

MASTER

LPV modelling and parameter estimation for reaction systems

Prikken, D.W.G.M.

Award date:
2018

[Link to publication](#)

Disclaimer

This document contains a student thesis (bachelor's or master's), as authored by a student at Eindhoven University of Technology. Student theses are made available in the TU/e repository upon obtaining the required degree. The grade received is not published on the document as presented in the repository. The required complexity or quality of research of student theses may vary by program, and the required minimum study period may vary in duration.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain



Systems & Control Master's Program
Department of Electrical Engineering
Control Systems Group

LPV Modelling and Parameter Estimation for Reaction Systems

Master Thesis

D.W.G.M. (Daimy) Prikken
0813303
d.w.g.m.prikken@student.tue.nl

Supervisors:
dr. L. (Leyla) Özkan
C.S. (Carlos) Méndez Blanco MSc
prof. dr. ir. P. M. J. (Paul) Van den Hof

Eindhoven
07/09/2018

Declaration concerning the TU/e Code of Scientific Conduct for the Master's thesis

I have read the TU/e Code of Scientific Conduct¹.

I hereby declare that my Master's thesis has been carried out in accordance with the rules of the TU/e Code of Scientific Conduct

Date

4-9-2018

Name

D. W. G. M. Peikken

ID-number

08.13303

Signature



Submit the signed declaration to the student administration of your department.

¹ See: <http://www.tue.nl/en/university/about-the-university/integrity/scientific-integrity/>
The Netherlands Code of Conduct for Academic Practice of the VSNU can be found here also.
More information about scientific integrity is published on the websites of TU/e and VSNU

Acknowledgements

First of all, I would like to thank dr. Leyla Özkan for her valuable help and supervision of my thesis and internship. Her passion for process control has fueled my interest in the field from an early stage on in my master.

I would also like to thank C. Méndez Blanco MSc for his daily supervision of my thesis. For his ever present and unconditional willingness to help that has guaranteed the successfulness of the thesis. For his devotedness to the project and the advices that he gave me.

Lastly, I want to thank my parents and grandparents for offering me the possibility to study, as well as to encourage me, along with the rest of the family and friends, to pursue my dreams. Their interest and willingness to help whenever they could and their advices has made it possible for me to successfully complete my studies.

Sincerely,
Daimy

Abstract

This work is concerned with obtaining control relevant process models and maintenance of these models for nonlinear reaction systems. In general, there are two types of modelling approaches. One approach is modelling based on physical laws (first principles) in which physical interpretation of variables and parameters is feasible and this aspect is highly valued by the industrial practitioners. However, this type of modelling can be very time consuming. The second approach is the data driven process modelling which is less expensive in terms of time in comparison to first principle models. But the physical interpretation of the parameters is not possible. In a recent work, extent transformation is used to decouple the nonlinear reaction system into governing physical phenomena and the resulting model is a Linear Parameter-Varying (LPV) system. Motivated with this LPV representation, in the first part of this graduation work, we have investigated the use of Orthogonal Basis Functions for the identification reaction systems. We have shown that this is indeed possible around a specific operating point. In the second part, we have focused on the practical parameter sensitivity and identifiability of reaction systems. Such analysis helps to rank the model parameters. Such information is useful in estimation of model parameters in aligning the process model with the process behavior. The applicability and reliability of the ranking methods are demonstrated on a Reactive Batch Distillation Column.

Summary

In this project, we have dealt with the modelling of reaction systems. A brief summary of this thesis is given in the following. We first introduce the thesis in chapter 1. In the introduction, the problem statements and research questions are stated.

In Chapter 2, all the background information is explained in order to have a good understanding of the rest of the thesis. In section 2.1, the difference between continuous and batch reactors is explained. Section 2.2 introduces the notions of extents of reaction and flow and how these can be used for the analysis of single phase and multiphase reaction systems. In section 2.3, the theory of extents is used to express a general reaction system as an LPV representation under some assumptions. The Reactive Batch Distillation Column system that is used in this thesis is introduced in section 2.4. Section 2.5 is about the so-called incremental identification procedure. This procedure facilitates the identification of reaction systems. An incremental identification procedure is required to identify the reaction kinetics, due to the nonlinear nature of the process. In this section, three different methods are introduced to perform this incremental identification. These three methods are the differential method using rate laws, the integral method using rate laws and the integral methods using extents. In the referenced literature, it is concluded that the latter method provides the best identification results, at the expense of heavier computational load. The example in this chapter demonstrates the identification procedure. By means of this example, it is concluded that simultaneous identification of reaction and the variable β , yielded the correct identified rate law. It is also concluded that signals with a low Signal-to-noise ratio, deteriorate the identification results.

In Chapter 3, Orthogonal Basis Function are introduced. They provide a means to identify a system and incorporate *a priori* knowledge. In section 3.1, the formulation of OBF's is explained and an example is provided that clarifies the use of OBF's for identification of linear systems. Out of multiple types of OBF's, it is concluded that the Laguerre basis is suitable for the reaction system in this thesis due to its low order transfer function. The theory behind LPV identification is also explained in this section. It is concluded that this application of LPV identification is unsuitable for the reaction system. The reason is that it is assumed that the scheduling variable is known or measured, but this assumption is not valid for reaction systems. The second reason is that the scheduling variable in these LPV systems is in either the B-matrix or C-matrix of the state space representation, while the scheduling variable in reaction systems is in the A-matrix of the state space representation, meaning it appears in the poles of the transfer function, rather than in the zeros.

Section 3.2 is dedicated to investigating whether the extent transformation yields a unique OBF. The conclusion here is that the extent representation does not yield a unique OBF. This is due to the fact that the transfer function that is obtained by the extent transformation is not all-pass. Besides the identification of linear systems, it is also possible to identify LPV systems using OBF's. In section 3.3, it is investigated if OBF identification is possible if reaction is viewed as a disturbance to the system. This is tested on two situations applied on a CSTR; one being a situation where the variable θ is controlled and one being a situation where mass is controlled. It is concluded that for both situations in a CSTR reactor, OBF identification is possible. This is due to the fact that the most impact of the disturbance is in the startup phase. In steady state the system can be

approximated with the OBF's. From the definition of α , it is concluded that the parameter cannot be modelled as a constant; it exhibits dynamic behaviour. This provides excellent identification results. The disadvantage is that physical interpretation is lost. Physical interpretation however, is valued a lot in process industry. Therefore in section 3.3.3, an investigation is executed to see if physical interpretation can be kept by writing out the explicit time responses. The conclusion here is that it is possible to approximate how much α and γ are going to change due to a change in inputs. It is however not possible to calculate what α and γ is in absolute values if there is no possibility to measure concentration data. As future work it could be investigated how an estimate of α and γ can be made without having concentration data. Section 3.4 suggests an identification method that can be investigated in the future for slow reaction systems.

Chapter 4 is about the identifiability of parameters and how these parameters can be ranked according to their contribution in outputs. Section 4.1 provides a method to verify if certain parameters in a system can be structurally identified. The conclusion here is that almost all parameters can be identified. It turned out that identifiability is not possible for parameters which appear in the differential equations as a product or in a matrix. Parameter Sensitivity is a method to identify which parameters have a large impact on certain outputs and rank those parameters according to their impact. For a CSTR, parameter sensitivity is investigated in section 4.2.1. The conclusion here is that the ranking results depends on inputs. Scaling can remove this difference in ranking for different situations. It is known that the ranking can also depend on initial conditions, control strategy or initial approximate values of the parameters. How to circumvent this can be investigated in future work.

Section 4.2.2 uses the same parameter sensitivity analysis to investigate the parameters of an RBD. It turns out that an RBD is a highly parametrised model with a large number of outputs. This makes the parameter sensitivity analysis difficult. Hence simplifications have to be made. This means that only sensitivities for temperature are computed. Moreover, this process is in batch regime and has no steady states. Therefore, time-varying parameters are present in this system. To use the same parameter sensitivity method as before, average values of these parameters have to be taken. The conclusion is that $h_{vap,mix}$ is the highest ranked parameter in every output. The rankings of $C_{p_{mix,i}}$ in stage i more or less corresponded more or less with reality where the highest ranked parameter is in the highest stage, being the reactor. Because this conclusion is not true case for all outputs and situations, it is assumed that this result is due to the averaging of the time-varying parameters. Therefore for future work it is necessary to investigate a parameter sensitivity method based on time-varying parameters.

Contents

Contents	vii
List of Figures	ix
List of Tables	xi
1 Introduction and Problem Statement	1
2 Modelling of Reaction Systems	4
2.1 Chemical Reactors	4
2.2 Extents of Reaction and Flow	5
2.2.1 Extents of Reaction	5
2.2.2 Reaction spaces	6
2.2.3 Computation of the Extents of Reaction and Inlet Flow	7
2.2.4 Computation of Extents of Reaction, Mass Transfer and Flow for Gas-Liquid Reaction Systems	7
2.3 LPV Model Representations of Reaction Systems	10
2.4 Reactive Batch Distillation Column	11
2.5 Incremental Identification of Reaction Systems	13
2.5.1 Example of incremental identification on a batch reactor	15
3 Extent representation and Orthogonal Basis Functions	20
3.1 Identification of linear and LPV systems using OBF's	20
3.2 Extents representation and a unique OBF	24
3.3 Identification of reaction systems using OBF's with reaction as disturbance	25
3.3.1 Identification of a CSTR with controlled θ	26
3.3.2 Identification of a CSTR with controlled mass	31
3.3.3 Estimation of α and γ by explicit expressions	34
3.4 2-step Identification method	36
4 Identifiability, Parameter Estimation and Sensitivity	37
4.1 Identifiability	37
4.2 Parameter Estimation and Sensitivity	39
4.2.1 Parameter Sensitivity of a CSTR	41
4.2.2 Parameter Sensitivity of a RBD	44
5 Conclusions and Future Work	46
Bibliography	47
Appendix	48

CONTENTS

A		49
A.1	Computation of transformation matrices	49
A.2	Table of parameters with nominal values	49

List of Figures

1.1	Outline of this thesis	2
2.1	Schematic representation of different types of reactors	5
2.2	Visual representation of the gas-liquid reaction system [3]	8
2.3	Reactive Batch Distillation Column [18]	11
2.4	Visual representation of identification methods. Path 1 depicts the integral method, path 2 the differential method and path 3 the extent-based method. [4]	14
2.5	Incremental identification with no noise	16
2.6	Incremental identification with a low SNR	17
2.7	Incremental identification with a high SNR	18
2.8	Incremental identification with no noise, simultaneously identifying concentrations and temperature	19
3.1	Bode magnitude diagram of the identification result using OBF's	22
3.2	Wiener LPV OBF model structure	22
3.3	Hammerstein LPV OBF model structure	23
3.4	Result of LPV identification procedure. Red line is both the input and scheduling variable. The blue line is the original output. The yellow line is the approximation of the output using a fourth order OBF approximation with the pole of the OBF in 0.8.	24
3.5	Inputs applied to the system	27
3.6	Input signals, time response for θ and reactor mass	28
3.7	Temperature response for controlled θ	28
3.8	First order identification result	28
3.9	Second order identification result	29
3.10	Second order identification result (error)	29
3.11	Second order identification result (error, no noise)	29
3.12	Second order identification result for γ	29
3.13	Second order identification results (Bode plots). 'tf1' corresponds to transfer function 3.19, 'tf2' corresponds to transfer function 3.20 and 'tf3' corresponds to transfer function 3.20.	30
3.14	Input signals, time response for θ and reactor mass	31
3.15	Temperature response for controlled mass	32
3.16	First order identification result	32
3.17	Second order identification result	32
3.18	Second order identification result (error)	32
3.19	Second order identification result (error, no noise)	32
3.20	Second order identification result for γ	32
3.21	Second order identification results (Bode plots). 'tf1' corresponds to transfer function 3.19, 'tf2' corresponds to transfer function 3.20 and 'tf3' corresponds to transfer function 3.20.	33
3.22	Time response of α	34

LIST OF FIGURES

3.23	Approximation results of $\frac{1}{\Delta\alpha}$	34
4.1	Nominal time responses of relevant signals (Situation 1)	42
4.2	Nominal time responses of relevant signals (Situation 2)	43

List of Tables

2.1	Parameter estimation results for various circumstances for candidate rate law 1 . . .	18
4.1	Parameter sensitivity rankings for number of moles for different situations	41
4.2	Parameter sensitivity rankings for temperature for different situations	41
4.3	Parameter sensitivity rankings for different temperature locations	44
4.4	Parameter sensitivity rankings for different temperature locations (Scaled according to scaling of [16])	45
A.1	System parameters and their nominal values	50

Chapter 1

Introduction and Problem Statement

The modelling of dynamic systems is an important practice in engineering. These models are developed to gain insight of the underlying phenomena. Once these dynamics are modelled, it is possible to manipulate the systems using controllers, in such a way that they behave as desired. In modelling, we can distinguish two methodologies. The first methodology is First Principle Modelling (FPM) which models are obtained using physical laws that govern the system's behaviour. Steps in this modelling process are as follows:

1. Develop a model using underlying physical laws.
2. Design experiments and perform the experiments
3. Acquire measurements from the experiment and process the measurements if necessary
4. Compare the measured data to the model and compute the unknown parameters.

Besides FPM, Data-Driven Modelling (DDM) is also possible. This type of modelling has become popular since the introduction of computers. For this process, the modelling steps 2, 3 and 4 of the FPM process are the same. The main difference between DDM and FPM is that in DDM the underlying system is regarded as a black box, meaning there is no knowledge about the physics of the system. Mostly linear models are used to approximate the dynamics of the underlying system. The disadvantage of this method is that for some systems, such as chemical processes, a linear model might not be sufficient for monitoring or to control the system in a wide operating regime.

In process industry, physical interpretation is greatly valued when modelling a reaction system. Therefore, FPM is preferred over DDM. The problem arises when it is only possible to use DDM instead of FPM; due to lack of measurements. The disadvantage is that by using DDM, generally physical interpretation is lost. The main research question in this thesis is therefore: ***"How can we identify reaction systems using data at hand and preserve physical interpretation?"***

In this thesis, a particular focus will be placed on the modelling and identification of reaction systems using so called extent transformations. Reaction systems are chemical systems in which one or multiple reactions occur. Interesting dynamics can be observed as the reaction dynamics, in general, are nonlinear. These nonlinearities make it challenging to identify and control reaction systems. The extents transformation decouples reaction systems into its governing physical phenomena. The extent-based representations have gained popularity in the recent years due to their excellent capabilities for identifying systems. These models can then be either used for the controlling of reaction systems, as already researched in [13], but also for the monitoring of processes.

For the latter, the model must be more accurately determined in comparison to control purposes. The main motivation to investigate the control of reaction systems is the growing importance to tightly control reaction systems in process industry. For increasing number of products, the purity and quality is crucial. Hence, the operating conditions of these processes must be tightly regulated.

In [11] it is shown that extent transformation can yield LPV models if reaction is regarded as a disturbance. The question here is whether this LPV model can be identified. Orthogonal Basis Functions (OBF's) can provide a means to do so. OBF's are a tool to identify linear systems using *a priori* knowledge of the system. Research into the approximation of linear systems using OBF's has been performed in [22] and [8]. The knowledge was extended to also use OBF's for the approximation of LPV systems [19],[20]. The latter research has broadened the opportunities for identifying and ultimately controlling systems. The problem here is that the structure of the model in these papers is different from the structure of the LPV model of reaction systems and the scheduling variable is not always known. Therefore the first subquestion is: ***"Is it possible to approximate a general nonlinear model of reaction systems using OBF's?"***. Besides being able to identify reaction systems using OBF's, it is also interesting to see if there a relation between extent transformation and OBF's. Hence the second subquestion is: ***"Do the extent transformations form a set of unique OBF's?"***.

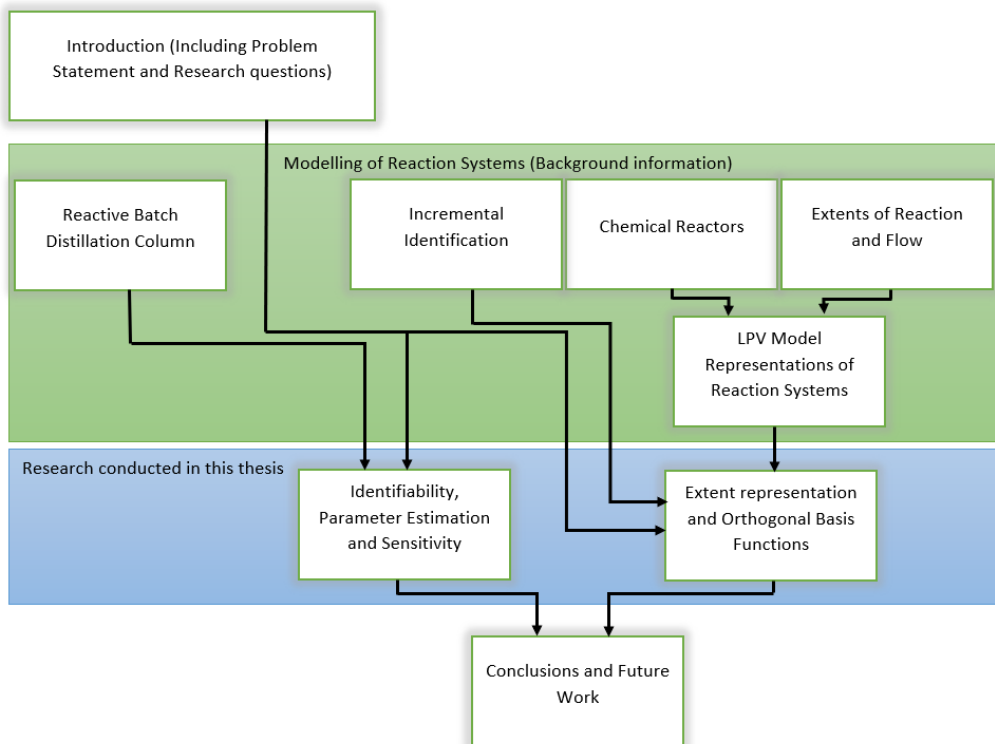


Figure 1.1: Outline of this thesis

A problem when modelling reaction systems is that this task can be expensive. Another problem is that it is not always possible in practice to identify the system and its parameters with the data at hand. Identifiability analysis provides a means to investigate whether systems are identifiable. Identifiability is the possibility to identify a unique set of parameters for which the model accurately describes the process. Hence if with the data at hand, the system is not identifiable, it may not be possible to maintain physical interpretation. The third subquestion is: ***"Which parameters or combination thereof can be identified?"***. There is substantial literature

on model identifiability; see for example [24] and [14]. The identifiability of reaction systems is challenging due to the nonlinear nature of them. It is necessary to investigate which parameters influence a certain output the most. This can be done by ranking the parameters according to their contribution to a certain output. The fourth subquestion here is: ***“Which parameters are more important to model?”***.

The outline of this thesis is displayed in Figure 1.1. Chapter 2 is the background information of this thesis. It is explained what types of chemical reactors exist, what extents of reaction is and how it is computed and how extent transformation yields an LPV representation. The case study of the Reactive Batch Distillation Column (RBD) that is going to be worked with in chapter 4 is explained. The incremental identification method is also introduced in this chapter to show which possibility there is to identify nonlinear reaction systems.

Chapter 3 is the first chapter that is concerned with the research of this thesis. The chapter starts by explaining how identification of linear and LPV systems is performed using Orthogonal Basis Functions. The relation between the extent representation and a unique OBF is investigated and the second subquestion is answered. Thereafter, it is investigated whether reaction systems can be approximated using OBF's in two different situations and the first subquestion is answered. Another 2-step identification method is proposed in case when reaction systems with slow reaction kinetics needs to be identified.

Chapter 4 is the second chapter that is concerned with the research of this thesis. First the notion of identifiability is explained. Subsequently, the third subquestion is answered by analysing several parameter sets of a Continuous Stirred-Tank Reactor (CSTR). Lastly, a parameter sensitivity analysis is performed to answer the fourth and last subquestion. This analysis is performed on both a CSTR and the RBD.

The thesis is concluded in Chapter 5, where besides conclusions, suggestions for possible future work are given.

Chapter 2

Modelling of Reaction Systems

This chapter provides background information on concepts and technologies used in this thesis. The first section is about chemical reactors. Before starting to elaborate on the modelling of reaction systems, a solid understanding of the different types of chemical reactors needs to be acquired. Thereafter, the so called extents of reaction and reaction spaces are introduced to show that reaction systems can be decoupled into their inherent physical phenomena. In the next subsections, the computations of these extents for single phase and multiphase reaction systems are given. Following this section of the extents of reaction and flow, the relevance of extent-based identification is discussed. The extents transformation can be used to form an LPV representation of reaction systems. The result of this is elaborated on in section 2.3. In this section, it will be explained why LPV representations are useful. In the final section the identification of systems using Orthonormal Basis Functions is addressed and the context in which they are used for in this thesis.

2.1 Chemical Reactors

Chemical reactors are the heart of any chemical process. They are of great relevance because material conversion takes place in this unit operation. Moreover, they are designed in such a way that the chemical reactions are performed in an optimal and safe manner. The performance of reactors dominate the economics of most processes. As a result, improving the performance of them has a great impact on the total costs. In general, there are two types of reactors: batch reactors and continuous reactors. The advantages of each of them is summarised as [17]:

- Continuous reactors have a better energy efficiency than batch reactors.
- Continuous reactors are easier to automate.
- Continuous reactors have a lower operation cost than batch reactors.
- Batch reactors are more versatile than continuous reactors.
- Batch reactors are used for small scale production (< 500 ton/year) while continuous reactors are used for large scale production (> 5000 ton/year).

The most common types of reactors are given in [15]:

- *Batch reactors.* This type of reactors have an agitator and do not have any inlet or outlet flows. The reactor is initially filled with components and under controlled conditions, the chemical reactions take place. It is, for example, possible to externally add or dissipate heat from the process. Batch reactors are often used because of their capability to produce

components with a high purity. Because there are no inlet or outlet flows, the change in moles is only due to reaction. This can be described mathematically as:

$$\dot{n}(t) = N^T \mathcal{V}(t)r(t) \quad (2.1)$$

where n is the number of moles, N the stoichiometric coefficient matrix, $\mathcal{V}(t)$ the volume of the mixture and $r(t)$ the reaction rate vector.

- *Semibatch reactors*. These reactors are similar to the batch reactor but now an inlet or outlet flow is present. Mathematically, the mole balance is:

$$\dot{n}(t) = N^T \mathcal{V}(t)r(t) \pm F(t) \quad (2.2)$$

where $F(t)$ is the inlet or outlet molar flow, depending on the type of semibatch reactor.

- *Continuous Stirred-Tank Reactor (CSTR)*. CSTR's are continuous reactors that have an agitator, an inlet flow and an outlet flow. It is possible to extend the equation 2.1 as:

$$\dot{n}(t) = F_{in}(t) - F_{out}(t) + N^T \mathcal{V}(t)r(t) \quad (2.3)$$

where $F_{in}(t)$ and $F_{out}(t)$ are respectively the molar inlet and outlet flow.

- *Plug Flow Reactor (PFR)*. This type of reactor is a tubular reactor instead of a tank. The propagation of the components along an axis is the same axis along which the concentrations change. The mass balance equation of the PFR of specie j can be written as:

$$\left(\frac{4v}{\pi D^2} \right) \frac{dC_j}{dz} = \nu_j r \quad (2.4)$$

where v is the volumetric flow, D the diameter of the tube, C_j the concentration and ν_j the stoichiometric coefficient of specie j and r the reaction rate.

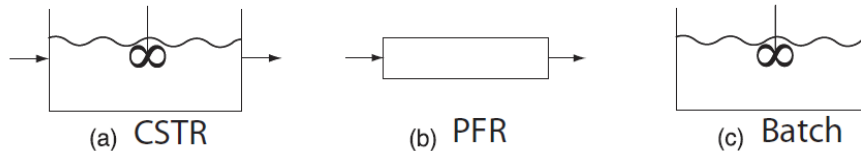


Figure 2.1: Schematic representation of different types of reactors

2.2 Extents of Reaction and Flow

2.2.1 Extents of Reaction

The concept of extents is introduced in [1]. To study the behaviour of chemical reactions, it can be useful to use the extent of reaction. The extent of reaction can also be referred to as the advancement of reaction. In a reaction, the change in extent of reaction is defined as the change in the number of a specie divided by the corresponding stoichiometric coefficient.

In homogeneous reaction systems with S species, R independent reactions, p inlet streams and one outlet stream, the mole balance equation can be written as:

$$\dot{n}(t) = N^T \mathcal{V}(t)r(t) + W_{in}u_{in}(t) - \frac{u_{out}(t)}{m(t)}n(t), \quad n(0) = n_0 \quad (2.5)$$

where $n(t) \in \mathbb{R}^{S \times 1}$ is the number of moles, $N \in \mathbb{R}^{R \times S}$ the stoichiometric coefficient matrix, $\mathcal{V}(t)$ the volume of the mixture, $r(t) \in \mathbb{R}^{R \times 1}$ the reaction rate vector, $W_{in} \in \mathbb{R}^{S \times p}$ the inlet composition

matrix, $u_{in}(t) \in \mathbb{R}^{p \times 1}$ and $u_{out}(t)$ the inlet and outlet mass flows and $m(t)$ the mass of the mixture. The extents of reaction is now defined as:

$$d\xi_r := \frac{dn_{s,r}}{\nu_{s,r}}, \quad \forall s = 1, \dots, S, \quad \forall r = 1, \dots, R, \quad \xi_r(0) = 0 \quad (2.6)$$

where $d\xi_r$ is the change in extent of reaction for the r th reaction, $dn_{s,r}$ the change in number of moles of the s th species caused by the r th reaction and $\nu_{s,r}$ the corresponding stoichiometric coefficient. In the case that there are no inlets nor outlets, which is the case in a batch reactor, the extent of reaction is expressed as:

$$\dot{\xi}_r = \mathcal{V}(t)r_r(t), \quad \xi_r(0) = 0 \quad (2.7)$$

Or in case of a semi-batch reactor with no inlets but only one outlet:

$$\dot{\xi}_r = \mathcal{V}(t)r_r(t) - \frac{u_{out}(t)}{m(t)}\xi_r, \quad \xi_r(0) = 0 \quad (2.8)$$

2.2.2 Reaction spaces

The space in which the number of moles evolve can be split into two reaction spaces:

- **Reaction variant set.** "Any set of R linearly independent variables that evolve in the reaction space constitutes a reaction variant set." [1]
- **Reaction invariant set.** "Any set of $(S - R)$ linearly independent variables that evolve in the space orthogonal to the reaction space constitutes a reaction invariant set." [1]

These definitions could be used to directly define the extents of reactions for batch and semi-batch reactors because they do not have an inlet flow. As soon as an inlet flow is present in a reactor, it does not make sense to use this inlet flow in the reaction variant nor reaction invariant set. The concept behind the extent of reaction is to describe the progression of solely the reaction. The concept of extent is therefore developed further to extents of reaction and extents of inlet flow. We therefore wish to look for the following transformation:

$$n \mapsto \begin{bmatrix} z_r \\ z_{in} \\ z_{inv} \end{bmatrix} = \begin{bmatrix} \mathcal{T}_1^\top \\ \mathcal{T}_2^\top \\ \mathcal{T}_3^\top \end{bmatrix} n \quad (2.9)$$

That leads to the following reaction variant z_r , inlet flow variant z_{in} and invariant z_{inv} :

$$\dot{z}_r = \underbrace{\mathcal{T}_1^\top N^\top}_{I_R} \mathcal{V}(t)r(t) + \underbrace{\mathcal{T}_1^\top W_{in}}_{0_{R \times p}} u_{in}(t) - \frac{u_{out}(t)}{m(t)} z_r, \quad z_r(0) = \mathcal{T}_1^\top n_0 \quad (2.10)$$

$$\dot{z}_{in} = \underbrace{\mathcal{T}_2^\top N^\top}_{0_{R \times R}} \mathcal{V}(t)r(t) + \underbrace{\mathcal{T}_2^\top W_{in}}_{I_p} u_{in}(t) - \frac{u_{out}(t)}{m(t)} z_{in}, \quad z_{in}(0) = \mathcal{T}_2^\top n_0 \quad (2.11)$$

$$\dot{z}_{inv} = \underbrace{\mathcal{T}_3^\top N^\top}_{0_{(S-R-p) \times R}} \mathcal{V}(t)r(t) + \underbrace{\mathcal{T}_3^\top W_{in}}_{0_{(S-R-p) \times p}} u_{in}(t) - \frac{u_{out}(t)}{m(t)} z_{inv}, \quad z_{inv}(0) = \mathcal{T}_3^\top n_0 \quad (2.12)$$

where z_r is expressed in $kmol$, z_{in} in kg and z_{inv} in $kmol$. These variants however cannot be interpreted as extents of reaction and extents of inlets because the initial conditions are nonzero. The definition of extents of reaction is the advancement of the reactions and by convention, the advancement of reaction starts at zero for the extent variable.

2.2.3 Computation of the Extents of Reaction and Inlet Flow

The expressions in section 2.2.2 can be interpreted as extents of reaction and inlet flow. A discounting factor λ is introduced. This factor subtracts the influence of the initial conditions. The transformation is then as follows [1]:

$$n \mapsto \begin{bmatrix} x_r \\ x_{in} \\ \lambda \end{bmatrix} = \begin{bmatrix} \mathcal{T}_{1,0}^\top \\ \mathcal{T}_{2,0}^\top \\ \tau_0^\top \end{bmatrix} n \quad (2.13)$$

with

$$\mathcal{T}_{1,0}^\top = \mathcal{T}_1^\top (I_S - n_0 \tau_0^\top), \quad \mathcal{T}_{2,0}^\top = \mathcal{T}_2^\top (I_S - n_0 \tau_0^\top), \quad \tau_0^\top = \frac{1_{S-R-p}^\top \mathcal{T}_3^\top}{1_{S-R-p}^\top \mathcal{T}_3^\top n_0} \quad (2.14)$$

The extent transformation for the CSTR then yields:

$$\dot{x}_r(t) = \mathcal{V}(t)r(t) - \frac{u_{out}(t)}{m(t)}x_r(t), \quad x_r(0) = 0 \quad (2.15)$$

$$\dot{x}_{in}(t) = u_{in}(t) - \frac{u_{out}(t)}{m(t)}x_{in}(t), \quad x_{in}(0) = 0 \quad (2.16)$$

$$\dot{\lambda}(t) = \frac{u_{out}(t)}{m(t)}\lambda(t), \quad \lambda(0) = 1 \quad (2.17)$$

It is also possible to define the extent of outlet as:

$$x_{out} = 1 - \lambda \quad (2.18)$$

The number of moles is now given as:

$$n(t) = N^\top x_r(t) + W_{in}x_{in}(t) + n_0\lambda(t) \quad (2.19)$$

Note that this transformation requires that $rank([N^\top \quad W_{in} \quad n_0]) = R + p + 1 < S$

2.2.4 Computation of Extents of Reaction, Mass Transfer and Flow for Gas-Liquid Reaction Systems

In [3], the theory of section 2.2.3 is extended to gas-liquid systems. This information is introduced because of the case study of the RBD in this thesis. Gas-liquid systems are common in process industry and to extend the previous knowledge to this type will create opportunities for using the extents of reaction.

To reduce the complexity of the model, a few assumptions are made:

- The gas and liquid phases are homogeneous.
- The reactor has a constant total volume.
- The reactions take place in the liquid phase only.
- The mass transfer phenomena are described by the two-film theory with no accumulation in the boundary layer. This implies steady state mass transfer.

In Figure 2.2, a representation is given of the resulting system based on these assumptions. Because of these assumptions, the mass transfer rate vector is given by:

$$\zeta = \begin{bmatrix} \zeta_{gl} \\ -\zeta_{tg} \end{bmatrix} \quad (2.20)$$

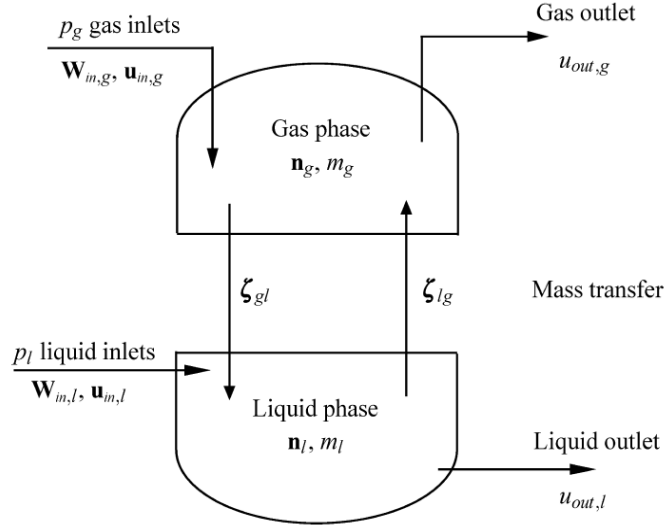


Figure 2.2: Visual representation of the gas-liquid reaction system [3]

where ζ_{gl} and ζ_{lg} represent the mass transfer rates from gas to liquid and liquid to gas respectively. These variables can take only a non-negative value. By convention, the mass transfer from gas to liquid is assigned with the positive sign. The mole balances can now be given as:

Gas phase

$$\dot{n}_g(t) = W_{in,g}u_{in,g}(t) - W_{m,g}\zeta(t) - \frac{u_{out,g}(t)}{m_g(t)}n_g(t), \quad n_g(0) = n_{g,0} \quad (2.21)$$

$$\dot{n}_g(t) = \bar{W}_{in,g}\bar{u}_{in,g}(t) - \frac{u_{out,g}(t)}{m_g(t)}n_g(t), \quad n_g(0) = n_{g,0} \quad (2.22)$$

Liquid phase

$$\dot{n}_l(t) = N^\top \mathcal{V}_l(t)r(t) + W_{in,l}u_{in,l}(t) + W_{m,l}\zeta(t) - \frac{u_{out,l}(t)}{m_l(t)}n_l(t), \quad n_l(0) = n_{l,0} \quad (2.23)$$

$$\dot{n}_l(t) = N^\top \mathcal{V}_l(t)r(t) + \bar{W}_{in,l}\bar{u}_{in,l}(t) - \frac{u_{out,l}(t)}{m_l(t)}n_l(t), \quad n_l(0) = n_{l,0} \quad (2.24)$$

with

$$\bar{W}_{in,g} = [W_{in,g} \quad -W_{m,g}], \quad \bar{W}_{in,l} = [W_{in,l} \quad W_{m,l}], \quad \bar{u}_{in,i} = \begin{bmatrix} u_{in,i} \\ \zeta \end{bmatrix} \quad (2.25)$$

where n_i is the S_i -dimensional vector of the number of moles, $W_{in,i}$ the $S_i \times p_i$ inlet composition matrix, $W_{m,i}$ the $S_i \times p_m$ mass transfer matrix, $u_{in,i}$ the p_i -dimensional inlet mass flow, $u_{out,i}$ the outlet mass flow of the i th phase, $i \in \{g, l\}$ and \mathcal{V}_l the volume of the liquid phase.

Now we look for the following extents transformations for the liquid and gas phase:

$$n_l \mapsto \begin{bmatrix} x_r \\ x_{in,l} \\ \lambda_l \end{bmatrix} = \underbrace{\begin{bmatrix} \mathcal{T}_{(1,l)_0}^\top \\ \mathcal{T}_{(2,l)_0}^\top \\ \tau_{(l)_0}^\top \end{bmatrix}}_{\mathcal{T}_{(l)_0}} n_l, \quad n_g \mapsto \begin{bmatrix} x_{in,g} \\ \lambda_g \end{bmatrix} = \underbrace{\begin{bmatrix} \mathcal{T}_{(2,g)_0}^\top \\ \tau_{(g)_0}^\top \end{bmatrix}}_{\mathcal{T}_{(g)_0}} n_g \quad (2.26)$$

with

$$\mathcal{T}_{(1,l)_0}^\top = \mathcal{T}_{(1,l)}^\top (I_{S_l} - n_{l,0} \tau_{(l)_0}^\top) \quad (2.27)$$

$$\mathcal{T}_{(2,l)_0}^\top = \mathcal{T}_{(2,l)}^\top (I_{S_l} - n_{l,0} \tau_{(l)_0}^\top) \quad (2.28)$$

$$\tau_{(l)_0}^\top = \frac{1_{S_l - R - p_l - p_m}^\top \mathcal{T}_{(3,l)}^\top}{1_{S_l - R - p_l - p_m}^\top \mathcal{T}_{(3,l)}^\top n_{l,0}} \quad (2.29)$$

$$\mathcal{T}_{(2,g)_0}^\top = \mathcal{T}_{(2,g)}^\top (I_{S_g} - n_{g,0} \tau_{(g)_0}^\top) \quad (2.30)$$

$$\tau_{(g)_0}^\top = \frac{1_{S_g - p_g - p_m}^\top \mathcal{T}_{(3,g)}^\top}{1_{S_g - p_g - p_m}^\top \mathcal{T}_{(3,g)}^\top n_{g,0}} \quad (2.31)$$

where p_m is the dimension of the mass transfer vector, $\mathcal{T}_{(1,l)_0}^\top$ is the transformation matrix of the reaction, $\mathcal{T}_{(2,i)_0}^\top$ is the transformation matrix of the inlet space in phase i , $\mathcal{T}_{(3,i)_0}^\top$ is the transformation matrix of the invariant space of phase i with discounted initial conditions $n_{i,0}$ and $\tau_{(i)_0}^\top$ the ratio between reaction and inlet invariant space at initial conditions in phase i . The computations of these matrices can be found in [3]. These transformations yield the following extents:

Gas phase:

$$\dot{x}_{in,g}(t) = u_{in,g}(t) - \frac{u_{out,g}(t)}{m_g(t)} x_{in,g}(t), \quad x_{in,g}(0) = 0 \quad (2.32)$$

$$\dot{x}_{m,g}(t) = \zeta(t) - \frac{u_{out,g}(t)}{m_g(t)} x_{m,g}(t), \quad x_{m,g}(0) = 0 \quad (2.33)$$

$$\dot{\lambda}_g(t) = -\frac{u_{out,g}(t)}{m_g(t)} \lambda_g(t), \quad \lambda_g(0) = 1 \quad (2.34)$$

Liquid phase:

$$\dot{x}_r(t) = \mathcal{V}_l(t)r(t) - \frac{u_{out,l}(t)}{m_l(t)} x_r(t), \quad x_r(0) = 0 \quad (2.35)$$

$$\dot{x}_{in,l}(t) = u_{in,l}(t) - \frac{u_{out,l}(t)}{m_l(t)} x_{in,l}(t), \quad x_{in,l}(0) = 0 \quad (2.36)$$

$$\dot{x}_{m,l}(t) = \zeta(t) - \frac{u_{out,l}(t)}{m_l(t)} x_{m,l}(t), \quad x_{m,l}(0) = 0 \quad (2.37)$$

$$\dot{\lambda}_l(t) = -\frac{u_{out,l}(t)}{m_l(t)} \lambda_l(t), \quad \lambda_l(0) = 1 \quad (2.38)$$

2.3 LPV Model Representations of Reaction Systems

In section 2.2.3, it was shown how to compute the extents of reaction and flow. This section shows how the extent transformation can be used to get LPV representations. The extent representation in equations 2.15, 2.16 and 2.17, can be extended to include an energy balance. This is done in order to make the model more general. The corresponding system of equations is given in [11]:

$$\dot{x}_r(t) = -\theta x_r(t) + \mathcal{V}(t)r(t) \quad (2.39)$$

$$\dot{x}_{in}(t) = -\theta x_{in}(t) + u_{in}(t) \quad (2.40)$$

$$\dot{\lambda}(t) = -\theta \lambda(t) \quad (2.41)$$

$$\dot{T}(t) = -\theta T(t) + \alpha u_{in}(t) - \beta \mathcal{V}(t)r(t) + \gamma Q_{in} \quad (2.42)$$

where $\theta = \frac{u_{out}(t)}{m}$, $\alpha = \frac{C_{p_{in}} T_{in}}{m C_{p_{mix}}(t)}$, $\beta = \frac{\Delta H_f^\ominus N^\top}{m C_{p_{mix}}(t)}$, $\gamma = \frac{1}{m C_{p_{mix}}(t)}$, $\Delta H_f^\ominus \in \mathbb{R}^{1 \times S}$ the vector of standard enthalpy, $C_{p_{in}} \in \mathbb{R}^{S \times p}$ the inlet heat capacity matrix, $C_{p_{mix}}(t)$ the heat capacity of the mixture in the reactor and $T(0) = T_0$. It is assumed here that $\alpha, \beta, \gamma, \theta$ and m are constant. These equations can be captured in three different Linear Parameter Varying (LPV) model representations.

Time scale separation. In this case it is assumed that the dynamics of x_r is faster than the dynamics of x_{in} ($\dot{x}_r = 0$).

$$\begin{bmatrix} \dot{x}_{in} \\ \dot{T} \end{bmatrix} = \begin{bmatrix} -\theta I_p & 0 \\ 0 & -\theta \end{bmatrix} \begin{bmatrix} x_{in} \\ T \end{bmatrix} + \begin{bmatrix} I_p & 0 \\ \alpha & \gamma \end{bmatrix} \begin{bmatrix} u_{in} \\ Q_{in} \end{bmatrix} + \begin{bmatrix} 0 \\ \beta \theta \end{bmatrix} x_r \quad (2.43)$$

$$\begin{bmatrix} n \\ T \end{bmatrix} = \begin{bmatrix} W_{in} & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} x_{in} \\ T \end{bmatrix} + \begin{bmatrix} N^\top \\ 0 \end{bmatrix} x_r + \begin{bmatrix} n_0 \\ 0 \end{bmatrix} \lambda \quad (2.44)$$

Change of variable. In case x_r is not faster than u_{in} , a change of variables is required. Let

$$z = \beta x_r + T \quad (2.45)$$

then

$$\dot{z} = -\theta z + \alpha u_{in} + \gamma Q_{in} \quad (2.46)$$

and

$$\begin{bmatrix} \dot{x}_{in} \\ \dot{z} \end{bmatrix} = \begin{bmatrix} -\theta I_p & 0 \\ 0 & -\theta \end{bmatrix} \begin{bmatrix} x_{in} \\ z \end{bmatrix} + \begin{bmatrix} I_p & 0 \\ \alpha & \gamma \end{bmatrix} \begin{bmatrix} u_{in} \\ Q_{in} \end{bmatrix} \quad (2.47)$$

$$\begin{bmatrix} n \\ T \end{bmatrix} = \begin{bmatrix} W_{in} & n_0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} x_{in} \\ \lambda \end{bmatrix} + \begin{bmatrix} N^\top & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} x_r \\ T \end{bmatrix} \quad (2.48)$$

Reaction rate as a disturbance. The reaction rate can also be seen as a disturbance. The LPV representation then becomes:

$$\dot{x} = A(\theta)x + Bu + d_1 \quad (2.49)$$

$$\begin{bmatrix} \dot{x}_r \\ \dot{x}_{in} \\ \dot{T} \end{bmatrix} = \begin{bmatrix} -\theta I_{R_I} & 0 & 0 \\ 0 & -\theta I_p & 0 \\ 0 & 0 & -\theta \end{bmatrix} \begin{bmatrix} x_r \\ x_{in} \\ T \end{bmatrix} + \begin{bmatrix} 0 & 0 \\ I_p & 0 \\ \alpha & \gamma \end{bmatrix} \begin{bmatrix} u_{in} \\ Q_{in} \end{bmatrix} + \begin{bmatrix} I_{R_I} \\ 0 \\ \beta \end{bmatrix} \mathcal{V}r \quad (2.50)$$

and

$$y = Cx + d_2 \quad (2.51)$$

$$\begin{bmatrix} n \\ T \end{bmatrix} = \begin{bmatrix} N^\top & W_{in} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_r \\ x_{in} \\ T \end{bmatrix} + \begin{bmatrix} n_0 \\ 0 \end{bmatrix} \lambda \quad (2.52)$$

where it is assumed that α, β and γ are constant. What we end up with is a LPV representation where the B and C matrix are constant and $A(\theta)$ is parameter varying.

2.4 Reactive Batch Distillation Column

Besides reaction, another major operation in process industry is distillation. Distillation is the operation of separating multiple species in a mixture based on their boiling points. This operation can also be combined with a reactor in order to form a so called Reactive Batch Distillation Column (RBD) as depicted in Figure 2.3. The RBD is capable of producing products with high added value. In such an RBD, equilibrium reactions take place. An equilibrium reaction has the following structure:



The balance of such a reaction is determined by the temperature. A balance to the right, signifies a lot of production of specie C and D , while a balance to the left signifies little production of specie C and D . The RBD steers the balance to the right hand side of an equilibrium reaction by increasing the reaction temperature and then distilling the mixture to end up with the desired product.

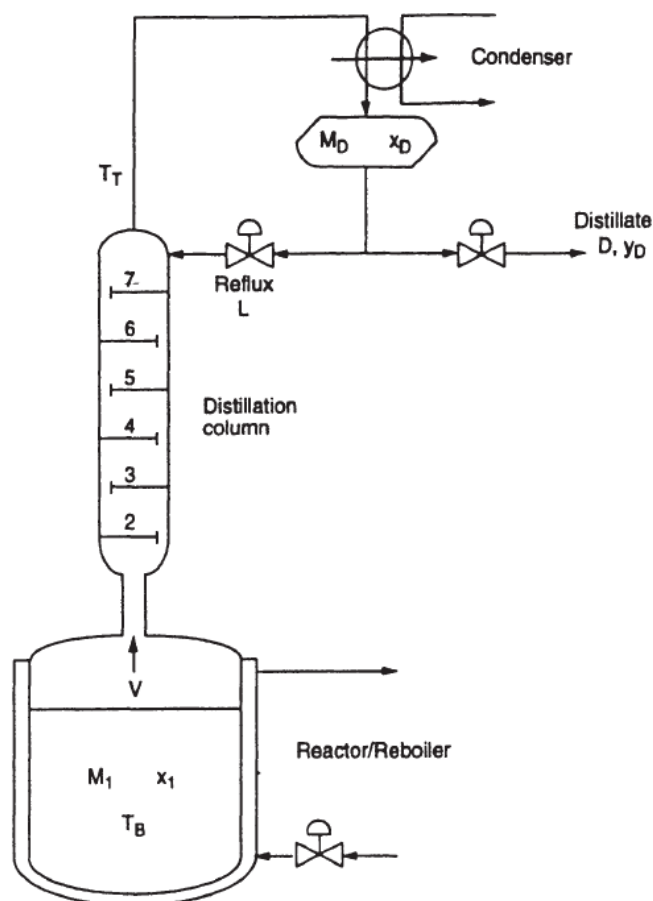


Figure 2.3: Reactive Batch Distillation Column [18]

For the modelling of the RBD, the following assumptions are made:

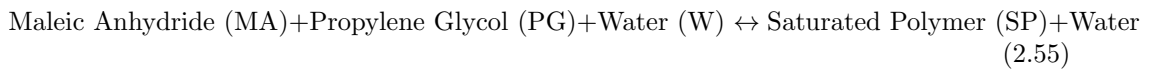
- Reaction only occurs in the reactor in the liquid phase
- The model balance of the reactor is given by equation 2.5
- For the distillation process, a stage equilibrium model is assumed:

$$\frac{dM_j x_{j,i}}{dt} = F_j f_{j,i} + L_{j-1} x_{j-1,i} + V_{j+1} y_{j+1,i} - (L_j x_{j,i} + V_j y_{j,i}) \quad (2.54)$$

where M is the total molar holdup, F_j , L_j and V_j are the total molar feed, liquid molar flow and vapour molar flow in stage j respectively. $f_{j,i}$, $x_{j,i}$ and $y_{j,i}$ are the compositions in the feed, the liquid phase and the gas phase respectively in stage j of specie i .

For the remainder of this thesis, a specific RBD will be used [13]. It is defined by the following characteristics:

- Number of species: $S = 14$
- Number of reactions: $R = 17$
- The general reaction is:



- Initial conditions:

- $M_{MA}(0) = 20$ kmol
- $M_{PG}(0) = 20$ kmol
- $M_W(0) = 10$ kmol
- $T(0) = 373$ K

- Number of stages: $NT = 6$
- One liquid phase inlet ($p = 1$) and one gas phase outlet ($v = 1$)
- Vapour holdup is negligible with respect to liquid holdup
- Constant atmospheric pressure
- Condenser (stage 2) is kept at constant temperature

For each stage of the process, the governing dynamics are:

Accumulator ($j = 1$) is the container where the top product is collected:

$$\text{Total mass balance: } \frac{dM_j}{dt} = L_j \quad (2.56)$$

$$\text{Component mass balance: } \frac{dM_j x_{j,i}}{dt} = L_j x_{j,i+1} \quad (2.57)$$

$$\text{Energy balance: } \frac{dM_j h_j}{dt} = L_j h_j \quad (2.58)$$

Condenser ($j = 2$) is the stage where vapour is condensed to a liquid:

$$\text{Total mass balance: } \frac{dM_j}{dt} = V_{j+1} - L_j \quad (2.59)$$

$$\text{Component mass balance: } \frac{dM_j x_{j,i}}{dt} = V_{j+1} y_{j+1,i} - L_j x_{j,i} \quad (2.60)$$

$$\text{Energy balance: } \frac{dM_j h_j}{dt} = V_{j+1} H_{j+1} - L_j h_j \quad (2.61)$$

Internal stages ($j = 3, 4$ and 5)

$$\text{Total mass balance: } \frac{dM_j}{dt} = L_{j-1} + V_{j+1} - (L_j + V_j) \quad (2.62)$$

$$\text{Component mass balance: } \frac{dM_j x_{j,i}}{dt} = L_{j-1} x_{j-1,i} + V_{j+1} y_{j+1,i} - (L_j x_{j,i} + V_j y_{j,i}) \quad (2.63)$$

$$\text{Energy balance: } \frac{dM_j h_j}{dt} = L_{j-1} h_{j-1} + V_{j+1} H_{j+1} - (L_j h_j + V_j H_j) \quad (2.64)$$

Reactor ($j = 6$)

$$\text{Total mass balance: } \frac{dM_j}{dt} = L_{j-1} - V_j \quad (2.65)$$

$$\text{Component mass balance: } \frac{dM_j x_{j,i}}{dt} = m_i(t) N^\top r(t) + L_{j-1} x_{j-1,i} - V_j y_{j,i} \quad (2.66)$$

$$\text{Energy balance: } \frac{dM_j h_j}{dt} = L_{j-1} h_{j-1} - V_j H_j - \Delta H_r + Q_i n \quad (2.67)$$

where $M_{j,i}$ is the liquid molar holdup of the i^{th} specie in the j^{th} stage, $x_{j,i}$ and $y_{j,i}$ are the liquid and vapour molar composition of the i^{th} specie in the j^{th} stage, respectively. h_j and H_j are the liquid and vapour molar enthalpy in the j^{th} stage and L_j and V_j the liquid and vapour flow respectively.

2.5 Incremental Identification of Reaction Systems

Chemical process models contain information about stoichiometry, kinetics, mass transfer and operation conditions (initial conditions, inlet and outlet flows, operational constraints). Particularly reaction kinetics and mass transfer are difficult to identify in models, because of nonlinearities and not being able to measure important physical quantities. The identification of these parameters can be executed by either a simultaneous or an incremental approach. The simultaneous approach chooses a candidate reaction rate expression from a library of rate expressions. The expression is then evaluated and compared to the measured data. This procedure has to be repeated for every candidate rate expression. Properties such as parameter and structural identifiability are crucial for determining parameter estimates [14]. The main advantage of simultaneous identification is that it leads to optimal parameter values [4]. This method however is computationally more costly because of the repetitive comparison of rate expressions and data. Choosing suitable initial parameter values can be problematic and yield convergence problems. Besides the simultaneous approach, the incremental approach can be used for the identification of the model which decomposes the problem into a set of subproblems [2],[6]. The first step in this process is to identify the reaction stoichiometry. The next step is to compute the rate profiles of reaction and mass transfer from measured data and the previously determined stoichiometry. This last step can be executed in three possible manners as described in Figure 2.4:

Differential method using rate laws. In this procedure, concentrations of the components are measured and differentiated. Besides the data about the concentrations, data about the inlet and outlet flows is obtained as well. Rewriting the equation 2.5, we can get:

$$-N^\top r(t) = \frac{1}{V(t)} \left(-\dot{n} + W_{in} u_{in}(t) - \frac{u_{out}(t)}{m(t)} n(t) \right) \quad (2.68)$$

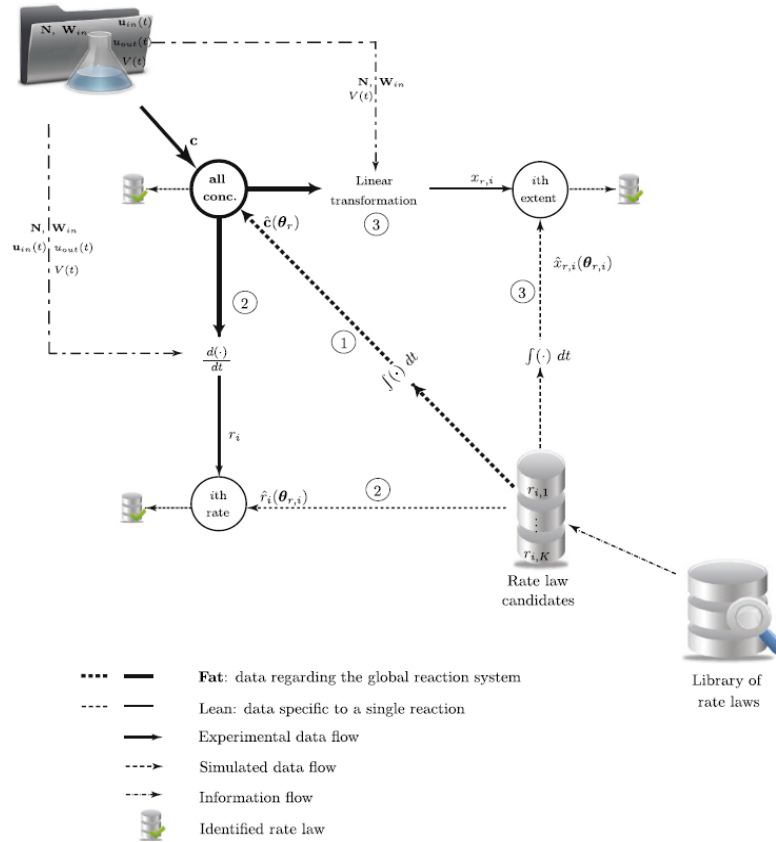


Figure 2.4: Visual representation of identification methods. Path 1 depicts the integral method, path 2 the differential method and path 3 the extent-based method. [4]

where the concentration is defined by the number of moles per volume. This equation shows that the reaction rate can be approximated by the differentiation of the concentrations. The estimated reaction rate is then compared to candidate rate laws by means of a least-squares method. The rate law that yields the smallest error is the final rate law. This rate law is then used for a global identification for parameters. Note here that the differentiation of noisy concentration measurements can cause problems for the identification procedure.

Integral method using rate laws. This procedure is similar to the differential method but the identification procedure is reversed. First a set of candidate rate laws are integrated and compared to the measured concentrations. The rate law that yields the smallest error in the least-squares sense is chosen as the rate law. The integral method is less vulnerable for noise, but is computationally more expensive.

Integral method using extents of reaction and mass transfer[4]. The concept of extents of reaction and mass transfer has been thoroughly explained in [1] and [3]. In this identification method, the extents are used for identification. The first step in the identification procedure is to identify the stoichiometry. Thereafter, the extents are computed from measured data as in section 2.2.1. In the next step, the nonlinear optimization problem is formulated as:

$$\min_{\theta_{r,i}} (x_{r,i} - \hat{x}_{r,i}(\theta_{r,i}))^T W_r (x_{r,i} - \hat{x}_{r,i}(\theta_{r,i})) \quad (2.69)$$

subject to

$$\dot{\hat{x}}_{r,i}(t) = V_l(t)r_i(c_l(t), \theta_{r,i}) - \frac{u_{out,l}(t)}{m_l(t)}\hat{x}_{r,i}(t) \quad (2.70)$$

$$\hat{x}_{r,i}(0) = 0, \quad \theta_{r,i}^L \leq \theta_{r,i} \leq \theta_{r,i}^U \quad (2.71)$$

where $x_{r,i}$ and $\hat{x}_{r,i}(\theta_{r,i})$ are the H -dimensional vectors of respectively the computed and simulated extent of reaction as a function of the unknown parameters $\theta_{r,i}$, W_r is an $H \times H$ -dimensional weighting matrix, $r_i(c_l(t), \theta_{r,i})$ the for $\theta_{r,i}$ evaluated rate expression as a function of measured concentrations and $\theta_{r,i}^L$ and $\theta_{r,i}^U$ the lower and upper bound of the parameters respectively. For the mass transfer, the nonlinear optimization problem is similar:

$$\min_{\theta_{m,j}} (x_{m,l,j} - \hat{x}_{m,l,j}(\theta_{m,j}))^\top W_m (x_{m,l,j} - \hat{x}_{m,l,j}(\theta_{m,j})) \quad (2.72)$$

subject to

$$\dot{\hat{x}}_{m,l,j}(t) = \zeta_j(c_l(t), c_g(t), \theta_{m,j}) - \frac{u_{out,l}(t)}{m_l(t)}\hat{x}_{m,l,j} \quad (2.73)$$

$$\hat{x}_{m,l,j}(0) = 0, \quad \theta_{m,j}^L \leq \theta_{m,j} \leq \theta_{m,j}^U \quad (2.74)$$

where $x_{m,l,j}$ and $\hat{x}_{m,l,j}(\theta_{m,j})$ are the H -dimensional vectors of respectively the computed and simulated extents of the j th mass transfer in the liquid space, W_m is an $H \times H$ -dimensional weighting matrix, ζ_j is the rate expression for the j th mass transfer and $\theta_{m,j}^L$ and $\theta_{m,j}^U$ the lower and upper bound of the parameters respectively. The integration of the differential equation requires information about the concentration. Because this data is needed continuously, the sampled data must be interpolated with continuous basis function $\phi_h(t)$ as follows:

$$c(t) = \sum_{h=0}^H c(t_h)\phi_h(t) \quad (2.75)$$

where $c(t)$ is the interpolated concentration data and $c(t_h)$ is the sampled concentration data. Global parameter identifiability implies that there is a unique set of parameters for which the model resembles the actual system best. Checking the parameter identifiability can be done beforehand. These methods have been investigated in [7], [9] and [24]. Parameter sensitivity can also be investigated to see which parameters affect the system dynamics the most [21].

In [5], an extensive research has been conducted on the performances of both the rate-based and extent-based identification. The following conclusions are drawn:

- The extent-based approaches give parameter estimates with tighter confidence intervals compared to rate-based approaches.
- Both extent-based and rate-based approaches can lead to biased estimates.
- Extent-based approaches can better distinguish rate law candidates than rate-based approaches.
- Extent-based approaches are computationally more costly than rate-based approaches.

2.5.1 Example of incremental identification on a batch reactor

In this example, the incremental identification will be demonstrated on a batch reactor. Assume a reaction system with balanced reaction:



with

$$N^T = \begin{bmatrix} -1 \\ -1 \\ 1 \\ 1 \end{bmatrix} \quad (2.77)$$

$$r(t) = k_f e^{-\frac{E_{af}}{RT(t)}} C_A(t) C_B(t) - k_r e^{-\frac{E_{ar}}{RT(t)}} C_C(t) C_D(t) \quad (2.78)$$

$$\dot{C}(t) = N^T r(t) \quad (2.79)$$

$$\dot{T}(t) = -\beta V(t) r(t) \quad (2.80)$$

The data that is used for identification is concentration data of all species and the volume of the reactor. The data is sampled at 0.1 s with a total of 2500 samples. The first step in an incremental identification procedure is to determine the stoichiometric matrix. For this case, this step is not necessary, as we assume it is known. Next, four different candidate rate laws are formulated:

- Candidate 1: $r(t) = k_f e^{-\frac{E_{af}}{RT(t)}} C_A(t) C_B(t) - k_r e^{-\frac{E_{ar}}{RT(t)}} C_C(t) C_D(t)$ (true system)
- Candidate 2: $r(t) = k_f e^{-\frac{E_{af}}{RT(t)}} C_A^2(t) C_B^2(t) - k_r e^{-\frac{E_{ar}}{RT(t)}} C_C(t) C_D(t)$
- Candidate 3: $r(t) = k_f e^{-\frac{E_{af}}{RT(t)}} C_A(t) C_B(t) - k_r e^{-\frac{E_{ar}}{RT(t)}} C_C^2(t) C_D^2(t)$
- Candidate 4: $r(t) = k_f e^{-\frac{E_{af}}{RT(t)}} C_A^2(t) C_B^2(t) - k_r e^{-\frac{E_{ar}}{RT(t)}} C_C^2(t) C_D^2(t)$

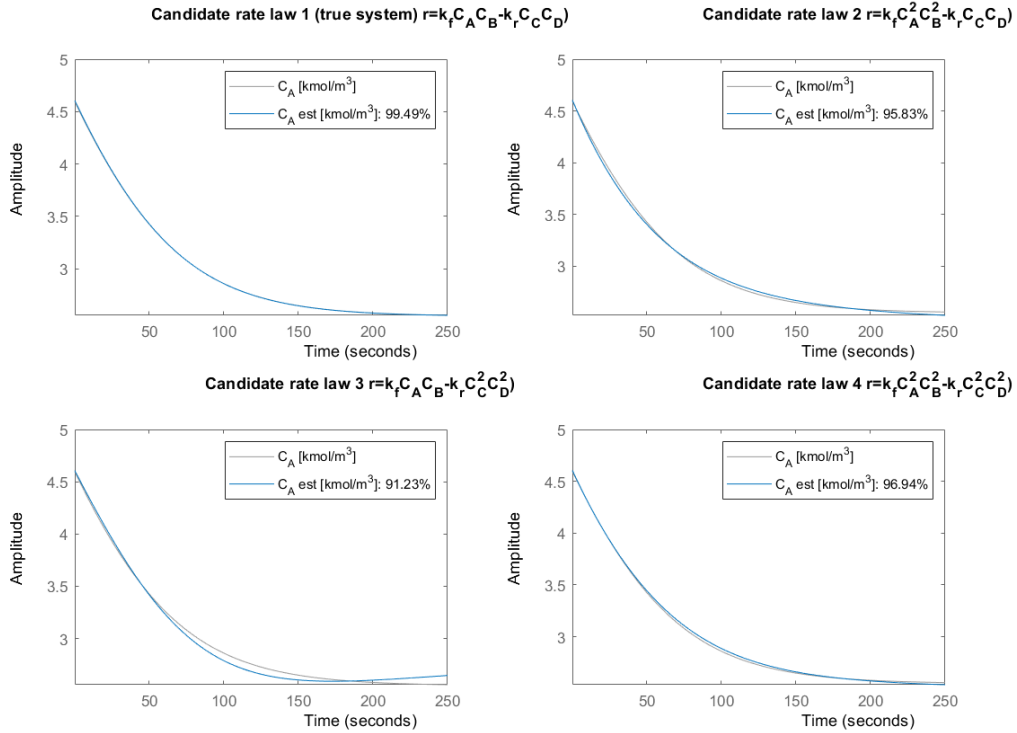


Figure 2.5: Incremental identification with no noise

The candidate rate law that matches the measured response best is chosen as rate law for the model. For this identification procedure, use was made of the integral method using concentrations, not extents. The identification results are displayed in Figures 2.5, 2.6, 2.7 and 2.8.

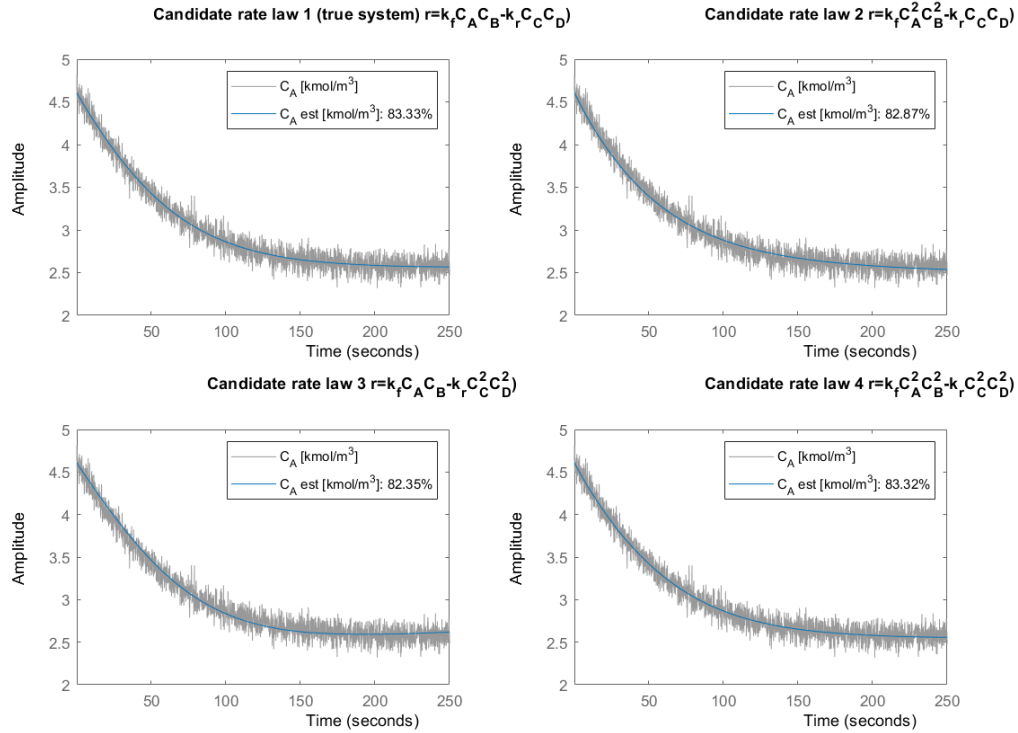


Figure 2.6: Incremental identification with a low SNR

This identification was performed with the MATLAB function `nlgreyest.m`. There are alternatives for identification such as least squares, but for simplicity, this method and function was used. `nlgreyest.m` estimates the parameters of a nonlinear grey-box model. The used measure for assessing the performance is the Normalized Root Mean Square (NRMS) which is the default measure for this function. The NRMS is defined as:

$$fit = \left(1 - \frac{\|y - \hat{y}\|}{\|y - \text{mean}(y)\|} \right) \cdot 100\% \quad (2.81)$$

where y is the measured data and \hat{y} is the fitted data. The numerical values of the fit are displayed in the legends of the Figures 2.5, 2.6, 2.7 and 2.8. For the ideal situation where there is no noise present, it is clear that the candidate rate law of the true systems reflects the true system best. In Figures 2.6 and 2.7 it is visible that for an decreasing Signal-to-Noise Ratio (SNR), the distinction between the candidate rate law becomes less. When concentration and temperature are both identified simultaneously with no noise as in Figure 2.8, the distinction between the rate laws is better. Table 2.1 provides the true systems parameter values and the estimates under the different circumstances. It shows that even though the distinction between rate laws is better for simultaneous identification, the estimated parameters are further away from the true system than the individual identification of the concentrations. The reason for this may also be that the value for β is estimated as a constant value, while it is a function of the number of moles in the reactor. It is therefore advised to first identify the rate law and subsequently determine β independently. The general conclusion here is that incremental identification is possible for the estimation of parameters related to reaction.

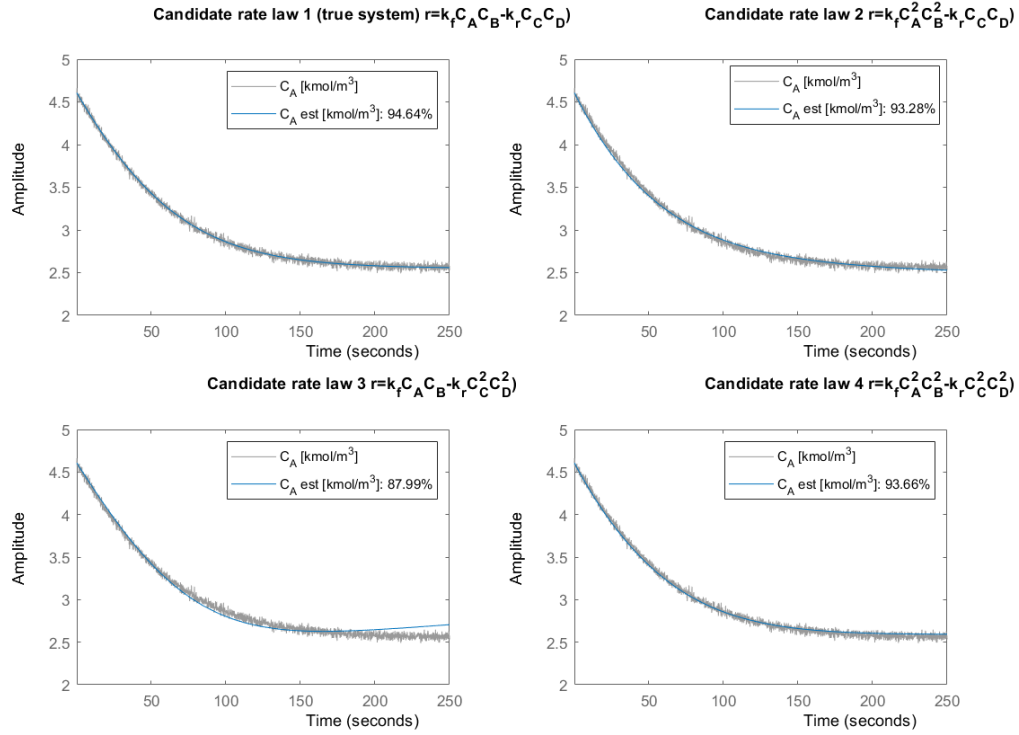


Figure 2.7: Incremental identification with a high SNR

Parameter	True system	Low SNR	High SNR	No noise	No noise, simultaneous
k_f	$6.060 \cdot 10^5$	$5.695 \cdot 10^5$	$5.465 \cdot 10^5$	$5.207 \cdot 10^5$	$9.860 \cdot 10^5$
k_r	$9.840 \cdot 10^6$	$6.564 \cdot 10^6$	$7.301 \cdot 10^6$	$8.161 \cdot 10^6$	$5.786 \cdot 10^5$
E_{af}	$6.380 \cdot 10^4$	$6.359 \cdot 10^4$	$6.347 \cdot 10^4$	$6.331 \cdot 10^4$	$6.528 \cdot 10^4$
E_{ar}	$7.171 \cdot 10^4$	$7.040 \cdot 10^4$	$7.076 \cdot 10^4$	$7.111 \cdot 10^4$	$6.270 \cdot 10^4$
β	-	-	-	-	$-3.539 \cdot 10^1$

Table 2.1: Parameter estimation results for various circumstances for candidate rate law 1

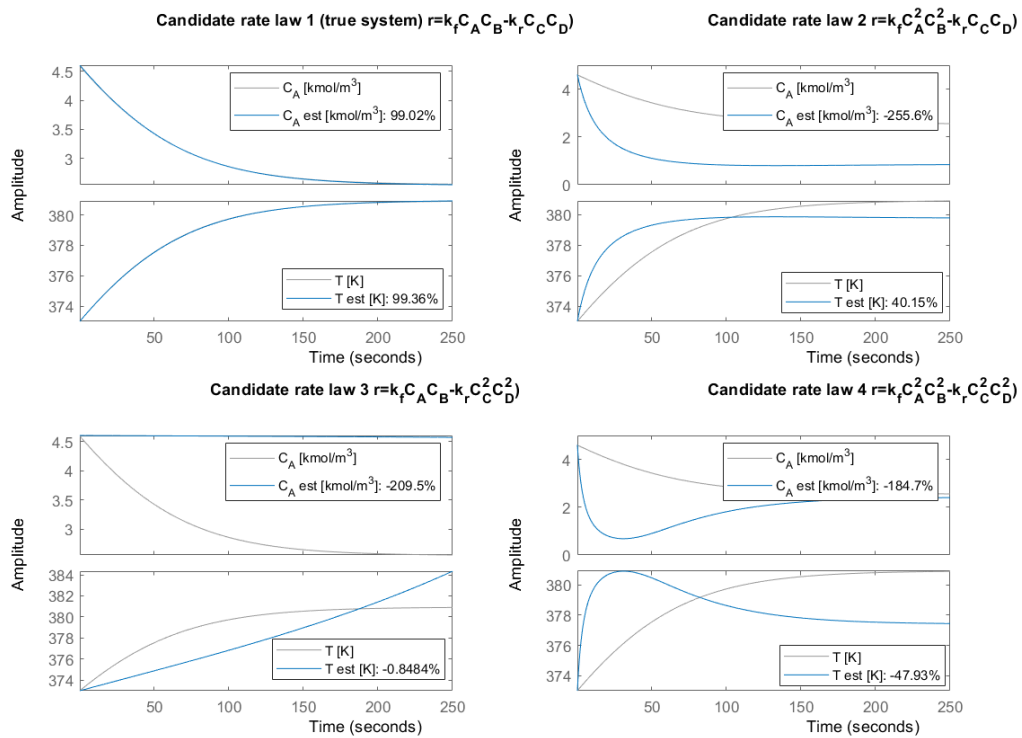


Figure 2.8: Incremental identification with no noise, simultaneously identifying concentrations and temperature

Chapter 3

Extent representation and Orthogonal Basis Functions

This chapter is concerned with the main research of this thesis. In section 2.3, three LPV representations were formulated using the extent transformation. The most suitable representation for this thesis is when reaction is regarded as a disturbance. In that LPV representation it was assumed that the parameters α , β and γ are constant. As a result, the $A(\theta)$ is varying with parameter θ and the B and C matrices are constant. Identifying the parameters α , β and γ can be done using system identification. Besides that, the model can also be approximated using Orthogonal Basis Functions (OBF's) [22],[8]. This yields a linear model. The problem here is that the reaction is a disturbance in identification of reaction systems. The parameter β is associated with this disturbance and can only be identified using the nonlinear method of incremental identification. The parameters α and γ are associated with the linear part of reaction systems. Therefore we would like to know if it is possible to identify reaction systems, namely α and γ , using OBF's. Hence our first subquestion is: *"Is it possible to approximate a general nonlinear model of reaction systems using OBF's?"*. It might also be convenient for identification to investigate whether there is a relation between extent transformations and OBF's. This poses the second subquestion of this thesis: *"Do the extent transformations form a set of unique OBF's?"*.

To answer these questions, it needs to be explained how identification of linear and LPV systems is performed. This is explained in section 3.1. Section 3.2 is the investigation to answer the second subquestion. In section 3.3, the first subquestion is investigated. Section 3.4 suggests a topic to investigate in the future in case when identification needs to be performed for slow reaction systems.

3.1 Identification of linear and LPV systems using OBF's

Every stable system has a unique series expansion in terms of a specific basis. Hence it is possible to approximate a system by a finite-length series expansion using basis functions [22]. Questions that are relevant for this research are the length of the series expansion and the selection of optimal orthogonal basis functions. In [22] it is concluded that the accuracy of the chosen basis functions can substantially improve the identification results in both bias and variance. The flexibility of the basis functions provide a possibility to use uncertain *a priori* knowledge into the procedure. As a result, the better the *a priori* knowledge is, the accuracy of the model is higher.

Consider a stable discrete transfer function $G(z)$. According to [22], there exists a unique series

expansion:

$$G(z) = \sum_{k=0}^{\infty} L_k f_k(z) \quad (3.1)$$

with $f_k(z)$ a sequence of orthonormal basis functions and L_k the corresponding expansion coefficients. The basis functions are orthogonal because of the property:

$$\frac{1}{2\pi} \int_{-\pi}^{\pi} f_k(e^{i\omega}) f_l(e^{-i\omega}) d\omega = \begin{cases} 1 & (k = l) \\ 0 & (k \neq l) \end{cases} \quad (3.2)$$

The transfer function $G(z)$ can be approximated with a finite number of coefficients and basis functions:

$$G(z) \approx \sum_{k=0}^n L_k f_k(z) \quad (3.3)$$

The power of this expansion is that with a relatively low order for the expansion, a good approximation can be given.

There exist several possibilities for orthogonal basis functions such as Takenaka-Malmquist, Hambo, Kautz, Laguerre and Pulse [19]. The system that is worked with in this thesis does not have complex poles or a large order transfer function. Therefore this thesis is restricted to the simpler OBF's like Laguerre or Pulse basis. The Pulse basis is the OBF $f_k(z) = z^{-k}$. The Laguerre orthogonal basis function is given by [23]:

$$f_k(z) = \frac{K}{z-a} \left(\frac{1-az}{z-a} \right)^k, \quad K = \sqrt{(1-a^2)T_s} \quad (3.4)$$

An important assumption here is that $G(\infty) = 0$, meaning that the transfer function is strictly proper. Another assumption is that the transfer function is stable. The variable a is a design variable. The value of a reflects the pole locations of the Laguerre basis functions and hence it should hold that $|a| \leq 1$.

Example: Identifying a first order transfer function. Assume a data generating system with the true transfer function as follows:

$$G_0(s) = \frac{10}{s+1} \quad (3.5)$$

It is now possible to approximate the transfer function $G(z)$ for a finite number of coefficients and basis functions. In this example, the Laguerre basis is used and the order n is chosen to be 4. For the variable a , a value of 0.8 is chosen. The sampling time is 0.1 second.

For the identification procedure, a white noise input signal is generated because it contains all the frequencies in the frequency spectrum. The following matrix equality can then be formed using the basis functions:

$$[\Phi_0(t) \quad \dots \quad \Phi_n(t)] \begin{bmatrix} L_0 \\ \vdots \\ L_n \end{bmatrix} + \begin{bmatrix} \varepsilon_0 \\ \vdots \\ \varepsilon_n \end{bmatrix} = \hat{y}(t) \quad (3.6)$$

$$[f_0(z,a)u(t) \quad \dots \quad f_n(z,a)u(t)] \begin{bmatrix} L_0 \\ \vdots \\ L_n \end{bmatrix} + \begin{bmatrix} \varepsilon_0 \\ \vdots \\ \varepsilon_n \end{bmatrix} = \hat{y}(t) \quad (3.7)$$

This equality can be solved in MATLAB. The results of the approximation can be found in Figure 3.1. What is clearly visible is that for an increasing value of n , the resemblance to the original system's frequency response improves.

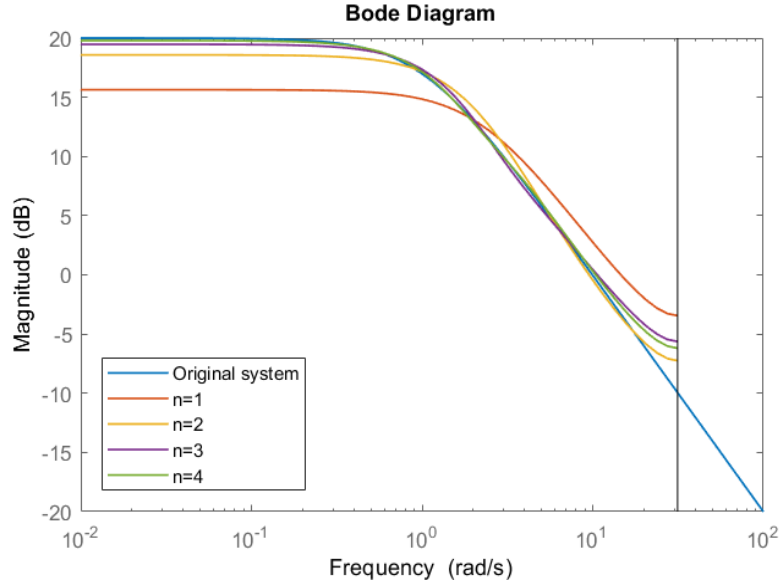


Figure 3.1: Bode magnitude diagram of the identification result using OBF's

It is also possible to identify an LPV system using fixed OBF's. For the identification procedure assume that the state space of the underlying system is given by:

$$\left[\begin{array}{c|c} A_d & B_d \\ \hline C_d(p) & D_d \end{array} \right] \quad \text{or} \quad \left[\begin{array}{c|c} A_d & B_d(p) \\ \hline C_d & D_d \end{array} \right] \quad (3.8)$$

where p is the scheduling variable. For the identification of the left state space system the Wiener-LPV OBF structure is used as in Figure 3.2. The identification of the right state space system is done with the Hammerstein-LPV OBF structure as in Figure 3.3 [19]. The procedure for identification is now demonstrated using an example. An important assumption here is that the data of input u , scheduling variable p and output y is known or can be measured.

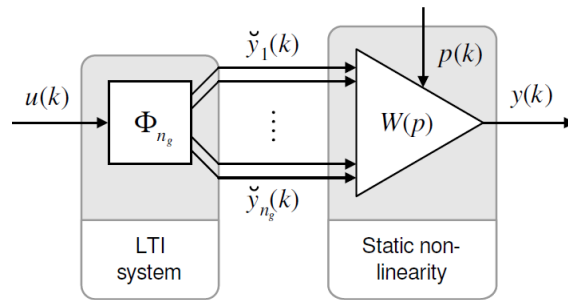


Figure 3.2: Wiener LPV OBF model structure

Example: C_d varying LPV model. Assume an LPV system as follows:

$$\left[\begin{array}{c|c} A_d & B_d \\ \hline C_d(p) & D_d \end{array} \right] = \left[\begin{array}{c|c} -0.9 & 1 \\ \hline p^2 & 0 \end{array} \right] \quad (3.9)$$

The approximation is given by:

$$\hat{y}(t) \approx \sum_{k=0}^n L_{k,l}(p(t)) f_k(z, a) u(t) \quad (3.10)$$

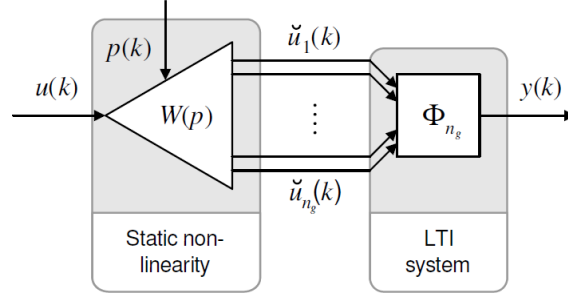


Figure 3.3: Hammerstein LPV OBF model structure

where $L_{k,l}(p(t))$ is modelled separately as:

$$L_{k,l}(p(t)) = \sum_{l=0}^m w_{k,l} \psi_l(t) \quad (3.11)$$

where $\psi_l(t)$ is an arbitrary continuous function with the property that $\psi_0(t) = 1$. In this case, the polynomial function $\psi_l(t) = (p(t))^l$ is used. The solution can now be computed by the following matrix equation:

$$\begin{bmatrix} y(0) \\ y(1) \\ \vdots \\ y(M) \end{bmatrix} = \begin{bmatrix} \Phi_0(0) & \dots & \Phi_0(0)(p(0))^l & \dots & \Phi_n(0) & \dots & \Phi_n(0)(p(0))^m \\ \Phi_0(1) & \dots & \Phi_0(1)(p(1))^l & \dots & \Phi_n(1) & \dots & \Phi_n(1)(p(1))^m \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \Phi_0(M) & \dots & \Phi_0(M)(p(M))^l & \dots & \Phi_n(M) & \dots & \Phi_n(M)(p(M))^m \end{bmatrix} \begin{bmatrix} w_{0,0} \\ w_{0,1} \\ \vdots \\ w_{1,0} \\ w_{1,1} \\ \vdots \\ w_{n,m} \end{bmatrix} \quad (3.12)$$

Where M is the number of samples, n the number of basis functions and m the polynomial order. The coefficients $w_{k,l}$ can then be computed by solving the matrix equality $Ax = b$. The approximation of the system in equation 3.9 is then given Figure 3.4 where $n = 4$, $a = 0.8$, $m = 2$ and $M = 500$. What can be seen here is that for a relatively low order of OBF, a good approximation is given by the identification procedure.

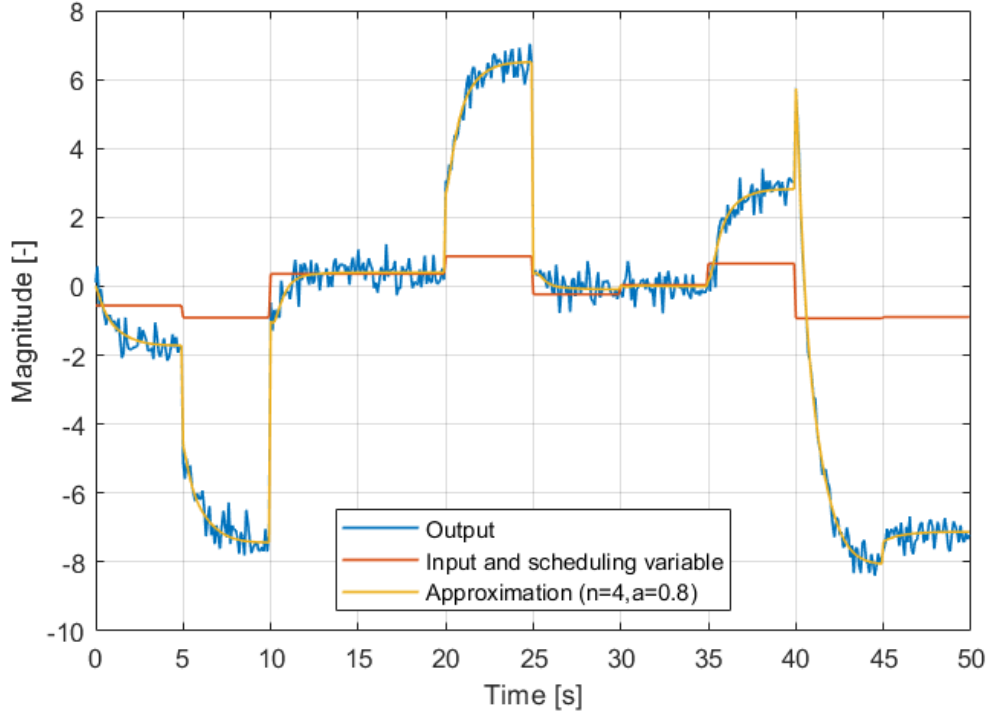


Figure 3.4: Result of LPV identification procedure. Red line is both the input and scheduling variable. The blue line is the original output. The yellow line is the approximation of the output using a fourth order OBF approximation with the pole of the OBF in 0.8.

3.2 Extents representation and a unique OBF

In this section, we investigate whether the extent representation yields an unique orthogonal basis function and thus answering the second subquestion. The continuous case where the extent representation is given by:

$$\begin{bmatrix} \dot{x}_r(t) \\ \dot{x}_{in}(t) \\ \dot{\lambda}(t) \end{bmatrix} = \begin{bmatrix} -\theta(t)I_R & 0 & 0 \\ 0 & -\theta(t)I_p & 0 \\ 0 & 0 & -\theta(t) \end{bmatrix} \begin{bmatrix} x_r(t) \\ x_{in}(t) \\ \lambda(t) \end{bmatrix} + \begin{bmatrix} 0 & I_R \\ I_p & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} u_{in}(t) \\ \mathcal{V}(t)r(t) \end{bmatrix}, \quad (3.13)$$

$$n(t) = [N^\top \quad W_{in} \quad n_0] \begin{bmatrix} x_r(t) \\ x_{in}(t) \\ \lambda(t) \end{bmatrix} \quad (3.14)$$

and $\theta = \frac{u_{out}(t)}{m(t)}$, which is assumed to be constant. $\mathcal{V}(t)r(t)$ is regarded as a disturbance d and $u_{in}(t)$ as an input u . In the frequency domain, the relation is given by:

$$n(s) = \frac{W_{in}}{s + \theta} u(s) + \frac{N^\top}{s + \theta} d(s) \quad (3.15)$$

The most important requirement for a function to be used as basis function is that the function is all-pass. This means that the magnitude of the transfer function must be equal to 1 for all frequencies:

$$\|G(j\omega)\| = 1 \quad \forall \omega \quad (3.16)$$

where $G(j\omega)$ is an all-pass transfer function. If the matrices W_{in} and N^\top in the transfer functions in 3.15 are neglected, the transfer function is $H(s) = \frac{1}{s + \theta}$. The transfer function $H(s)$ is not equal

to 1 for all frequencies. The only way a function is all-pass is when the frequencies of the zero and pole are mirrored in the imaginary axis of the complex plane:

$$\tilde{G}(s) = \frac{s - \theta}{s + \theta} \quad (3.17)$$

where $\tilde{G}(s)$ is a first order all-pass transfer function.

3.3 Identification of reaction systems using OBF's with reaction as disturbance

In this section, an investigation whether identification is possible if the reaction is regarded as a disturbance, is conducted. This section is therefore an investigation of the first subquestion. If the reaction is regarded as a disturbance, the state space system is given by equations 2.49 and 2.52. The accompanying transfer functions are then given by:

$$\frac{n(s)}{u_{in}(s)} = \frac{W_{in}}{s + \theta} \quad (3.18)$$

$$\frac{T(s)}{u_{in}(s)} = \frac{\alpha}{s + \theta} \quad (3.19)$$

$$\frac{T(s)}{Q_{in}(s)} = \frac{\gamma}{s + \theta} \quad (3.20)$$

It is worthwhile to investigate what the impact of the disturbance is in this setting, if one desires to identify the parameters α and γ . Therefore we assume a reaction system with equilibrium reaction:



with

$$W_{in} = \begin{bmatrix} \frac{1}{M_A} & 0 \\ 0 & \frac{1}{M_B} \\ 0 & 0 \\ 0 & 0 \end{bmatrix}, \quad N^T = \begin{bmatrix} -1 \\ -1 \\ 1 \\ 1 \end{bmatrix} \quad (3.22)$$

$$r(t) = k_f e^{-\frac{E_{af}}{RT(t)}} C_A(t) C_B(t) - k_r e^{-\frac{E_{ar}}{RT(t)}} C_C(t) C_D(t) \quad (3.23)$$

Note here that the reaction vector uses dynamic reaction coefficients to make the situation more realistic. The nominal values of the parameters are given in Table A.1. The measured quantities are:

- Volume \mathcal{V}
- Reactor temperature T
- Stoichiometric matrix N
- Inlet composition matrix W_{in}
- Inlet mass flow u_{in}
- Heat duty Q_{in}
- Inlet temperature T_{in}
- Inlet flow heat capacity C_{pin}
- Volumetric outlet flow F_{out}

The only quantities that are generally not measured are the concentrations of each species or the number of moles of each species. This absence of measurements obliges the identification of the

parameters α and γ . In an ideal situation, where concentration could be measured, α and γ could be calculated by means of the following relations:

$$\alpha(t) = \frac{C_{pin} T_{in}}{m(t) C_{pmix}(t)} = \frac{C_{pin} T_{in}}{C_p M_w n(t)} = \frac{C_{pin} T_{in}}{C_p M_w C(t) \mathcal{V}(t)} \quad (3.24)$$

$$\gamma(t) = \frac{1}{m(t) C_{pmix}(t)} = \frac{1}{C_p M_w n(t)} = \frac{1}{C_p M_w C(t) \mathcal{V}(t)} \quad (3.25)$$

$$n(t) = \begin{bmatrix} n_A(t) \\ n_B(t) \\ n_C(t) \\ n_D(t) \end{bmatrix}, \quad C(t) = \begin{bmatrix} C_A(t) \\ C_B(t) \\ C_C(t) \\ C_D(t) \end{bmatrix}, \quad C_p = \begin{bmatrix} C_{p,A} \\ C_{p,B} \\ C_{p,C} \\ C_{p,D} \end{bmatrix}^T \quad (3.26)$$

$$C_{pin} = C_p \begin{bmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 \\ 0 & 0 \end{bmatrix}, \quad M_w = \begin{bmatrix} M_A & 0 & 0 & 0 \\ 0 & M_B & 0 & 0 \\ 0 & 0 & M_C & 0 \\ 0 & 0 & 0 & M_D \end{bmatrix} \quad (3.27)$$

3.3.1 Identification of a CSTR with controlled θ

We would like to investigate the identification for a case where θ is constant. Unfortunately, a realistic situation where θ can be fixed does not exist. Besides that, it is undesirable to have θ constant due to possible disturbances. A better alternative is to control θ . In our original definition, θ is given as:

$$\theta(t) = \frac{u_{out}(t)}{m(t)} \quad (3.28)$$

Looking at this equation from a practical point of view this would mean that data about $u_{out}(t)$ and $m(t)$ should be measured in order to control θ . Measuring the mass in a reactor can be cumbersome. Also measuring outlet mass-flow is more difficult than measuring volumetric outlet flow. Rewriting the previous equation for θ yields a beneficial result:

$$\theta(t) = \frac{u_{out}(t)}{m(t)} = \frac{\frac{F_{out}(t)}{\rho_{mix}}}{\frac{V(t)}{\rho_{mix}}} = \frac{F_{out}(t)}{V(t)} \quad (3.29)$$

where $F_{out}(t)$ is volumetric outlet flow and $V(t)$ is the volume of the tank. These quantities are most often measured in industry. $V(t)$ is determined from the level controllers of the reactor and the physical design of the reactor. Volumetric outlet flow can be measured by flow meters. It is now possible to control θ using these quantities.

The most important parameters that we need to approximate using identification in 3.19, 3.20 and 3.20 are α and γ . W_{in} tends to be known, so does not need to be identified. α and γ both appear in the differential equation of energy balance, so temperature data is used for the identification procedure. In the simulation of the identification procedure, three step inputs are applied simultaneously at $t = 0$, resulting in a startup phase. The identification is performed on the data after the startup phase for $t \geq 1500$ s. For the identification of α and γ the inputs of Figure are applied to the system. The temperature response of these steps can be seen in Figure 3.7. In the first attempt to estimate α and γ , a first order approximation is made for the transfer function in equation 3.20, hence assuming α and γ are constant. The identification result is displayed in Figure 3.8. The approximation of γ as a constant is fairly well. The identification of α is not good enough. There appears to be a peak upward after a step is applied, signifying non-minimum phase behaviour. The reason for this can be found in the definition of α in equation 3.24. The variable α is related to the number of moles in an inverse relation. The effect of this inverse relation is related to the non-minimum phase behaviour. In theory it should therefore

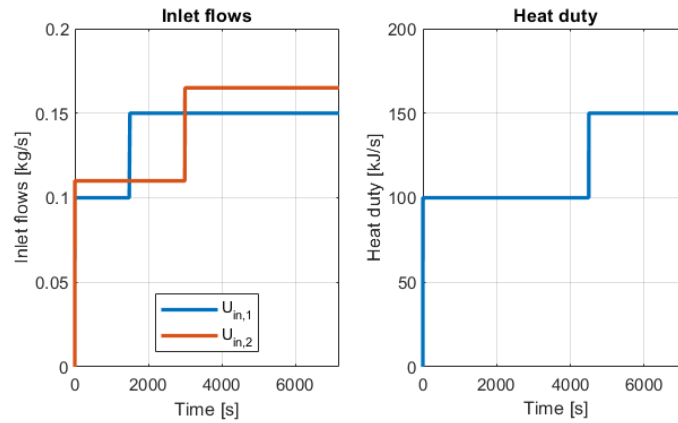


Figure 3.5: Inputs applied to the system

be possible to identify α as a dynamic variable. This is done in Figure 3.9, where the transfer functions in 3.20 and 3.20 are modelled as being second-order transfer functions. Now the fit in the time domain is more accurate as the non-minimum phase behaviour is captured. The benefit is that the transfer function in 3.19 can be approximated locally. The downside is that the physical interpretation of this transfer function is lost. The identified bode plots are given in Figure 3.13. One characteristic that is striking is significant decrease of mass in Figure 3.6 due to a controlled θ . This is a situation that is undesirable in practice. Therefore in the next section, the identification will be executed in a situation with controlled mass.

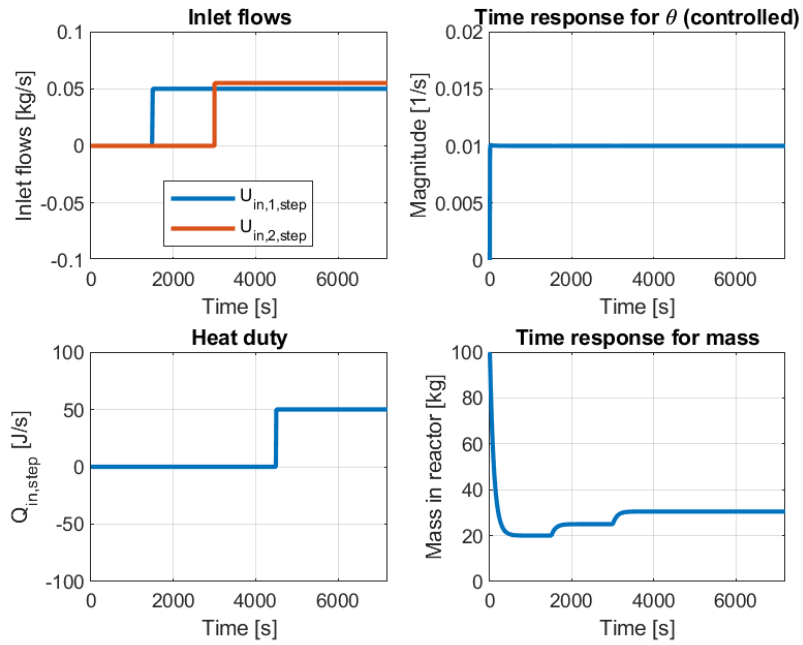


Figure 3.6: Input signals, time response for θ and reactor mass

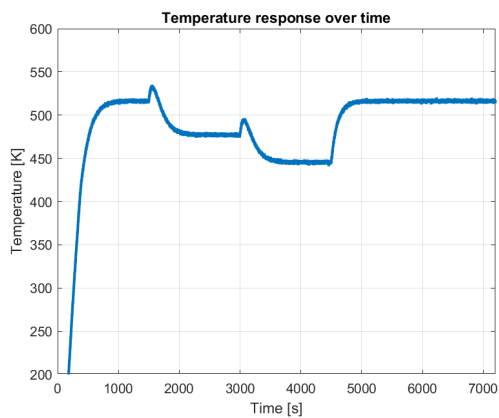


Figure 3.7: Temperature response for controlled θ

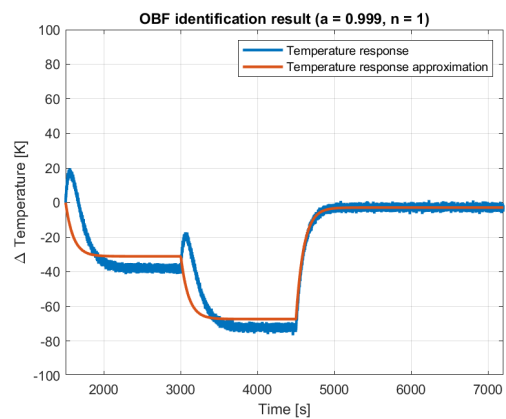


Figure 3.8: First order identification result

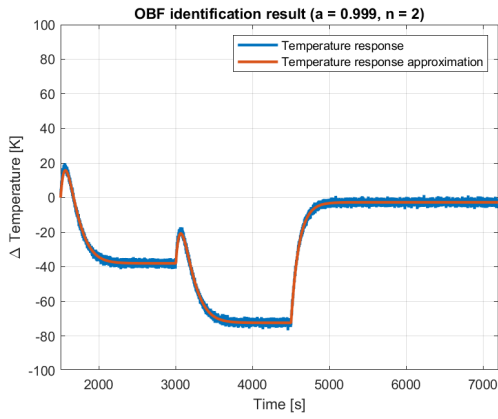


Figure 3.9: Second order identification result

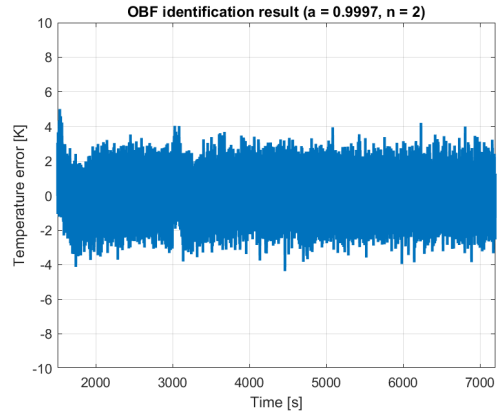


Figure 3.10: Second order identification result (error)

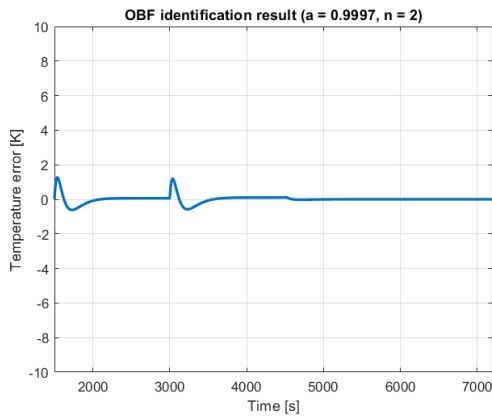


Figure 3.11: Second order identification result (error, no noise)

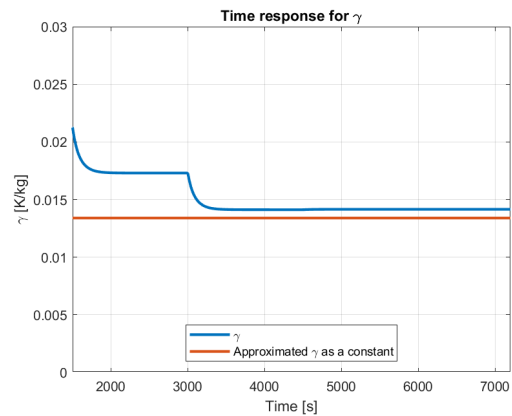


Figure 3.12: Second order identification result for γ

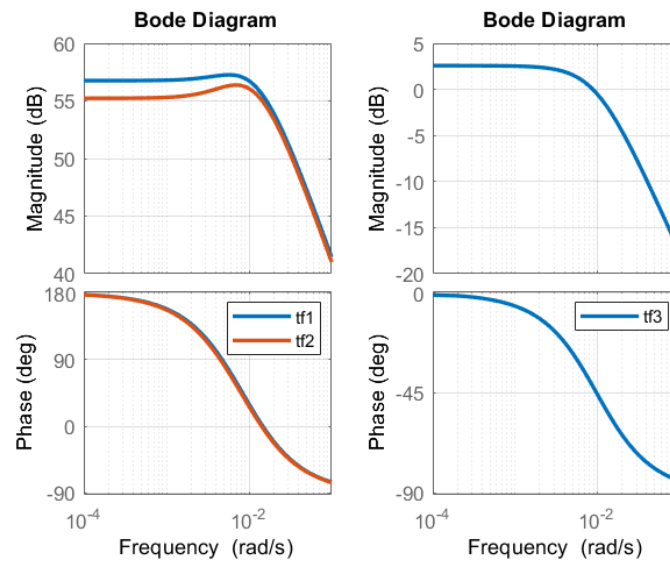


Figure 3.13: Second order identification results (Bode plots). 'tf1' corresponds to transfer function 3.19, 'tf2' corresponds to transfer function 3.20 and 'tf3' corresponds to transfer function 3.20.

3.3.2 Identification of a CSTR with controlled mass

The situation where mass is controlled is more common in process industry than the situation where θ is controlled. As a result, θ is not constant anymore. The fluctuations in θ however are not that significant so identification could still be possible with a fixed θ . The first order identification result is displayed in Figure 3.16 and the second order identification result is displayed in Figures 3.17, 3.18 and 3.20. One observation here is that the non-minimum phase behaviour that was encountered in the controlled θ situation is not observed. Another observation is that the difference between first order and second order is not significant. The difference between the estimated γ and the actual measured γ is significant. But this yields no significant mismatch in the time response. This is due to the very small value of γ . The bode plots of the three transfer functions are given in Figure 3.21. The conclusion here is that controlling the mass is also a viable solution for identifying the parameters. The condition then is that the larger the magnitude of the applied inputs, the larger the variations in θ will be and hence the identification result will deteriorate.

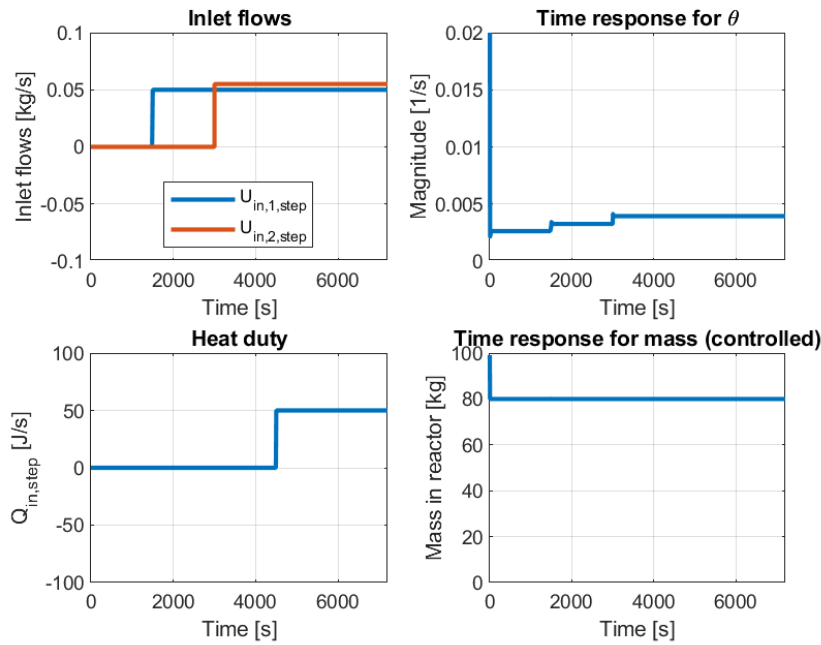


Figure 3.14: Input signals, time response for θ and reactor mass

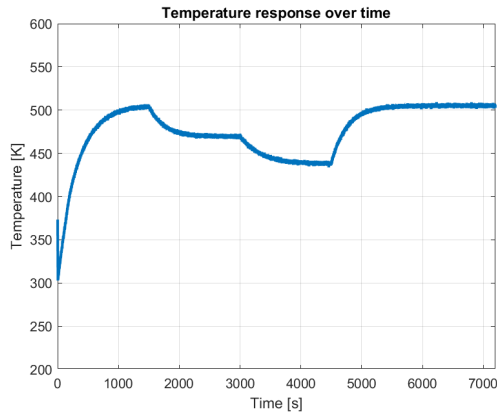


Figure 3.15: Temperature response for controlled mass

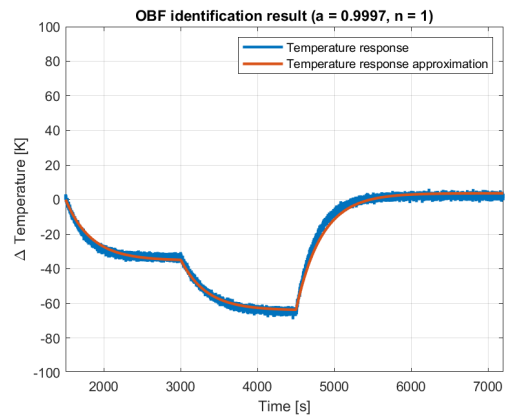


Figure 3.16: First order identification result

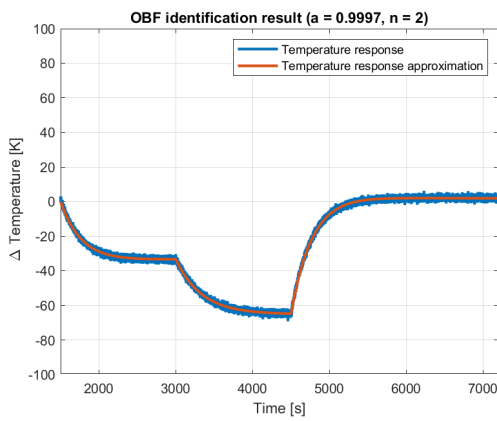


Figure 3.17: Second order identification result

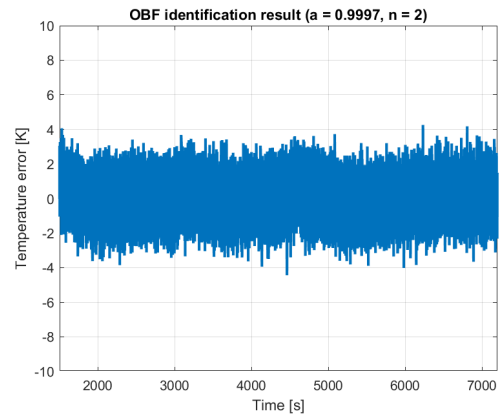


Figure 3.18: Second order identification result (error)

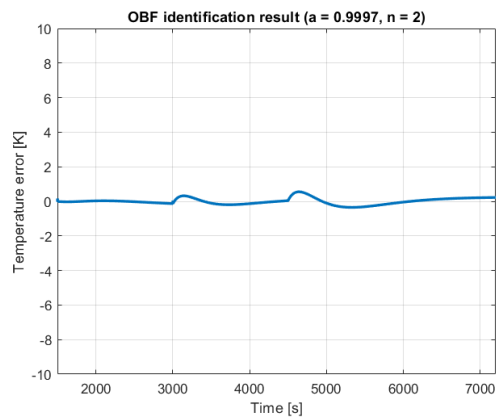


Figure 3.19: Second order identification result (error, no noise)

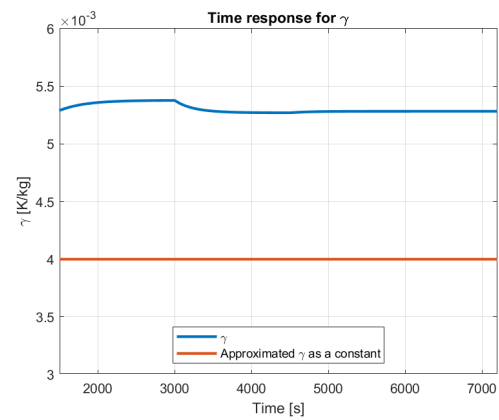


Figure 3.20: Second order identification result for γ

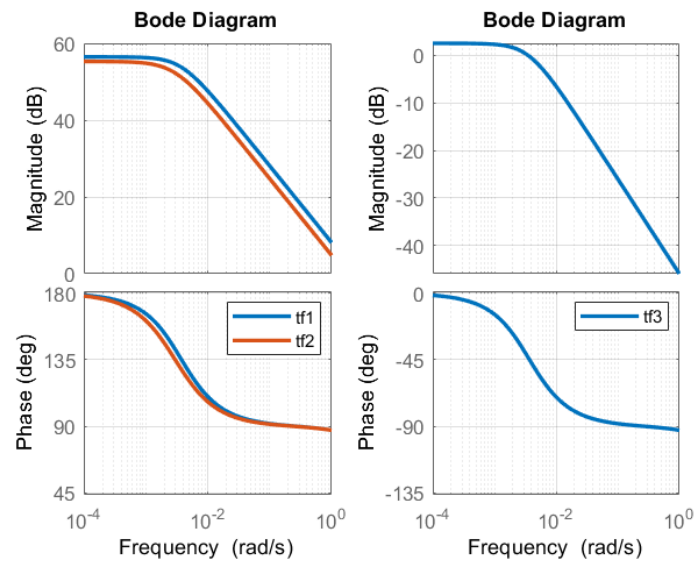


Figure 3.21: Second order identification results (Bode plots). 'tf1' corresponds to transfer function 3.19, 'tf2' corresponds to transfer function 3.20 and 'tf3' corresponds to transfer function 3.20.

3.3.3 Estimation of α and γ by explicit expressions

In sections 3.3.1 and 3.3.2, it was concluded that approximating transfer functions 3.20 and 3.20 as a second order transfer functions improves the identification result. The disadvantage is that physical interpretation is lost when using this method. The physical interpretation however, is important in understanding the reactor dynamics. In this section, the physical interpretation will be searched for by writing out the explicit expressions for the time responses of the quantities that define α and γ . This is done using the Laplace transform.

If the reaction part of equation 2.5 is neglected, the explicit time response to a step input is as follows:

$$\mathcal{L}\{\dot{n}(t)\} = \mathcal{L}\left\{W_{in}u_{in}(t) - \frac{u_{out}(t)}{m(t)}n(t)\right\} \quad (3.30)$$

$$s \cdot n(s) - n_0 = W_{in}u_{in}(s) - \theta n(s) \quad (3.31)$$

$$n(s) = \frac{W_{in}}{s + \theta}u_{in}(s) + \frac{n_0}{s + \theta} \quad (3.32)$$

$$\mathcal{L}\{n(s)\}^{-1} = \mathcal{L}\left\{\frac{W_{in}}{s + \theta}\frac{\kappa}{s} + \frac{n_0}{s + \theta}\right\}^{-1} \quad (3.33)$$

$$n(t) = \frac{W_{in}\kappa}{\theta}\left(1 - e^{-\theta t}\right) + n_0e^{-\theta t} \quad (3.34)$$

where $\mathcal{L}\{\cdot\}$ and $\mathcal{L}\{\cdot\}^{-1}$ are the Laplace and inverse Laplace transform, respectively. $\kappa \in \mathbb{R}^{p \times 1}$ is a vector of magnitudes of the step inputs. The interest lies now in the first term of equation 3.34, which is the forced response due to the step inputs. The reason why the second term is not important is because this term signifies the number of moles at $t = 0$. Since the startup phase is discarded as in sections 3.3.1 and 3.3.2, the identification starts at $t = 1500$ s and hence focus is placed on the first term. If this first term is substituted in expressions 3.24 and 3.25, the deviation in α and γ due to the forced input is expressed as:

$$\Delta\alpha(t) = \frac{C_{p_{in}}T_{in}\theta}{C_pM_wW_{in}\kappa(1 - e^{-\theta t})} \quad (3.35)$$

$$\Delta\gamma(t) = \frac{\theta}{C_pM_wW_{in}\kappa(1 - e^{-\theta t})} \quad (3.36)$$

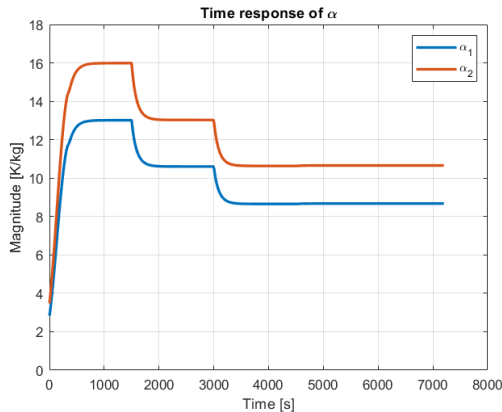


Figure 3.22: Time response of α

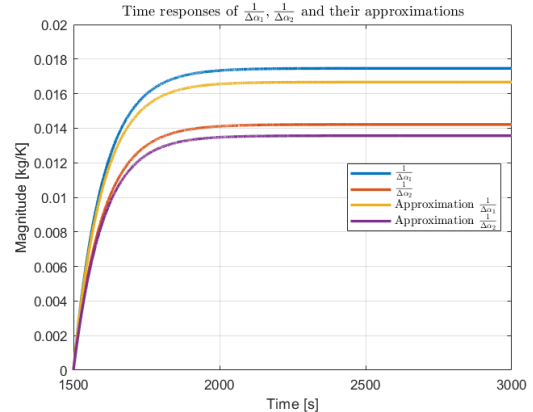


Figure 3.23: Approximation results of $\frac{1}{\Delta\alpha}$

The question now is whether this simplification is accurate enough to do identification. To test this, the same example as in section 3.3.1 is used with two inputs and a controlled θ . The time response for α is given in Figure 3.22. The expressions for $\Delta\alpha$ and $\Delta\gamma$ gives infinite or NaN result

because of the division by 0 at $t = 0$. To circumvent this problem, analysis is performed on $\frac{1}{\Delta\alpha}$. The results for γ are omitted because apart from a constant $C_{pin}T_{in}$, the results are the same. The time window for which we analyse the approximation is $1500 \leq t \leq 3000$ s. In Figure 3.23, the approximation results are displayed. With this simplification it is visible that the approximation is good. The error is caused by the reaction that shifts the balance of the reaction and causes different concentrations. Now, the change in α is displayed but not the absolute value of α . This has to be known prior to applying the step input. In this case, it is assumed that the value is known from one concentration sample that was taken just before applying the step. If this data is unknown then it is not yet known how to calculate α via explicit expressions. This can be investigated in the future.

3.4 2-step Identification method

In our identification situation in the previous section, it turned out that reaction was not a significant disturbance on the temperature. It is questionable whether the reaction is a disturbance in the first place. It was stated that the reaction is a disturbance because it is the only dynamics that makes the state space representation nonlinear. After all, if one neglects the reaction in the state space representation, one ends up with a linear system representation. It is also not possible to identify reaction using OBF's. But actually the reaction does not need to be seen as a disturbance if one looks at the structure of the reaction vector in equation 2.78. The concentration data can be measured or derived from experiment data of the number of moles and volume. The only unknown parameters are k_f, k_r, E_{af} and E_{ar} . But these can be identified by an incremental identification procedure as explained in section 2.5.

Hence in this section, a 2-step identification method is proposed. This method is proposed in a situation where a slow reaction systems needs to be identified. The first step is to perform the incremental identification procedure as explained in section 2.5. Once the parameters k_f, k_r, E_{af} and E_{ar} are known, the disturbance can be estimated in real-time. With the following input signals:

$$u_{in}(t) = -W_{in}^+ N^\top \mathcal{V}(t) \bar{r}(t) + \tilde{u}_{in}(t) \quad (3.37)$$

$$Q_{in}(t) = \frac{\left(\alpha W_{in}^+ N^\top + \beta \right) \mathcal{V}(t) \bar{r}(t)}{\gamma} + \tilde{Q}_{in}(t) \quad (3.38)$$

where $\bar{r}(t)$ is the estimated disturbance vector, the state space simplifies to:

$$\dot{n}(t) = -\theta n(t) + W_{in} \tilde{u}_{in}(t) \quad (3.39)$$

$$\dot{T}(t) = -\theta T(t) + \alpha \tilde{u}_{in}(t) + \gamma \tilde{Q}_{in}(t) \quad (3.40)$$

Which is linear system that can easily be identified. The only problem is that the controller is dependent of α, β and γ which are also the parameters that need to identified. How to further use this 2-step identification method can be investigated in future work.

Chapter 4

Identifiability, Parameter Estimation and Sensitivity

One of the problems when modelling reaction systems is that modelling is expensive. Besides that, it is not always possible to identify the system with the data at hand. Therefore, in this chapter we will investigate which parameters are identifiable and hence answer subquestion three: *”Which parameters or combination thereof can be identified?”*. This investigation is done in section 4.1. It is necessary to investigate which parameters are most influential on a certain output. This can be done by ranking the parameters according to their output contribution. Ranking parameters according to their influence is referred to as parameter sensitivity. In sections 4.2.1 and 4.2.2, the parameter sensitivity will be investigated of a CSTR and an RBD, respectively. This will answer the fourth subquestion: *”Which parameters are more important to model?”*.

4.1 Identifiability

In this section, we are going to investigate the identifiability of parameters in a dynamic model of chemical processes. This will eventually give insights in whether a model is structurally and qualitatively identifiable. The first notion means that a parameter can be uniquely identified in the first place. The second notion is related to how good an estimate of the parameter can be given. Only the first notion is treated in this thesis.

In [12], a method is given to determine if a system is structurally identifiable. Assume an underlying system that is described by the set of differential equations:

$$\frac{dx}{dt} = f(x, u, p) \quad (4.1)$$

where $f(x, u, p)$ are a set of parametric functions that are described in terms of states (x), inputs (u) and parameters (p). In the following example, which is used to demonstrate the structural identifiability, a CSTR is used with the following dynamics:

$$f(x, u, p) = \begin{bmatrix} \dot{n}(t) \\ \dot{T}(t) \end{bmatrix} = \begin{bmatrix} -\theta n(t) + N^T \mathcal{V}(t)r(t) + W_{in}u_{in}(t) \\ -\theta T(t) + \alpha u_{in}(t) - \beta \mathcal{V}(t)r(t) + \gamma Q_{in}(t) \end{bmatrix} \quad (4.2)$$

and the reaction as in 3.23. It is now possible to formulate a sensitivity matrix R as follows:

$$R = \begin{bmatrix} \frac{\partial f(x, u, p)}{\partial p_1} & \cdots & \frac{\partial f(x, u, p)}{\partial p_n} \\ \frac{\partial f(x, u, p)}{\partial p_1} & \cdots & \frac{\partial f(x, u, p)}{\partial p_n} \\ \vdots & \vdots & \vdots \end{bmatrix} \quad (4.3)$$

The columns of R have an infinite length in theory but after a certain amount of differentiations, the rank of the matrix is not increasing anymore. With a weighting matrix Q the matrix F can be formulated by:

$$F = R^\top QR \quad (4.4)$$

The rank of this matrix determines whether a parameter set is fully identifiable or not. If the rank of this matrix is less than the number of parameters, not all parameters are identifiable. For several parameter sets, the identifiability is established through the method explained above. For this, 5 different parameter sets are distinguished:

- Situation 1:

$$p_1 = [k_f \quad k_r \quad E_{af} \quad E_{ar} \quad \alpha \quad \beta \quad \gamma] \rightarrow \text{Rank}(F) = 7 \quad (4.5)$$

- Situation 2:

$$\alpha = \frac{C_{pin} T_{in}}{D_1} \quad (4.6)$$

$$\beta = \frac{D_2}{D_1} \quad (4.7)$$

$$\gamma = \frac{1}{D_1} \quad (4.8)$$

$$D_1 = mC_{pmix} \quad (4.9)$$

$$D_2 = \Delta H_f^\ominus N^\top \quad (4.10)$$

$$p_2 = [k_f \quad k_r \quad E_{af} \quad E_{ar} \quad D_1 \quad D_2] \rightarrow \text{Rank}(F) = 6 \quad (4.11)$$

- Situation 3:

$$\alpha = \frac{C_{pin} T_{in}}{mC_{pmix}} \quad (4.12)$$

$$\beta = \frac{D_2}{mC_{pmix}} \quad (4.13)$$

$$\gamma = \frac{1}{mC_{pmix}} \quad (4.14)$$

$$D_2 = \Delta H_f^\ominus N^\top \quad (4.15)$$

$$p_3 = [k_f \quad k_r \quad E_{af} \quad E_{ar} \quad D_2 \quad C_{pmix}] \rightarrow \text{Rank}(F) = 6 \quad (4.16)$$

- Situation 4:

$$\alpha = \frac{C_{pin} T_{in}}{mC_{pmix}} \quad (4.17)$$

$$\beta = \frac{\Delta H_f^\ominus N^\top}{mC_{pmix}} \quad (4.18)$$

$$\gamma = \frac{1}{mC_{pmix}} \quad (4.19)$$

$$\Delta H_f^\ominus = [H_a \quad H_b \quad H_c \quad H_d] \quad (4.20)$$

$$p_4 = [k_f \quad k_r \quad E_{af} \quad E_{ar} \quad C_{pmix} \quad H_a \quad H_b \quad H_c \quad H_d] \rightarrow \text{Rank}(F) = 6 \quad (4.21)$$

- Situation 5:

$$\alpha = \frac{C_{p_{in}} T_{in}}{C_p M_w n(t)} \quad (4.22)$$

$$\beta = \frac{D_2}{C_p M_w n(t)} \quad (4.23)$$

$$\gamma = \frac{1}{C_p M_w n(t)} \quad (4.24)$$

$$D_2 = \Delta H_f^\ominus N^\top \quad (4.25)$$

$$p_5 = [k_f \quad k_r \quad E_{af} \quad E_{ar} \quad D_2 \quad C_{p,a} \quad C_{p,b} \quad C_{p,c} \quad C_{p,d}] \rightarrow \text{Rank}(F) = 8 \quad (4.26)$$

The definitions for $C_{p_{in}}$, C_p and M_w are as in section 3.3.

In the first situation, the rank is equal to the number of parameters. Hence all the specified parameters of p_1 are identifiable. In situation 2, it is assumed that $C_{p_{in}}$ and T_{in} are known and that parameters D_1 and D_2 need to be identified besides the four parameters from the reaction. The full rank of F , proves that structural identifiability is guaranteed in this situation. Situation 3 is an extension of situation 2 where besides data about $C_{p_{in}}$ and T_{in} also data about the mass is measured. Again there is full rank. In Situations 4 and 5, structural identifiability is not guaranteed. When $C_{p_{in}}$, C_p and D_2 are written terms of matrices, and the elements of these matrices are in the parameter sets, the system is not structurally identifiable. This is due to the fact that the product of matrices in which these parameters appear, yields a number such as $mC_{p_{mix}}$ and $\Delta H_f^\ominus N^\top$. From this number, the matrix ΔH_f^\ominus cannot be calculated.

4.2 Parameter Estimation and Sensitivity

In the previous section, an analysis was performed to establish whether certain parameters can be identified or not. This notion is referred to as structural identifiability. In this section, the parameter sensitivity is analysed. In certain industries, such as process industry, the modelling of systems is costly. The amount of parameters in such systems can be vast. To reduce the complexity of the model and the amount of parameters, parameter sensitivity analysis is performed to investigate which parameters are most important in the dynamics of the underlying system. This section contains two parameter sensitivity analyses of a CSTR and the Reactive Batch Distillation Column (RBD).

The parameter sensitivity analysis can be decomposed into the following steps:

1. Obtain a parameter set with approximate values of the parameters.
2. For each parameter i in the parameter set, the model is simulated with small deviations in the approximate value of the parameter. Then the response of the j^{th} output is collected for a deviation with a higher value than the approximate value $y_j(p_{0,i} \cdot (1 + \Delta), t)$ and for a deviation with a smaller value than the approximate value $y_j(p_{0,i} \cdot (1 - \Delta), t)$, where $p_{0,i}$ is the approximate value of the i^{th} parameter and Δ is the deviation in the parameter.
3. Compute the following derivative:

$$\frac{\partial y_j(p_i, t)}{\partial p_i} \approx \frac{y_j(p_{0,i} \cdot (1 + \Delta), t) - y_j(p_{0,i} \cdot (1 - \Delta), t)}{2\Delta} \quad (4.27)$$

4. Obtain a parameter sensitivity matrix, similar to the sensitivity matrix of section 4.1:

$$S = \begin{bmatrix} \frac{\partial y_1(p_1, t_0)}{\partial p_1} & \cdots & \frac{\partial y_1(p_k, t_0)}{\partial p_k} \\ \vdots & \vdots & \vdots \\ \frac{\partial y_l(p_1, t_0)}{\partial p_1} & \cdots & \frac{\partial y_l(p_k, t_0)}{\partial p_k} \\ \vdots & \vdots & \vdots \\ \frac{\partial y_1(p_1, t_m)}{\partial p_1} & \cdots & \frac{\partial y_1(p_k, t_m)}{\partial p_k} \\ \vdots & \vdots & \vdots \\ \frac{\partial y_l(p_1, t_m)}{\partial p_1} & \cdots & \frac{\partial y_l(p_k, t_m)}{\partial p_k} \end{bmatrix} = [S_1 \quad \dots \quad S_k] \quad (4.28)$$

with k parameters, l outputs and m time samples.

5. Rank the parameters by the orthogonalization method explained in [10].

The orthogonalization method is a method that ranks the parameters on their norm and linear dependence simultaneously. The procedure occurs as follows: Assume a sensitivity matrix, composed of the column vectors a, b and c :

$$S = [a \quad b \quad c] \quad (4.29)$$

If a has the largest norm, a normalised vector $q_1 = a_1/||a_1||$ is subtracted from b and c to create two orthogonal vectors to a :

$$\tilde{b} = b - (q_1' b)q_1, \quad \tilde{c} = c - (q_1' c)q_1 \quad (4.30)$$

Out of these two vectors, the vector with the largest norm is selected again and subtracted. In this case the largest norm is from \tilde{c} :

$$\bar{b} = \tilde{b} - (q_2' \tilde{b})q_2, \quad q_2 = \tilde{c}/||\tilde{c}|| \quad (4.31)$$

where $||\cdot||$ is the Euclidean norm. The following decomposition can be performed:

$$SE = QR \quad (4.32)$$

$$S \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} = [q_1 \quad q_2 \quad q_3] \begin{bmatrix} q_1' a & q_1' c & q_1' b \\ 0 & q_2' c & q_2' b \\ 0 & 0 & q_3' b \end{bmatrix} \quad (4.33)$$

which can be further reduced to:

$$E' S' S E = \bar{R}' D' D \bar{R} \quad (4.34)$$

$$E' S' S E = \begin{bmatrix} 1 & 0 & 0 \\ \frac{q_1' c}{q_1' a} & 1 & 0 \\ \frac{q_1' b}{q_1' a} & \frac{q_2' b}{q_2' c} & 1 \end{bmatrix} \begin{bmatrix} (q_1' b)^2 & 0 & 0 \\ 0 & (q_2' c)^2 & 0 \\ 0 & 0 & (q_3' b)^2 \end{bmatrix} \begin{bmatrix} 1 & \frac{q_1' c}{q_1' a} & \frac{q_1' b}{q_1' a} \\ 0 & 1 & \frac{q_2' b}{q_2' c} \\ 0 & 0 & 1 \end{bmatrix} \quad (4.35)$$

The E matrix can be interpreted as the ranking of the parameters. The column that has a 1 in the first row belongs to the parameter that is most sensitive to changes. The column that has the 1 in the last row belongs to the parameter that is least sensitive to parameter changes. The coefficients in R relate to how much the parameters correlate. Coefficients with a value close to 1, have a high positive correlation while coefficients with a value close to -1 have a strong negative correlation. Coefficients close to 0 have almost no correlation.

4.2.1 Parameter Sensitivity of a CSTR

In this section, the parameter sensitivity of a CSTR is investigated. As an example, the same situation as in section 3.3.1 is used. The only difference is that in this case, no step are applied for $t > 0$ s. For the analysis, a distinction is made between the parameter sensitivity ranking for the number of moles E_n and for the temperature E_T . The main motivation for this is scaling. The range of values for temperatures are of a different order of magnitude than the number of moles. The result can be found in Tables 4.1 and 4.2 in the column of situation 1.

Sit. 1	Sit. 2	Sit. 1(Scaled)	Sit. 2(Scaled)
H_a	$C_{p,c}$	k_f	k_f
$C_{p,c}$	$C_{p,d}$	E_{af}	E_{af}
k_r	k_r	$C_{p,a}$	$C_{p,a}$
k_f	$C_{p,a}$	E_{ar}	E_{ar}
H_c	$C_{p,b}$	$C_{p,b}$	$C_{p,b}$
E_{ar}	k_f	$C_{p,c}$	$C_{p,c}$
$C_{p,a}$	E_{ar}	H_a	H_a
$C_{p,d}$	H_a	$C_{p,d}$	$C_{p,d}$
E_{af}	E_{af}	H_b	H_b
H_d	H_b	H_c	H_c
H_b	H_c	H_d	H_d
$C_{p,b}$	H_d	k_r	k_r

Table 4.1: Parameter sensitivity rankings for number of moles for different situations

Sit. 1	Sit. 2	Sit. 1(Scaled)	Sit. 2(Scaled)
H_b	$C_{p,c}$	H_b	$C_{p,c}$
$C_{p,d}$	H_b	$C_{p,d}$	H_b
E_{ar}	E_{ar}	E_{ar}	E_{ar}
$C_{p,a}$	$C_{p,b}$	$C_{p,a}$	$C_{p,b}$
E_{af}	$C_{p,a}$	E_{af}	$C_{p,a}$
H_c	k_r	H_c	k_r
k_f	E_{af}	k_f	k_f
$C_{p,b}$	H_a	$C_{p,b}$	H_a
k_r	k_f	k_r	E_{af}
H_d	H_d	H_d	H_d
H_a	H_c	H_a	H_c
$C_{p,c}$	$C_{p,d}$	$C_{p,c}$	$C_{p,d}$

Table 4.2: Parameter sensitivity rankings for temperature for different situations

From these rankings it is not possible to draw conclusions about which parameters are more important. The first problem is that the time response of the number of moles is not independent of the time response of the temperature. The temperature influences the reaction and hence the number of moles indirectly.

The second problem is that this method relies on absolute differences in signals, rather than relative changes. Therefore, absolute differences in the time responses can have a large impact on the sensitivity. The conditions that influence this absolute sensitivity are for example the inputs. To prove this, a second sensitivity analysis is performed on a situation with different inputs than in the first situation. The result can be found in Tables 4.1 and 4.2 in the column of situation 2. What can be seen is that for different inputs, the ranking in parameters is different.

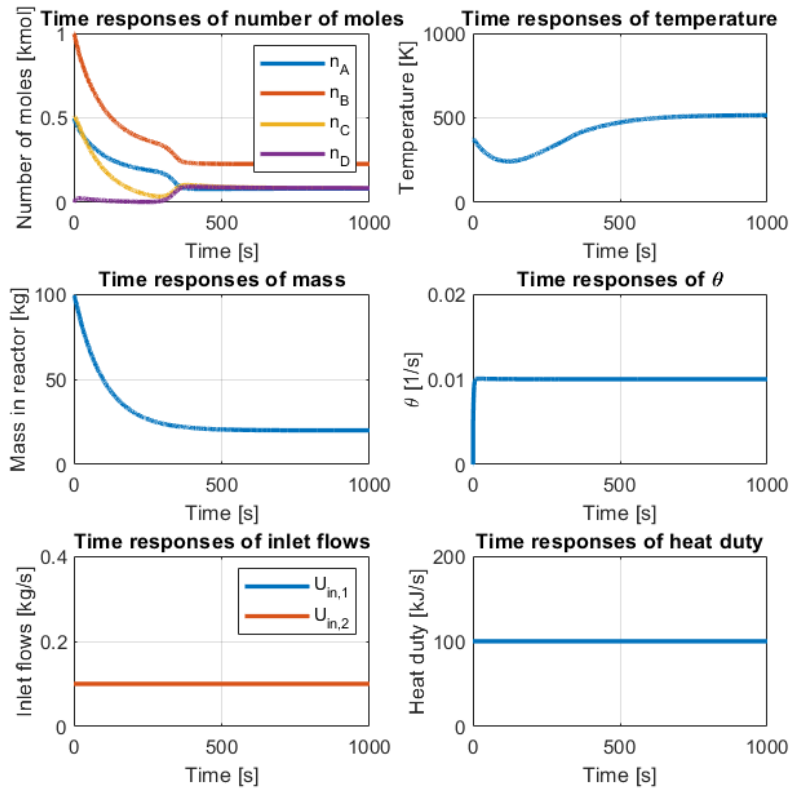


Figure 4.1: Nominal time responses of relevant signals (Situation 1)

So far, it is visible that for this parameter sensitivity method for absolute differences, it is difficult to draw sound conclusions that are valid under different circumstances. The input signals have an impact on the ranking of the parameters. It is known that also other conditions influence the ranking. These are:

- Initial conditions
- Control strategy
- Initial approximate values of the parameters

How to solve this problem and get a more sound conclusion can be investigated in a future work. It is worthwhile to investigate whether scaling can give a more sound ranking that is valid under multiple situations. In Tables 4.1 and 4.2, the sensitivity matrices of situation 1 and 2 are scaled as follows:

$$\bar{S}_n = \frac{S_n}{n(t)}, \quad \bar{S}_T = \frac{S_T}{T(t)} \quad (4.36)$$

where \bar{S}_n is the absolute sensitivity matrix of number of moles divided by the nominal time response of $n(t)$ and \bar{S}_T is the absolute sensitivity matrix of temperature divided by the nominal time response of $T(t)$. The nominal responses are the responses for nominal values of the parameters. In this way, the changes are relative rather than absolute. What can be seen in Table 4.1 is that for both situation with different inputs, the rankings are the same. For the ranking of the temperatures in Table 4.2, this is not the case. What is noteworthy is that some parameters appear high in the ranking for the different situations. Examples of high ranking parameters in

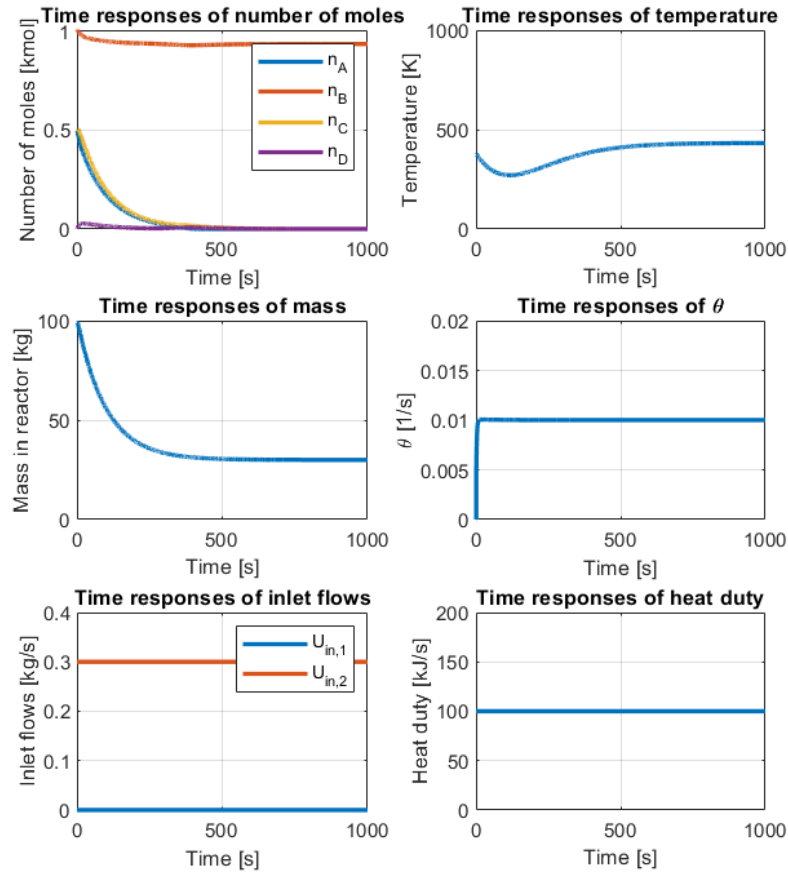


Figure 4.2: Nominal time responses of relevant signals (Situation 2)

temperature are E_{ar} , $C_{p,a}$ and $C_{p,b}$. Examples of low ranking parameters in temperature are H_a and H_d .

In general it is difficult to find a numeric parameter ranking method that ensures one ranking that applies for numerous different situations. It is for now unknown whether this is the case for all systems or specific systems. This system is coupled through the temperature dependent reaction coefficients and concentration dependent coefficients such as α , β and γ . Some kind of decoupling of this system might give a more unified ranking for the parameters.

4.2.2 Parameter Sensitivity of a RBD

In this section, the parameter sensitivity analysis will be performed on the Reactive Batch Distillation Column. For the RBD, the parameter set is the same as in section 4.2.1, because the distillation process does not yield any extra parameters. The number of outputs is large. As specified in section 2.4, there are 14 species hence 14 concentrations or number of moles. Besides that, every stage has a different temperature. This means that in total there are $(14 + 1) \cdot 6 = 90$ possible outputs and sensitivities to analyse. To simplify the analysis, the concentration outputs are ignored. The reason for this is that concentration is difficult to gain measurements of in industry. Therefore only temperatures are considered for parameter sensitivity analysis of the RBD. Rather than performing the analysis on the same parameters as in section 4.2.1, analysis is performed on the variables:

$$p_{RBD} = \begin{bmatrix} h_{vap,mix} \\ C_{p_{mix},1} \\ C_{p_{mix},2} \\ C_{p_{mix},3} \\ C_{p_{mix},4} \\ C_{p_{mix},5} \\ C_{p_{mix},6} \end{bmatrix} \quad (4.37)$$

where $h_{vap,mix}$ is the heat of vapourisation of the mixture and $C_{p_{mix},i}$ is the heat capacity of the mixture in stage i . The parameters k_f, k_r, E_{af} and E_{ar} are related to reaction and, hence, to the number of moles and concentrations. Because these outputs are neglected for the parameter sensitivity, these parameters are also neglected. The parameters related to temperature such as heat enthalpies and capacities are neglected because this would mean that the analysis has to be performed for at least $2 \cdot 14 = 28$ parameters. With the system that is discussed here, the simulation would last too long. Regarding equation 2.42, the variables $C_{p_{mix},i}$ are the most important variable for temperature response. Therefore the heat capacity of the mix in each stage is chosen as parameter. This implies that the analysis is done with time-varying parameters. For time-varying parameters it is not possible to apply a method as in section 4.2.1, where the outputs are simulated for approximate parameter values. Therefore, the first step in the analysis is to obtain averaged values of the parameters in equation 4.37, denoted as $p_{RBD,0}$:

$$p_{RBD,0} = \begin{bmatrix} 44000 & (J/mol) \\ 122.68 & (J/K) \\ 135.95 & (J/K) \\ 177.57 & (J/K) \\ 197.24 & (J/K) \\ 225.29 & (J/K) \\ 245.42 & (J/K) \end{bmatrix} \quad (4.38)$$

The second step is now to perform the same parameter analysis as in section 4.2.1. The selected outputs are the temperature in stages 3 (top tray of distillation) and the temperature in the reactor. The ranking are as follows: What can be seen here is that $h_{vap,mix}$ is the most important

Temperature stage 3 (top tray)	Temperature stage 6 (Reactor)
$h_{vap,mix}$	$h_{vap,mix}$
$C_{p_{mix},6}$	$C_{p_{mix},6}$
$C_{p_{mix},4}$	$C_{p_{mix},4}$
$C_{p_{mix},2}$	$C_{p_{mix},3}$
$C_{p_{mix},5}$	$C_{p_{mix},5}$
$C_{p_{mix},3}$	$C_{p_{mix},2}$
$C_{p_{mix},1}$	$C_{p_{mix},1}$

Table 4.3: Parameter sensitivity rankings for different temperature locations

parameter in both stages. Besides that, the ordering of the $C_{p_{mix}}$ is more or less from bottom to top. This means that the most important $C_{p_{mix}}$ is in stage 6 (reactor) and the least important in stage 1 (the accumulator). This conclusion is realistic in reality as the property of flows are from reactor to the accumulator. What is remarkable is that this line of reasoning is not true for all stages because $C_{p_{mix,5}}$ is ranked lower than $C_{p_{mix,4}}$ in both sensitivities of temperature. The reason for this is unclear. The only explanation is that it is due to taking the average of the $C_{p_{mix}}$ in all stages.

In [16], a similar sensitivity analysis is performed but with some scaling. The sensitivity is calculated as follows:

$$\tilde{S}_{i,j} = \frac{p_i}{y_j(p_i, t)} \frac{dy_j(p_i, t)}{dp_i} \quad (4.39)$$

This implies a multiplication with the approximate value of the parameter and division over the nominal time response of the output. The result of the sensitivity analysis with this scaling can be found in Table 4.4.

Temperature stage 3 (top tray)	Temperature stage 6 (Reactor)
$h_{vap,mix}$	$h_{vap,mix}$
$C_{p_{mix,6}}$	$C_{p_{mix,6}}$
$C_{p_{mix,4}}$	$C_{p_{mix,4}}$
$C_{p_{mix,2}}$	$C_{p_{mix,3}}$
$C_{p_{mix,5}}$	$C_{p_{mix,5}}$
$C_{p_{mix,3}}$	$C_{p_{mix,2}}$
$C_{p_{mix,1}}$	$C_{p_{mix,1}}$

Table 4.4: Parameter sensitivity rankings for different temperature locations (Scaled according to scaling of [16])

The ranking in Table 2.52 is exactly the same ranking as in Table 4.3, meaning that the scaling has no effect in this situation.

What has been done in the parameter sensitivity for the RBD is that time-varying parameters are taken as constant parameters and that the analysis is performed around the mean values of the time-varying parameters. What has not been investigated is a method which facilitates parameter analysis on time-varying parameters, rather than mean values. This can be investigated in the future.

Chapter 5

Conclusions and Future Work

For each of the four subquestions, the conclusions will be repeated and possible future work is suggested.

Is it possible to approximate a general nonlinear model of reaction systems using OBF's?

If reaction is viewed as a disturbance, OBF identification is possible. Due to the definition of α , it can not be modelled as a constant, but should be modelled as a dynamic variable. If α is modelled as a dynamic variable, physical interpretation is lost. Physical interpretation can be kept to a certain level if the step responses are written explicitly. Then it is possible to approximate how much α and γ are going to change due to a step input, but it is still unknown what the absolute change of these parameters is, if there is no information about the concentrations. As a future work, it is therefore possible to investigate how to estimate α and γ if concentration data is not available and physical interpretation must be kept. Another suggestion that was made for future work is the 2-step identification procedure. This procedure can create possibilities to identify slow reaction systems using OBF's.

Do the extent transformations form a set of unique OBF's?

The conclusion here is that the extent transformation does not yield a unique OBF. This is because the transfer function is not all-pass and can therefore not be extended.

Which parameters or combination thereof can be identified?

Almost all parameters can be identified. It is however not possible for parameters that appear in the differential equations as a product or in a matrix.

Which parameters are more important to model?

For a CSTR it was concluded that the ranking of parameters depends on the chosen inputs. Scaling provides a solution in getting a more consistent result for different situations. It is known that initial conditions, control strategy or initial approximate values of the parameters also play a role on the ranking. In future work it can be investigated how a more consistent ranking can be given. Because RBD is a highly parametrised model with a large number of outputs, parameter sensitivity analysis is difficult. Therefore, only sensitivities for temperature are computed. Because this process is in batch regime and has no steady states, time-varying parameters are present in this system. To use the same parameter sensitivity method as before, average values of these parameters have to be taken. The conclusion is that heat of vaporisation is the most important parameter. The rankings of $C_{pmix,i}$ in stage i corresponds more or less with reality where the highest ranked parameter is in the highest stage. Because this conclusion is not consistent for all cases, it is suggested that for future work it is necessary to investigate a parameter sensitivity method based on time-varying parameters.

Bibliography

- [1] Michael Amrhein, Nirav Bhatt, Balasubrahmanyam Srinivasan, and Dominique Bonvin. Extents of reaction and flow for homogeneous reaction systems with inlet and outlet streams. *AIChE Journal*, 56(11):2873–2886, 2010. 5, 6, 7, 14
- [2] André Bardow and Wolfgang Marquardt. Incremental and simultaneous identification of reaction kinetics: Methods and comparison. *Chemical Engineering Science*, 59(13):2673–2684, 2004. 13
- [3] Nirav Bhatt, Michael Amrhein, and Dominique Bonvin. Extents of reaction, mass transfer and flow for gas-liquid reaction systems. *Industrial and Engineering Chemistry Research*, 49(17):7704–7717, 2010. ix, 7, 8, 9, 14
- [4] Nirav Bhatt, Michael Amrhein, and Dominique Bonvin. Incremental identification of reaction and mass-transfer kinetics using the concept of extents. *Industrial and Engineering Chemistry Research*, 50(23):12960–12974, 2011. ix, 13, 14
- [5] Nirav Bhatt, Nimet Kerimoglu, Michael Amrhein, Wolfgang Marquardt, and Dominique Bonvin. Incremental identification of reaction systems—A comparison between rate-based and extent-based approaches. *Chemical Engineering Science*, 83:24–38, 2012. 15
- [6] Marc Brendel, Dominique Bonvin, and Wolfgang Marquardt. Incremental identification of kinetic models for homogeneous reaction systems. *Chemical Engineering Science*, 61(16):5404–5420, 2006. 13
- [7] Florin Paul Davidescu and Sten Bay Jørgensen. Structural parameter identifiability analysis for dynamic reaction networks. *Chemical Engineering Science*, 63(19):4754–4762, 2008. 15
- [8] Peter S.C. Heuberger, Paul M.J. Van den Hof, and Bo Wahlberg. Modelling and Identification with Rational Orthogonal Basic Functions. *IFAC Proceedings Volumes*, pages 445–455, 2000. 2, 20
- [9] Lennart Ljung and Torkel Glad. On global identifiability for arbitrary model parametrizations. *Automatica*, 30(2):265–276, 1994. 15
- [10] Berit Floor Lund and Bjarne A. Foss. Parameter ranking by orthogonalization—Applied to nonlinear mechanistic models. *Automatica*, 44(1):278–281, 2008. 40
- [11] Alejandro Marquez Ruiz, Carlos S. Mendez Blanco, and Leyla Özkan. Control of Homogeneous Reaction Systems using Extent-Based LPV Models. 2018. 2, 10
- [12] Kevin A. P. McLean and Kim B. McAuley. Mathematical modelling of chemical processes—obtaining the best model predictions and parameter estimates using identifiability and estimability procedures. *Canadian Journal of Chemical Engineering*, 90(2):351–366, 2012. 37
- [13] Carlos S. Méndez Blanco. Master’s Thesis: Control of Reactive Batch Distillation Columns via Extents Transformation, 2017. 1, 12

- [14] Luc Pronzato and Eric Walter. *Identification of parametric models from experimental data*. 1997. 3, 13
- [15] Lanny D. Schmidt. *The Engineering of Chemical Reactions*. Oxford University Press, 1998. 4
- [16] Stephan Seefeld and William R. Stockwell. First-order sensitivity analysis of models with time-dependent parameters: An application to PAN and ozone. *Atmospheric Environment*, 33(18):2941–2953, 1999. xi, 45
- [17] Sigurd Skogestad. *Chemical and Energy Process Engineering*. CRC Press, 2008. 4
- [18] Eva Sørensen and Sigurd Skogestad. Batch Processing Systems Engineering. chapter Control Strategies for a Combined Batch Reactor/Batch Distillation Process, pages 274–294. Springer-Verlag, 1996. ix, 11
- [19] Roland Tóth, Peter S.C. Heuberger, and Paul M.J. Van den Hof. LPV System Identification with Globally Fixed Orthonormal Basis Functions. *Proceedings of the IEEE Conference on Decision and Control*, pages 3646–3653, 2007. 2, 21, 22
- [20] Roland Tóth, Peter S.C. Heuberger, and Paul M.J. Van den Hof. Asymptotically optimal orthonormal basis functions for LPV system identification. *Automatica*, 45(6):1359–1370, 2009. 2
- [21] Tamas Turányi. Sensitivity Analysis of Complex Kinetic Systems. Tools and Applications. *Journal of Mathematical Chemistry*, 5:203–248, 1990. 15
- [22] Paul M.J. Van den Hof, Peter S.C. Heuberger, and József Bokor. System identification with Generalized Orthonormal Basis Functions. *Automatica*, 31(12):1821–1834, 1995. 2, 20
- [23] Bo Wahlberg. System Identification Using Laguerre Models. *IEEE Transactions on Automatic Control*, 36(5):551–562, 1991. 21
- [24] Eric Walter and Luc Pronzato. On the identifiability and distinguishability of nonlinear parametric models. *Mathematics and Computers in Simulation*, 42(2-3):125–134, 1996. 3, 15

Appendix A

A.1 Computation of transformation matrices

- Using SVD, the matrix $[N^\top \quad W_{in}]$ can be decomposed:

$$[N^\top \quad W_{in}] = [U_{1,1} \quad U_{1,2}] \begin{bmatrix} \Sigma_1 \\ 0 \end{bmatrix} V_1^\top \quad (\text{A.1})$$

$$\mathcal{T}_3 = U_{1,2}$$

- Using SVD, the matrix $[N^\top \quad \mathcal{T}_3]$ can be decomposed:

$$[N^\top \quad \mathcal{T}_3] = [U_{2,1} \quad U_{2,2}] \begin{bmatrix} \Sigma_2 \\ 0 \end{bmatrix} V_2^\top \quad (\text{A.2})$$

$$\mathcal{T}_2 = U_{2,2}(W_{in}U_{2,2})^+$$

- $\mathcal{T}_1 = (N^\top + (I_s - W_{in}\mathcal{T}_2^\top))^\top$

A.2 Table of parameters with nominal values

Parameter name	Symbol	Nominal value	Unit
Forward activation energy	E_{af0}	$6.380 \cdot 10^4$	$J \cdot mol^{-1}$
Reverse activation energy	E_{ar0}	$7.171 \cdot 10^4$	$J \cdot mol^{-1}$
Pre-exponential forward reaction coefficient	k_f	$6.060 \cdot 10^5$	$m^3 \cdot kmol^{-1} \cdot s^{-1}$
Pre-exponential reverse reaction coefficient	k_r	$9.840 \cdot 10^6$	$m^3 \cdot kmol^{-1} \cdot s^{-1}$
Gas constant	R	$8.314 \cdot 10^0$	$J \cdot mol^{-1} \cdot K^{-1}$
Heat capacity specie A	$C_{p,A}$	$2.043 \cdot 10^0$	$J \cdot K^{-1}$
Heat capacity specie B	$C_{p,B}$	$2.510 \cdot 10^0$	$J \cdot K^{-1}$
Heat capacity specie C	$C_{p,C}$	$1.973 \cdot 10^0$	$J \cdot K^{-1}$
Heat capacity specie D	$C_{p,D}$	$4.190 \cdot 10^0$	$J \cdot K^{-1}$
Standard heat enthalpy specie A	H_A	$-4.845 \cdot 10^5$	J
Standard heat enthalpy specie B	H_B	$-2.394 \cdot 10^5$	J
Standard heat enthalpy specie C	H_C	$-4.459 \cdot 10^5$	J
Standard heat enthalpy specie D	H_D	$-2.858 \cdot 10^5$	J
Inlet temperature	T_{in}	$3.000 \cdot 10^2$	K
Density specie A	ρ_A	$1.050 \cdot 10^3$	$kg \cdot m^{-3}$
Density specie B	ρ_B	$7.920 \cdot 10^2$	$kg \cdot m^{-3}$
Density specie C	ρ_C	$9.320 \cdot 10^2$	$kg \cdot m^{-3}$
Density specie D	ρ_D	$1.000 \cdot 10^3$	$kg \cdot m^{-3}$
Molecular weight specie A	M_A	$6.005 \cdot 10^1$	$kg \cdot kmol^{-1}$
Molecular weight specie B	M_B	$3.204 \cdot 10^1$	$kg \cdot kmol^{-1}$
Molecular weight specie C	M_C	$7.418 \cdot 10^1$	$kg \cdot kmol^{-1}$
Molecular weight specie D	M_D	$1.800 \cdot 10^1$	$kg \cdot kmol^{-1}$

Table A.1: System parameters and their nominal values