmol/K	$\rho_{l,r} =$	7.28223 kmol/m ³
Compressor		$\epsilon_1 =$	1.0399157 kmol/h/m ³
$\kappa =$	0.7166374645	$\epsilon_2 =$	1.0113731 kmol/h/m ³
$T_{ref} =$	273.15 K	$\epsilon_2 =$	1.00 kmol/h/m ³
Separator		$\gamma_{D,r} =$	0.996011
$\rho_{l,s} =$	10.29397546 kmol/m ³	$\gamma_{E,r} =$	1.0
$\gamma_{D,s} =$	1.001383	$\gamma_{F,r} =$	1.078
$\gamma_{E,s} =$	1.001383	$\gamma_{G,r} =$	0.999
$\gamma_{F,s} =$	1.001383	$\gamma_{H,r} =$	0.999
$\gamma_{G,s} =$	1.001383	$T_{cw,r,in} =$	308.0 K
$\gamma_{H,s} =$	0.992188	$UA_r =$	127.6 kW/K
$V_s =$	99.1 m ³	$m_{cw,r} =$	93.7 m ³ /h
$T_{cw,s,in} =$	313.0 K	$Cp_{cw} =$	4.18 kJ/kg/K
$UA_s =$	152.7 kW/K	$HoF_1 =$	-136033.04 kJ/kmol
$m_{cw,s} =$	49.37 m ³ /h	$HoF_2 =$	-93337.9616 kJ/mol
		$HoF_3 =$	0.0 kJ/mol
Stripper			
$\rho_{l,str} =$	8.6496 kmol/m ³	$a_{6,2} =$	-0.00010
$m_{cw,str} =$	230.31 kg/h	$a_{6,3} =$	3.69×10^{-7}
$a_{4,0} =$	0.548012	$a_{7,0} =$	0.001393
$a_{4,1} =$	0.011351	$a_{7,1} =$	0.000217
$a_{4,2} =$	-0.00011	$a_{7,2} =$	1.37×10^{-5}
$a_{4,3} =$	3.51×10^{-7}	$a_{7,3} =$	1.84×10^{-9}
$a_{5,0} =$	0.620794	$a_{8,0} =$	-0.01568
$a_{5,1} =$	0.010197	$a_{8,1} =$	0.000976
$a_{5,2} =$	-0.00010	$a_{8,2} =$	-7.64×10^{-6}
$a_{5,3} =$	3.69×10^{-7}	$a_{8,3} =$	8.32×10^{-8}
$a_{6,0} =$	0.628854		
$a_{6,1} =$	0.010049		

Table D.9: Results comparison between *modular* approach and Ricker and Lee (1995b).

Holdup	Base Case		Mode 1 (50/50)		Mode 2 (10/90)	
	This work	Ref [†]	This work	Ref [†]	This work	Ref [†]
$N_{A,m}$	47.236	48.838	54.379	52.847	56.721	59.874
$N_{B,m}$	11.646	13.493	24.767	24.189	12.951	14.107
$N_{C,m}$	36.755	40.030	31.779	30.924	31.958	33.449
$N_{D,m}$	10.392	10.442	9.759	9.729	1.898	2.206
$N_{E,m}$	29.283	28.488	27.465	26.940	43.185	43.729
$N_{F,m}$	3.097	2.514	6.634	6.747	9.534	9.645
$N_{G,m}$	6.093	5.403	8.823	8.125	1.515	1.708
$N_{H,m}$	2.143	2.517	4.361	3.870	6.817	7.440
T_m	368.367	359.250	388.951	370.523	366.052	359.250
$N_{A,r}$	4.296	3.972	4.593	4.315	7.299	6.090
$N_{B,r}$	1.702	1.665	3.006	2.834	2.409	1.956
$N_{C,r}$	2.918	2.888	1.860	1.750	2.951	2.432
$N_{D,r}$	0.191	0.169	0.112	0.106	0.012	0.016
$N_{E,r}$	11.733	10.641	9.857	9.025	8.233	9.972
$N_{F,r}$	1.520	1.295	3.353	3.117	2.763	3.285
$N_{G,r}$	76.388	67.260	76.667	68.626	8.539	10.927
$N_{H,r}$	71.486	68.196	75.049	65.786	80.491	95.896
T_r	394.791	395.166	398.272	398.357	393.684	397.350
$N_{A,s}$	26.333	28.895	28.974	31.005	36.724	32.039
$N_{B,s}$	10.167	12.119	18.986	20.415	11.500	10.291
$N_{C,s}$	18.563	21.022	11.634	12.487	14.777	12.794
$N_{D,s}$	0.069	0.097	0.059	0.080	0.007	0.008
$N_{E,s}$	4.173	5.905	4.275	5.967	4.770	5.680
$N_{F,s}$	0.627	0.719	1.693	2.057	1.576	1.871
$N_{G,s}$	15.495	20.492	22.852	28.442	3.284	4.032
$N_{H,s}$	11.138	16.195	18.032	22.117	23.880	28.679
T_s	355.704	353.250	368.281	368.971	367.284	363.450
$N_{G,str}$	21.492	21.754	27.766	27.757	4.351	4.363
$N_{H,str}$	17.549	17.510	17.698	17.716	32.035	32.037
T_{str}	338.859	337.863	339.621	339.635	338.456	338.550

[†] = Ricker and Lee (1995b)

Nomenclature

A_i, B_i, C_i	Antoine constants of component i	
$a_{c,j}$	Coefficient in split fraction factor correlation	
Bi	Biot number for heat transfer $h_p R/k_e$	[-]
C	Controllability matrix	[-]
C_i	Concentration of component i	kmol m^{-3}
CP_i^j	Heat capacity of component i in phase j	$\text{kJ kmol}^{-1} \text{K}^{-1}$
F_j	Flowrate of stream j	kmol s^{-1} or kmol h^{-1}
$F_{i,j}$	Flowrate of component i in stream j	kmol s^{-1} or kmol h^{-1}
f_i	Feed ratio of component i w.r.t variable of reference	[-]
H_i	Enthalpy of component i	kJ
HK_c	Heavy-key component in distillation column c	[-]
HoF_k	Heat of formation of reaction k	kJ kmol^{-1}
HoV_s	Heat duty due to vaporization in separator	kW
HoV_{str}	Vapour heat duty in stripper	kW
$H_{vap,i}$	Heat of vaporization of component i	kJ kmol^{-1}
h_p	Heat transfer coefficient	$\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$
K_i	Equilibrium constant of component i	[-]
k_e	Effective thermal conductivity	$\text{kJ h}^{-1} \text{m}^{-1} \text{K}^{-1}$
k_k	Reaction rate constant in reaction k	h^{-1} or $\text{kmol m}^{-3} \text{h}^{-1}$
L_c	Level of unit c	m
LK_c	Light-key component in distillation column c	[-]
MW_i	Molecular weight of component i	kg kmol^{-1}
$m_{cw,c}$	Cooling water flowrate to unit c	kmol h^{-1}
$N_{i,c}$	Holdup of component i in unit c	kmol
Da	Damköhler number	[-]
P_c	Total pressure in unit c	MPa or mmHg
\mathbf{p}	Vector of parameters	
p_i	Productivity of component i	[-]
$p_{i,c}$	Partial pressure of i in equipment c ; productivity	MPa or mmHg
\dot{Q}	Heat duty	kW
Q	Volumetric flowrate	$\text{m}^3 \text{h}^{-1}$
R	Pellet radius	m
R_g	Gas constant	$\text{kJ kmol}^{-1} \text{K}^{-1}$

R_k	Rate of reaction of reaction k	kmol s^{-1} kmol h^{-1}	or
\widehat{R}_k	Dimensionless rate of reaction of reaction k	[-]	
S_{im}	Selectivity of component i w.r.t to component m	[-]	
T_j	Temperature of stream j	K	
T_b°	Basis temperature	K	
t	Time	min or h	
UA	Specific heat transfer rate coefficient	kW K^{-1}	
\mathbf{u}	Vector of design (manipulated) variables		
V	Volume	m^3	
\mathbf{x}	Vector of state variables		
x_i	Conversion of component i	[-]	
$x_{i,j}$	Mole fraction in the liquid of component i in stream j	[-]	
Y_i	Yield of component i	[-]	
\mathbf{y}	Vector of output (controlled) variables		
y_i	Dimensionless recycle flowrate of component i	[-]	
$y_{i,j}$	Mole fraction in the vapour of component i in stream j	[-]	
$z_{i,j}$	Bulk mole fraction of component i in stream j	[-]	

Greek Symbols

$\alpha_{i,j}$	Recovery factor of component i w.r.t. stream j	[-]	
β	Dimensionless heat of reaction, $-\Delta H_r C_o / \rho C_p T_o$	[-]	
β_c	Vapour fraction in unit c	[-]	
γ_k	Arrhenius number in reaction k	[-]	
$\gamma_{i,c}$	Activity coefficient of component i in unit c	[-]	
$\Delta H_{f,i,k}^\circ$	Heat of formation of component i of reaction k at 295 K	kJ kmol^{-1}	
$\Delta H_{r,k}$	Heat of reaction of reaction k	kJ kmol^{-1}	
ϵ_k	Pre-exponential factor in reaction k	$\text{kmol h}^{-1} \text{m}^{-3}$	
θ_j	Dimensionless temperature in stream j	[-]	
κ	Compression factor	[-]	
λ	Purge factor, eigenvalue	[-]	
$\nu_{i,k}$	Stoichiometric coefficient of component i in reaction k	[-]	
ξ_k	Extent of reaction of reaction k	kmol h^{-1}	
$\xi_{v,k}$	Dimensionless extent of reaction of reaction k	[-]	
ρ	Density	kmol m^{-3}	
σ	Purge relationship, $1/(1 - \lambda)$	[-]	
τ	Residence time	min or h	
Φ_i	Split factor for component i in the stripper	[-]	
ψ	Split exchange	[-]	

Subscripts

<i>c</i>	Operation unit index
<i>cw</i>	Cooling media
<i>DOF</i>	Degrees of freedom
<i>i</i>	Component index
<i>j</i>	Stream index
<i>k</i>	Reaction index
<i>m</i>	Mixing zone
<i>r</i>	Reactor
<i>s</i>	Separator
<i>str</i>	Stripper

Superscripts

<i>cr</i>	Critical value
<i>l</i>	Liquid phase
<i>m</i>	Condition of state-multiplicity
<i>sat</i>	Saturation conditions
<i>v</i>	Vapour phase

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