May 2019

A Model-Based Framework for the Smart Manufacturing of Polymers

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A MODEL-BASED FRAMEWORK FOR THE SMART MANUFACTURING OF POLYMERS

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

The Department of Chemical Engineering

by

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August 2019
To God, Our Lady “La Dolorosa del Colegio” and my family.
ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor Prof. José A. Romagnoli for his guidance, encouragement, and support during my doctoral studies. Also, I am thankful with the committee members of my doctoral dissertation Prof. Warren T. Liao, Prof. James A. Dorman, and Prof. Luis A. Escobar for evaluating and reviewing my research. I am grateful for having the honor of collaborated with Prof. Roberto Baratti and Prof. Stefania Tronci from the University of Cagliari (Italy), and Prof. João B. P. Soares and Prof. Amanda L. T. Brandão from the University of Alberta (Canada) and Pontifícia Universidade Católica do Rio de Janeiro (Brazil), respectively. Finally, my humble recognition and deepest thankfulness to my research group PSE at LSU for their friendship, continuous assistance, and countless fond memories.

I would like to thank my beloved ones who encouraged me during this process especially my parents Marco & Gina, my sister Paula, and my family & friends.

My special acknowledgement to the Cain Department of Chemical Engineering at Louisiana State University for opening me their doors.
TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................ iii

LIST OF TABLES .................................................................................................................... vi

LIST OF FIGURES ................................................................................................................... vii

ABSTRACT .............................................................................................................................. x

1 INTRODUCTION ..................................................................................................................... 1
   1.1 Background ...................................................................................................................... 1
   1.2 Dissertation motivation ................................................................................................. 4
   1.3 Dissertation organization ............................................................................................. 7
   1.4 Contributions of dissertation ....................................................................................... 9
   1.5 References ...................................................................................................................... 11

2 MODELLING AND OPTIMAL OPERATION OF POLYMERIZATION PROCESSES ........ 14
   2.1 Introduction .................................................................................................................. 14
   2.2 Parameter estimation: the gEST function ..................................................................... 16
   2.3 Parameter estimation: heuristic strategies .................................................................... 18
   2.4 Optimal operation in polymerization ............................................................................ 23
   2.5 References ..................................................................................................................... 26

3 CONTROL STRATEGIES IN POLYMERIZATION ......................................................... 30
   3.1 Introduction .................................................................................................................. 30
   3.2 Exact linearizing control in polymerization .................................................................. 34
   3.3 Feedback control of weight-average molecular weight ............................................. 44
   3.4 References ..................................................................................................................... 47

4 NONLINEAR STATE ESTIMATION IN POLYMERIZATION ........................................... 50
   4.1 Introduction .................................................................................................................. 50
   4.2 The hybrid discrete-time extended Kalman filter ....................................................... 53
   4.3 The geometric observer ............................................................................................... 58
   4.4 Data-driven parameter estimation ............................................................................... 62
   4.5 References ..................................................................................................................... 66

5 FRAMEWORK DESIGN FOR THE SMART MANUFACTURING OF POLYMERS .... 70
   5.1 Introduction .................................................................................................................. 70
   5.2 Integrated model-centric framework for polymer synthesis ..................................... 72
   5.3 Module development, implementation & functionality .............................................. 75
   5.4 References ..................................................................................................................... 79

6 CASE STUDY 1: ACRYLAMIDE-WATER-POTASSIUM PERSULFATE SYSTEM .... 80
   6.1 Mechanistic model ....................................................................................................... 80
   6.2 Metaheuristic parameter estimation ............................................................................ 86
   6.3 Experimental equipment and setup .............................................................................. 90
6.4 Results for open-loop experiments with \( h \)-DEKF .......................................................... 92
6.5 Results for closed-loop experiments with \( h \)-DEKF ...................................................... 98
6.6 Results: GO design and implementation ................................................................. 104
6.7 References ............................................................................................................. 117

7  CASE STUDY 2: COPOLYMERIZATION OF ETHYLENE WITH 1,9-DECADIENE. 119
7.1 Fundamental model ............................................................................................ 119
7.2 Experimental equipment and setup ...................................................................... 125
7.3 Online estimation of significant kinetic parameters ............................................. 128
7.4 References ............................................................................................................. 145

8  CONCLUSIONS AND FUTURE PERSPECTIVES .................................................. 147
8.1 Conclusions .......................................................................................................... 147
8.2 Future directions ................................................................................................... 153
8.3 References ............................................................................................................. 154

APPENDIX: ADDITIONAL INFORMATION .......................................................... 155
   A.1 Significant parameter selection: global sensitivity analysis .............................. 155
   A.2 References ........................................................................................................ 159

AUTHOR PUBLICATIONS ......................................................................................... 160

VITA ............................................................................................................................. 162
LIST OF TABLES

Table 4.1. Parameter values for ParLMSRBF-R for global optimization .................................................. 57
Table 6.1. Kinetic and thermodynamic parameters of the mathematical model. ................................. 84
Table 6.2. Experiment initial conditions for different trajectories .............................................................. 85
Table 6.3. GA, DE and PSO performance and CPU time ............................................................................. 88
Table 6.4. F-Test and t-Test for DE vs GA, DE vs PSO. ............................................................................ 89
Table 6.5. Kinetic and thermodynamic parameters of the mathematical model. ................................. 90
Table 6.6. PID + h-DEKF control action improvement. ........................................................................... 104
Table 6.7. Average minimum singular values and condition number for full-order observer calculated along increasing $M_w$ trajectory ......................................................................................... 107
Table 6.8. Average minimum singular values and condition number: 4 innovated states with passive structure calculated along an increasing $M_w$ trajectory ................................................................. 110
Table 7.1. Kinetic rate constants for the copolymerization of ethylene with 1,9-decadiene. ...... 123
Table 7.2. Kinetic and thermodynamic parameters for the copolymerization of ethylene with 1,9-decadiene using dimethylsilyl (N-tert-butylamido) (tetramethylcyclopentadienyl) titanium dichloride (CGC)/MAO ........................................................................................................... 124
Table 7.3. Ethylene concentration and total moles of ethylene in toluene at different temperatures .................................................................................................................................................. 127
Table 7.4. Initial conditions for simulations and experiments ................................................................. 127
LIST OF FIGURES

Figure 1.1. World plastics production: 1950 - 2016 ................................................................. 2
Figure 1.2. Integrated model-based framework for smart manufacturing. ............................. 6
Figure 1.3. Self-contained intelligent system for the smart manufacturing of polymers. ........ 6
Figure 2.1. GA pseudo-code .................................................................................................. 19
Figure 2.2. DE pseudo-code .................................................................................................. 21
Figure 2.3. PSO pseudo-code .................................................................................................. 22
Figure 2.4. Schematic representation of a generic optimization problem for polymerization processes .......................................................................................................................... 25
Figure 3.1. Schematic of the conventional control and linearizing control. ............................... 34
Figure 3.2. Schematic of the nonlinear controller implementation for computational testing. .... 36
Figure 3.3. Control of $N_m$ by manipulating $T$ ................................................................ 38
Figure 3.4. Control of $N_m$ by manipulating $F_m$ ............................................................... 40
Figure 3.5. Control of $N_m$ by manipulating $F_i$ ................................................................. 42
Figure 3.6. Block diagram for weight-average molecular weight control ................................ 45
Figure 4.1. Schematic representation of the ParLMSRBF-R algorithm. .................................. 57
Figure 4.2. Data-driven parameter estimation architecture. ....................................................... 66
Figure 5.1. Schematic of the integrated simulation, parameter estimation, and optimization for polymeric systems .................................................................................................................. 73
Figure 5.2. Framework design for the smart manufacturing of polymers. Integration between experimental apparatus and computational in/offline tools ......................................................... 74
Figure 5.3. Flow diagram of the functionality of the tailor made module .................................. 76
Figure 5.4. Experimental apparatus and ACOMP system. ......................................................... 77
Figure 5.5. ACOMP monitoring system and in-house GUI for the smart manufacturing of polymers ................................................................................................................................. 78
Figure 6.1. Final chain length distribution of optimal trajectories. ............................................... 85
Figure 6.2. Convergence profile and standard deviation for DE, GA and PSO. ......................... 88
Figure 6.3. Laboratory pilot plant setup .................................................................................. 91
Figure 6.4. ParLMSRBF-R algorithm convergence profile of one run when searching optimal $e_w$ for auto-tuned error-driven free-parameters. ................................................................ 92
Figure 6.5. Eigenvalues of the estimation error dynamics for different OL experiments .......... 93
Figure 6.6. Results for the increasing $M_w$ trajectory in open-loop experiments ...................... 95
Figure 6.7. Results for the constant $M_w$ trajectory in open-loop experiments ......................... 96
Figure 6.8. Results for the decreasing $M_w$ trajectory in open-loop experiments ..................... 97
Figure 6.9. Results for increasing $M_w$ trajectory closed-loop showing measurements for open-loop, PID and $h$-DEKF + PID .................................................................................. 100
Figure 6.10. Results for constant $M_w$ trajectory closed-loop showing measurements for open-loop, PID and $h$-DEKF + PID .................................................................................. 101
Figure 6.11. Results for decreasing $M_w$ trajectory closed-loop showing measurements for open-loop, PID and $h$-DEKF + PID .................................................................................. 102
Figure 6.12. Evolution of the chain length distribution during closed-loop experiments ............ 103
Figure 6.13. Comparison between experimental data, full-order 1,2,2 GO (low characteristic frequency, average characteristic frequency and high characteristic frequency), and the nonlinear model (dashed line) for an increasing $M_w$ trajectory ......................................................... 108
Figure 6.14. Number-average molecular weight comparison for: nonlinear model; $h$-DEKF; full-order GO; 4-order GO with passive structure; 3-order GO with passive structure .......... 111
Figure 6.15. Comparison between the experimental chain length distribution by GPC standard calibration and the estimated by: $h$-DEKF; full-order GO; 4-order GO with passive structure; 3-order GO with passive structure ........ 112
Figure 6.16. Comparison between experimental data, 4-order GO with passive structure, $h$-DEKF and nonlinear model for increasing $M_w$ trajectory .............................................................. 113
Figure 6.17. Comparison between experimental data, 4-order GO with passive structure, $h$-DEKF, and nonlinear model for the first decreasing $M_w$ trajectory .............................................. 115
Figure 6.18. Comparison between experimental data, 4-order GO with passive structure, $h$-DEKF, and nonlinear model for the second decreasing $M_w$ trajectory .......................................... 116
Figure 7.1. Experimental unit for polyolefin synthesis, schematic ........................................... 126
Figure 7.2. Framework for the online estimation of significant kinetic parameters ................. 128
Figure 7.3. Global sensitivity indices: first-order and total sensitivity index

Figure 7.4. Condition number of the observability matrix for homopolymerizations at 120 °C, 130 °C, 140 °C

Figure 7.5. Homopolymerization at 120 °C. Experimental measurements, nonlinear model, and estimated by EKF, iLU-GO and RCMR

Figure 7.6. Homopolymerization at 130 °C. Experimental measurements, nonlinear model, and estimated by EKF, iLU-GO and RCMR

Figure 7.7. Homopolymerization at 140 °C. Experimental measurements, nonlinear model, and estimated by EKF, iLU-GO and RCMR

Figure 7.8. Estimation of a single significant parameter. Comparison between theoretical, and estimated kinetic parameters at 120 °C, 130 °C, 140 °C

Figure 7.9. Estimation of two significant parameters. Comparison between theoretical, and estimated kinetic parameters at 120 °C, 130 °C, 140 °C

Figure 7.10. Comparison of the monomer flow rate between the experimental values, fundamental model, estimated with a single parameter, and estimated with two parameters

Figure 7.11. Comparison of the final average properties at different temperatures for experimental values, fundamental model, estimated with a single parameter, and estimated with two parameters

Figure 7.12. Estimation of a single significant parameter. Comparison between theoretical, and estimated kinetic parameters at different initial diene concentrations for the copolymerization experiment A and copolymerization experiment B

Figure 7.13. Estimation of two significant parameters. Comparison between theoretical, and estimated kinetic parameters at different initial diene concentrations for the copolymerization experiment A and copolymerization experiment B

Figure 7.14. Comparison of the monomer flow rate during copolymerization between the experimental values, fundamental model, estimated with a single parameter, and estimated with two parameters at different initial diene concentrations

Figure 7.15. Comparison of average polymer properties at different initial diene concentrations between experimental values, fundamental model, estimated with a single parameter, and estimated with two parameters
ABSTRACT

It is hard to point a daily activity in which polymeric materials or plastics are not involved. The synthesis of polymers occurs by reacting small molecules together to form, under certain conditions, long molecules. In polymer synthesis, it is mandatory to assure uniformity between batches, high-quality of end-products, efficiency, minimum environmental impact, and safety. It remains as a major challenge the establishment of operational conditions capable of achieving all objectives together. In this dissertation, different model-centric strategies are combined, assessed, and tested for two polymerization systems.

The first system is the synthesis of polyacrylamide in aqueous solution using potassium persulfate as initiator in a semi-batch reactor. In this system, the proposed framework integrates nonlinear modelling, dynamic optimization, advanced control, and nonlinear state estimation. The objectives include the achievement of desired polymer characteristics through feedback control and a complete motoring during the reaction. The estimated properties are close to experimental values, and there is a visible noise reduction. A 42% improvement of set point accomplishment in average is observed when comparing feedback control combined with a hybrid discrete-time extended Kalman filter (h-DEKF) and feedback control only. The 4-state geometric observer (GO) with passive structure, another state estimation strategy, shows the best performance. Besides achieving smooth signal processing, the observer improves 52% the estimation of the final molecular weight distribution when compared with the h-DEKF.

The second system corresponds to the copolymerization of ethylene with 1,9-decadiene using a metallocene catalyst in a semi-batch reactor. The evaluated operating conditions consider different diene concentrations and reaction temperatures. Initially, the nonlinear model is validated
followed by a global sensitivity analysis, which permits the selection of the important parameters. Afterwards, the most important kinetic parameters are estimated online using an extended Kalman filter (EKF), a variation of the GO that uses a preconditioner, and a data-driven strategy referred as the retrospective cost model refinement (RCMR) algorithm. The first two strategies improve the measured signal, but fail to predict other properties. The RCMR algorithm demonstrates an adequate estimation of the unknown parameters, and the estimates converge close to theoretical values without requiring prior knowledge.
1 INTRODUCTION

1.1 Background

The chemical industry is one of the most important manufacturing businesses in the world. Only in the US, its growth perspective in volume of chemicals produced per year is projected to be 2.7% for the next decade (ACC, 2016). The immediate future looks even more promising projecting an estimated growth of 3.4% and 3.6% for 2018 and 2019, respectively. Roughly, the US is the largest producer of chemicals in the globe. By 2023, the American chemistry revenues might exceed the $700 billion US dollars (ACC, 2018). However, the most dynamic growth is occurring in the Gulf Coast region. Indeed, the state of Louisiana holds about 18% of all US produced chemical products, and it is home of more than 100 major refineries and chemical plants. In 2017, the chemical industry in Louisiana was responsible of 29,109 direct employments, without considering an additional 8.3 indirect jobs created per chemical industry job (Scott, 2018). Moreover, polymer synthesis grasps an important share of the chemical industry spectrum. Besides products of massive consumption such as polyolefins (polyethylene and polypropylene), other specialty products are gaining interest because of new applications that include 3-D printing, aerospace, nanoscience, and environmental consciousness (biopolymers and blends), which projects a solid growth of polymer production. With a continuous expansion for more than a half century, the global production of plastics has increased exponentially in the past decades, and it is expected to double in the coming two decades. Figure 1.1 exhibits the plastics production data worldwide from 1950 to 2016 (almost seventy years), including polymeric materials (thermoplastics and polyurethanes), and other plastics (thermosets, adhesives, coatings and sealants). PET fibers, PA fibers, PP fibers and poly-acrylic fibers are not included in the reported information (PlasticsEurope, 2013; 2015; 2016; 2017).
With the advent of more sophisticated systems, the chemical manufacturing industry requires to encompass its goals towards an efficient, high adaptable and smart manufacturing philosophy. Process complexity, dynamics-based economics and profoundly different performance objectives require the solid application of networked and real-time information-based technologies (Stephanopoulos & Reklaitis, 2011). Production facilities should evolve to knowledge-embedded enterprises able to predict various scenarios. This will allow performance enhancement and avoid incidents by using distributed intelligence and local decision-making with global impact (Davis et al., 2012). These trends combine operation technologies with information technology, the Internet of things (IoT), artificial intelligence (AI), advanced analytics, and will

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**Figure 1.1.** World plastics production: 1950 - 2016.
even include in the scope the problems of other plants aiming the incorporation of full enterprise integration. Therefore, the smart manufacturing philosophy represents a vividly intensified knowledge-enabled industrial enterprise in which all business and operations aim to achieve substantial improvement from an energy, safety, sustainability, and profitability perspective (Bogle, 2017).

Model-based and data-driven approaches are feasible strategies for the smart manufacturing of standardized polymers. Indeed, it is becoming a trend to use the available process data (data sheets, historical data, and online measurements) to gain knowledge on a process of interest (Qin, 2014; Thomas et al., 2018). Nevertheless, in polymer synthesis one significant constraint is the lack of economical and smart sensors able to provide online information of relevant polymer properties. On the other hand, detailed fundamental models describing the dynamics of a process are of significant importance. These models, depending on their complexity and detail, can provide a general idea of the system or a comprehensive high-resolution perspective of the polymerization process under study (Wang & Hutchinson, 2011; Ghadipasha et al., 2016). Model-based strategies have enormous potential including the capability of being employed in operational and enterprise-wide optimization (Grossmann, 2005; Geraili et al., 2016), advanced control strategies (Romagnoli & Palazoglu, 2005), enhanced monitoring, and property estimation (Salas et al., 2018). Even though model-based strategies face the issue that most models in polymer science are of high complexity, and they require certain treatment before deployment, by combining different strategies under the umbrella of smart manufacturing there is a bright perspective of a new scope of technological tools for decision-making and problem-solving in polymer synthesis design and operations.
1.2 Dissertation motivation

Mathematical models are essential and ubiquitous when implementing smart manufacturing strategies. Indeed, process models provide a solid background in assessing uncertainty in decisions, gaining knowledge on the process dynamics, and innovating the operational conditions. In this context, industry 4.0 is committed to knowledge discovery and rapid innovation (Tao et al., 2018). Thus, it will always be better to count with an educated description of the system under study in the form of fundamental models. There are numerous applications in which models are useful: from experimental design in small scale, kinetic parameters estimation, operating conditions setup to supply chain design and even enterprise-wide optimization. How powerful a model-based strategy is depends on the available resolution, computational power accessibility, and ultimately the main objectives for its deployment.

In the case of polymerization processes, the mathematical models that describe their dynamics are of high complexity and mostly nonlinear. Most polymerizations follow the principles of living polymers (Szwarc, 1968; Szwarc, 1998) where intermediate reactions occur and are hardly observable; nonetheless, these steps permit a complete understanding of the evaluated process and provide guidelines to infer relevant polymer properties. As in other manufacturing industries, polymer synthesis seeks the production of high quality and standardized products for the complete satisfaction of final customers. To achieve these production goals numerous optimal model-based policies (Zeaiter et al., 2002; Srour et al., 2007; Flores-Tlacuahuac & Biegler, 2008) and advanced control strategies (Padilla & Alvarez, 1997; Gentric et al., 1999) have been proposed for generating operating conditions that lead to target properties while optimizing operational costs, energy usage, and operational time. It is important to mention that the molecular weight distribution (MWD) is polymer property that has demonstrated relevant significance. The MWD
presupposes key physical and mechanical properties such as the elasticity modulus, glass transition temperature and material strength (Landel & Nielsen, 1993; McKeen, 2014; Gentekos et al., 2016; Gao et al., 2017). The presence of impurities in feedstock materials, and other operational disturbances might compromise the molecular structure of polymers. A solid understanding of significant properties during synthesis can prevent final products to shift from target values.

The ultimate need of model-based smart manufacturing strategies for polymer synthesis is the core motivation of this doctoral dissertation. Many successful and promising strategies have been studied separately, but they have not been fully integrated towards satisfying the current needs of the polymer manufacturing industry. A typical approach in polymer synthesis, is to establish optimal policies (recipes) such that by following simple measurable trajectories (temperature, density or viscosity) key properties are drawn. In addition, numerous publications have studied state estimation combined with control strategies, but the majority of these studies rely on computational experiments and do not count with online real-time measurements from state-of-the-art sensors. Exploiting model-base strategies simultaneously with smart sensors, as portrayed in Figure 1.2, bequeaths the strength, reliability, and confers the necessary support for settling the paradigm shift proposed in Figure 1.3, a self-contained intelligent system for the smart manufacturing of polymers with seamless communications. In this sense, models and model-based strategies have the capability of running simultaneously with a chemical plant (in real-time operation) while taking advantage of the experimental data generated by smart sensors. The main aims in this work include to improve the operation, control, and monitoring system holding the joint purpose of optimizing energy usage, enhance labor safety, reduce environmental impact, and to overall improve the profitability of the business.
Figure 1.2. Integrated model-based framework for smart manufacturing.

Figure 1.3. Self-contained intelligent system for the smart manufacturing of polymers.
1.3 Dissertation organization

This dissertation is structured in eight chapters. The first chapter highlights the motivation and main aims of this work, and includes a justification of the need of model-based smart manufacturing strategies for polymer manufacturing.

Chapter 2 highlights the importance of mechanistic models in polymerization and introduces strategies towards the estimation of the model’s kinetic parameters using the existing experimental data. In this section, different strategies and algorithms for parameter estimation are discussed. The gEST function available in the software gPROMS is presented as a formal tool for fitting the polymerization model. In addition, suitable metaheuristic algorithms including the genetic algorithm, differential evolution algorithm, and particle swarm optimization are introduced. These heuristic methodologies demonstrate good performance and easy implementation. Once the model is validated, dynamic optimization strategies search for optimal operating policies. For dynamic optimization, the gOPT tool available in gPROMS is tested. This tool uses control vector parametrization to compute optimal trajectories of operationally controlled variables.

Chapter 3 presents advanced control practices for polymer synthesis. An introductory explanation of control in polymer synthesis is provided. In this context, control strategies permit to achieve target (set point) polymer properties by manipulating certain variables. Nonlinear controllers are introduced and their response is portrayed for different pairing between controlled and manipulated variables. Finally, the advantage of real-time measurements from state-of-the-art sensors is highlighted. Feedback control of weight-average molecular weight is described, and its development explained for the production of target polymers.
Chapter 4 introduces nonlinear state/parameter estimation strategies for polymerization. Nonlinear estimation permits to embed the experimental data with a fundamental model of interest in an elegant manner. Signal processing and online state/parameter estimation is possible by using suitable computational algorithms that are adapted to the system. In addition, unmeasured properties of interest can be reconstructed online by the filters/observers. Different algorithms, which demonstrate adaptability to high nonlinear system, are implemented and tested for state and parameter estimation.

Chapter 5 shows the design and buildup of model-centric frameworks for the smart manufacturing of polymers. The interaction and connectivity among the different strategies is highlighted. The architecture design, development, and deployment permit to expose the particularities found in each framework while an adequate functionality of the integrated system is guaranteed. The model-based frameworks are constructed such that real experimental data can be robustly included while different polymerization system can be adapted. The frameworks are meant to remain generic.

Chapter 6 introduces a case study for the aqueous free-radical polymerization of acrylamide using potassium persulfate as initiator. The experiments performed for this system had as sensor the Automatic Continuous Online Monitoring of Polymerization reactions (ACOMP) system, which corresponds to a state-of-the-art smart sensor able to provide relevant experimental data in real-time. Considering the advantages and limitations of the system, the proposed framework for the smart manufacturing of acrylamide includes nonlinear modelling, dynamic optimization, nonlinear state estimation, and advanced control. All the different tools are designed around the sensor in order to maximize its features and functionality.
Chapter 7 introduces a case study for the synthesis of polyolefins. The copolymerization of ethylene and 1,9-decadiene with a metallocene catalyst system has as only online measurement the flow rate of monomer. To exploit the available measurement a global sensitivity analysis identifies the most representative kinetic parameters of the system. The identified significant kinetic parameters are then estimated online using an extended Kalman filter (EKF), a variation of the geometric observer (GO), and the retrospective cost model refinement (RCMR) algorithm. Additional polymer properties are estimated and compared with available offline measurements. Results focus on the findings generated by implementing a data-driven parameter estimation strategy (RCMR) for the first time in polymerization processes.

Chapter 8 provides conclusions on the development of model-centric smart manufacturing frameworks oriented to the synthesis of polymers. Additionally, future perspectives in the area are highlighted from which data-driven strategies appear to be promising in the near future. Nevertheless, the need of fundamental models is justified as it guaranteed an educated understanding of the problem.

1.4 Contributions of dissertation

The original contributions from this thesis dissertation include:

- A novel framework that integrates nonlinear modelling, multi-objective dynamic optimization, nonlinear state estimation, and advanced control, which are formulated, implemented, and tested around a state-of-the-art sensor. The framework seeks to achieve target (set point) weight-average molecular weight trajectories. The ACOMP system is combined for the first time with a nonlinear state estimator for full polymer characterization and signal processing. A number of optimal policies (recipes) are generated and
experimentally tested in a pilot plant that synthetizes polyacrylamide in semi-batch fashion using potassium persulfate as initiator.

- A *hybrid* variation of the discrete-time extended Kalman filter (*h*-DEKF) is formulated considering an auto-tune error-driven procedure. Model errors are obtained using a stochastic global optimization technique which guarantees a smooth tuning of the filter and adequate online performance.

- A GO is formulated and tested using experimental data from the ACOMP system for a semi-batch free-radical polymerization reactor that synthetizes polyacrylamide. The available measurements include the weight-average molecular weight, the concentration of monomer, and the volume of internal contents. Different combinations between innovated states and measurements offer a number of possible structures of the GO. The computation of the minimum singular values and condition numbers permit to select the most promising structures. To overcome inadequacies observed in full-order architectures, low order GOs with passive structures are explored. The best observer is selected, compared with a standard estimation strategy and tested under various experimental operating conditions. The observer performance is evaluated qualitatively and quantitatively as a tradeoff between dynamic property estimation and signal processing.

- A strategy for the online estimation of significant kinetic parameters is proposed and assessed for the copolymerization of ethylene with 1,9-decadiene using a metallocene catalyst at different reaction temperatures and concentrations of the diene. A global sensitivity analysis is performed to all the kinetic parameters, in which a pivot matrix is implemented to avoid unfeasible points due to the high nonlinearities of the studied system. The first and total sensitivity indices permit the selection of the most significant parameters.
which are later reconstructed. After verifying stability, real experimental data is used to validate the proposed strategy.

- A normalized GO which uses a pre-conditioning strategy (incomplete LU decomposition) is assessed and evaluated for parameter estimation. The robustness and dynamic response of the method is compared with an EKF.

- A data-driven strategy for the online estimation of important kinetic parameters, referred as the RCMR algorithm, was assessed and tested. The RCMR algorithm is adapted and implemented to estimate the significant kinetic parameters of the model in real-time. After verifying stability and robustness, real experimental data permitted to validate the performance of the algorithm. Results demonstrate the estimated kinetic parameters converge close to theoretical values without requiring prior knowledge on the polymerization model or the original kinetic values.

1.5 References

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June 2018.


2 MODELLING AND OPTIMAL OPERATION OF POLYMERIZATION PROCESSES

2.1 Introduction

To count with a mathematical representation of a polymerization system represents an advantageous tool for understanding the process when seeking the implementation of advanced model-based strategies. The use of mechanistic models requires to follow certain steps before they are reliable and fully useful for a number of applications including experimental design (policy formulation), dynamic optimization, advanced control strategies and nonlinear state estimation. For developing a fundamental model, initial steps include the understanding of the process characteristic (geometry of the experimental apparatus or equipment, reaction mechanism, type of reactor, degree of mixing), the mandatory energy and mass balances, and the mathematical representation of key properties such as the number-average and weight-average molecular weights (Baillagou & Soong, 1985; Pinto & Ray, 1995).

Another polymer property of high importance is the molecular weight distribution (MWD). The MWD is crucial as it explains physical, rheological and thermal properties, including thermal stability, material strength and processability (Nguyen & Kausch, 1999; Heidemeyer & Pfeiffer, 2002; Isayev, 2016). Even though the weight-average molecular weight is usually the most important property when characterizing a polymer distribution, there are some cases in which average properties do not contain enough relevant information. If a bimodal or broad distribution is foreseen (Schork, 2014), the computation of the distribution is essential and needs to be addressed following a different approach. Several strategies have been suggested for modelling the distribution of polymers including orthogonal collocation approach (Galvan & Tirrell, 1986), Monte-Carlo based simulation (He et al., 1997) and deconvolution (Soares et al., 1995; 1997). An
inherent limitation, however, is the high complexity of some of these calculations, which can become computationally expensive and even unfeasible in certain polymerization systems (Brandão et al., 2017). A simplified version of this property can be captured by the chain length distribution which uses the finite molecular weight moments method proposed Crowley et al. (1997a; 1997b) in conjunction with the kinetic rate equations. The aforementioned method is applicable in batch and semi-batch operations.

Once the model is formulated, the kinetic rate constants, noteworthy parameters of the system, require to be adjusted or fitted for the particular polymerization processes under study. These parameters require to be determined precisely since small variations can result in considerable errors. Information in regard to the kinetic rate constants may be obtained from literature or acquired experimentally (Ryan & Dutta, 1979; Asua et al., 1990). In some cases, this task might become difficult because of the non-availability of data from the literature, or the unfeasibility to obtain representative measurements due to the lack of experimental facilities. There are many aspects that can affect the kinetic rate parameters during polymerizations including operating conditions and the presence of inhibitors. Thus, descriptive values of rate constants should be determined utilizing a convenient parameter estimation technique. This is an important prerequisite which makes the mechanistic model reliable.

After the mechanistic model has been validated, different manipulations are possible including the generation of optimal recipes. By applying dynamic optimization, optimal policies can be formulated in order to achieve different objectives. The accomplishment of target properties or making an efficient use of feedstock materials can be guaranteed when optimal operational conditions are followed during the reaction.
2.2 Parameter estimation: the gEST function

The parameter estimation is often formulated as an optimization problem in which the main aim include the maximization of the probability that the model is going to predict similar values as the ones obtained experimentally. According to Li et al. (2004), an effective parameter estimation is achievable for nonlinear models if the following conditions are met:

- The system should be structurally identifiable, which means that each set of parameter values will result in unique output trajectories, and

- The parameters that exert a weak effect on the estimated measured variables, and the parameters which effect on the measured output is linearly dependent need to be detected in order to be removed from the formulation because their effect is not accurate or individually quantified.

The maximum likelihood criterion is a broadly utilized parameter estimation procedure. The software gPROMS, containing the gEST function, can be utilized for parameter estimation using data collected from different sets of experimental runs (Ng et al., 1999). Each experiment is described by fixed conditions that contain particular initial conditions or combinations of controlled and manipulated variables. Important settings include:

1) The initial conditions, which in polymerizations can be the initial loading monomer, co-monomer, initiator, catalyst or solvent,

2) The variations of the controlled variables,

3) The values of the time invariant parameters, and

4) The total reaction time.
Assuming independent, normally distributed measurement errors ($\epsilon_{ijk}$) with zero mean and standard deviations ($\sigma_{ijk}$), the maximum likelihood is seized by the objective function in Eq. (2.1).

$$\phi = \frac{N}{2} \ln(2\pi) + \frac{1}{2} \min_\theta \left\{ \sum_{i=1}^{NE} \sum_{j=1}^{NV_i} \sum_{k=1}^{NM_{ij}} \left[ \ln(\sigma_{ijk}^2) + \frac{(\tilde{z}_{ijk} - z_{ijk})^2}{\sigma_{ijk}^2} \right] \right\}$$

(2.1)

Where $N$ describes the total number of measurements taken during all the experiments, $\theta$ is the set of model parameters to be estimated which may be subjected to a given lower and upper bound. $NE$, $NV_i$ and $NM_{ij}$ are the total number of experiments, the number of measured variables in the $i$th experiment, and the number of measurements of the $j$th variable in the $i$th experiment, respectively. $\sigma_{ijk}^2$ is the variance of the $k$th measurement of variable $j$ in experiment $i$ while $\tilde{z}_{ijk}$ is the $k$th measured value of variable $j$ in experiment $i$ and $z_{ijk}$ is the $k$th model-predicted value of variable $j$ in experiment $i$ (Ghadipasha, 2016).

According to Nowee et al. (2007), the variable $\sigma_{ijk}^2$ has dependency on the error structure of the experimental data, which can be homoscedastic (constant) or heteroscedastic (depend on the variables magnitude). If $\sigma_{ijk}^2$ is fixed, the maximum likelihood problem is simplified into a least square criterion. If a purely heteroscedastic model applied the error, it would have the structure in Eq. (2.2).

$$\sigma_{ijk}^2 = \omega_{ijk}^2 (\tilde{z}_{ijk})^\gamma$$

(2.2)

Which implies that if the magnitude of the measured variable increases, the variance of $\tilde{z}_{ijk}$ will also increase. The parameter $\omega_{ijk}^2$ and $\gamma$ are determined as part of the optimization during the estimation process.
2.3 Parameter estimation: heuristic strategies

Metaheuristic strategies are intelligent approaches to search optimal points from highly nonlinear problems of dimensionality of a few of tens. They treat the mathematical model as a black box, which reduces computational effort while having the advantage of a relatively easy implementation. By using exploitation and exploration of the solution domain, better optimal solutions are achievable (Yi et al., 2013; Salas et al., 2017). Metaheuristic methods are algorithms, usually nature-inspired, that intend to solve complex optimization problems. Because of their initialization stage, these algorithms are considered as part of stochastic optimization techniques (Bianchi et al., 2009). For kinetic parameter estimation, metaheuristic methods have been employed in reacting systems (Majumdar et al., 2005; Hu et al., 2012). Therefore, for polymerization processes, metaheuristic algorithms appear to be a promising and easy to implement strategy for kinetic parameter estimation (Lee et al., 1999; Prata et al., 2009). In the following subsections, relevant metaheuristic strategies are explained towards kinetic parameter estimation in polymer synthesis.

2.3.1 Genetic algorithm

The genetic algorithm (GA) is a metaheuristics method based on natural selection. It was first proposed by Holland (1975) and further developed by Holland & Goldberg (1989). In the literature, numerous applications have been suggested for this algorithm in diverse fields of science and engineering (Weile & Michielssen, 1997; Nicklow et al., 2009; Liao et al., 2011). In general, the GA searches for optimal points from a population, which is guided by output values and probabilistic rules (Kapanoglu, 2007). The algorithm initializes by random encoded chromosomes in which each chromosome corresponds to a different output. Individuals, represented by their associated outputs, are ranked. The algorithm selects individuals for reproduction based on their
success and takes a fraction of the population to crossover following a continuous random selection. This operator produces two complementary offspring as linear combinations of the parents. To avoid local optima, another proportion of the populations experiences mutation. In the mutation step, the algorithm uses a boundary strategy. The mutation operator replaces the genome with either lower or upper random bound based on a mutation rate.

For the next generation, the best solutions are kept and used to generate a new population. New offspring are generated in the crossover as well as in the mutation. The algorithm ends with a preselected maximum number of generations or when termination criteria is met. Figure 2.1 introduces the pseudo-code of the GA summarizing its steps. Here, $z_{l,O}^{P_1}$ and $z_{l,O}^{P_2}$ are two randomly chosen parents, $z_{l,O}^{O_1}$ and $z_{l,O}^{O_2}$ are the generated children, $\eta$ denotes a crossover factor which varies in the interval $[-\gamma, 1 + \gamma]$. The extra range crossover factor $\gamma$ is a selected scalar value.

---

**Step 1 Initialization**

Initialize the generation number $G = 0$.
Randomly initialize $NP$ individuals (target vectors $z_{l,G} = \{z_{l,G}^1, ..., z_{l,G}^{NP}\}$ for $l = 1, 2, ..., NP$) within the search range $[z_{min}^l, z_{max}^l]$, where $z_{min} = \{z_{min}^1, ..., z_{min}^D\}$ and $z_{max} = \{z_{max}^1, ..., z_{max}^D\}$.

FOR $i = 1$ to $NP$
    FOR $j = 1$ to $D$
        $z_{l,G}^j = z_{min}^j + \text{rand}(0,1)(z_{max}^j - z_{min}^j)$
    END FOR
END FOR

**Step 2 Generation**

WHILE stopping criterion is not satisfied.

- Crossover Step: / generate two off-springs through linear combination of two parents
  $$
  z_{l,G}^{O_1} = \eta z_{l,G}^{P_1} + (1-\eta)z_{l,G}^{P_2} \\
  z_{l,G}^{O_2} = (1-\eta)z_{l,G}^{P_1} + \eta z_{l,G}^{P_2}
  $$

- Mutation Step: / generate a mutation vector (boundary mutation) within the search range $[z_{min}, z_{max}]$

- Selection Step: / select a target vector with better objective function as the individual for the next generation.

Increment generation number $G = G + 1$

END WHILE

**Figure 2.1. GA pseudo-code**
2.3.2 Differential evolution algorithm

The Differential Evolution (DE) algorithm, developed by Storn & Price (1997), is a heuristic optimization technique able to solve nonlinear and non-differentiable problems. The main advantages include simple implementation, speed and robustness, which makes it highly applicable for parameter estimation of reacting systems (Wang et al., 2001; Babu & Angira, 2006), including a continuous polymer reactor (Lee et al., 1999). As explained by Liao et al. (2012), the DE algorithm involves the evolution of a population of solutions using certain operators that include mutation, crossover and selection.

The initial population of the DE algorithm can follow a uniform distribution over the solution domain. Each solution vector in the population serves as the target vector in one generation. For each target vector, the mutation operator generates a new parameter vector called the mutated vector by adding a weighted difference between two population vectors to a third vector. These three vectors are selected randomly and must differ from the target. A scaling factor $\beta$ controls the amplification of the differential variation between the second and the third randomly chosen vectors. Selecting $\beta$ randomly improves the convergence behavior especially for noisy objective functions (Price et al., 2006). For crossover, a uniform arrangement builds trial vectors from values copied from two different vectors. Finally, the vector with the best cost function is selected as the target vector for the next generation.

Figure 2.2 depicts the pseudo-code of the DE algorithm. Here, the $CR$ resembles the crossover rate, and $j_{rand}$ is a random integer from 1 to $D$ (dimensionality of the problem).
Step 1 Initialization

Initialize the generation number $G = 0$.
Randomly initialize $NP$ individuals (target vectors $z_{i,G} = \{z_{i,G}^1, ..., z_{i,G}^D\}$ for $i = 1, 2, ..., NP$) within the
search range $[z_{min}, z_{max}]$, where $z_{min} = \{z_{min}^1, ..., z_{min}^D\}$ and
$z_{max} = \{z_{max}^1, ..., z_{max}^D\}$.
FOR $i = 1$ to $NP$
  FOR $j = 1$ to $D$
    $z_{i,G}^j = z_{min}^j + \text{rand}(0,1)(z_{max}^j - z_{min}^j)$
  END FOR
END FOR

Step 2 Generation

WHILE stopping criterion is not satisfied.
  o Mutation Step: / generate a mutation vector
    $w_{i,G} = \{w_{i,G}^1, ..., w_{i,G}^D\}$
    FOR $i = 1$ to $NP$
      $w_{i,G} = z_{r_1,G} + \beta(z_{r_2,G} - z_{r_3,G})$
    END FOR
  o Crossover Step: / generate a trial vector $v_{i,G} = \{v_{i,G}^1, ..., v_{i,G}^D\}$
    FOR $i = 1$ to $NP$
      FOR $j = 1$ to $D$
        $v_{i,G}^j = \begin{cases} z_{i,G}^j & \text{if } \text{rand}(0,1) \leq CR \text{ or } j = j_{rand} \\ w_{i,G}^j & \text{otherwise} \end{cases}$
      END FOR
    END FOR
  o Selection Step: / select a trial or target
    vector with better objective function as the
    individual for the next generation.
    FOR $i = 1$ to $NP$
      $z_{i,G+1} = \begin{cases} v_{i,G} & \text{if } F_{obj}(v_{i,G}) \leq F_{obj}(z_{i,G}) \\ z_{i,G} & \text{otherwise} \end{cases}$
    END FOR
Increment generation number $G = G + 1$
END WHILE

Figure 2.2. DE pseudo-code

2.3.3 Particle swarm optimization

Particle swarm optimization (PSO) is derived from a study on artificial intelligence
exploiting social interaction concepts (Eberhart & Kennedy, 1995; Poli et al., 2007), and it has
demonstrated applicability in the optimization of chemical processes (Ourique et al., 2002). A
swarm is a population of homogenous simple agents, which perform elemental tasks and interact
among themselves and the environment. It represents collective behavior as a consequence of the
self-organization and local interactions (Mariani & Walczak, 2015). PSO is classified as a
stochastic optimization approach containing a swarm of candidate solutions. In this algorithm, each potential solution is defined as a particle that represents a point in a space of dimensionality $D$. The position of a particle is given by a vector, and the population of candidate solutions constitutes a swarm. During the search of an optimal solution, the particles define trajectories in the parameter space.

Figure 2.3 shows the pseudo-code of the PSO. The velocity vector ($V_i$) is given for the $i^{th}$ particle in the solution domain. This vector governs the movement of each particle, and it is constituted by the terms momentum, cognitive component, and social component. Here, $p_i$ is the current best solution, $g$ is the global best solution obtained by the swarm, and $\theta_i$ the inertia weight, which decreases by a certain damping ratio $\xi$ in each iteration and supports in balancing the global exploration and local exploitation.

![PSO pseudo-code](image)

**Figure 2.3. PSO pseudo-code**
The factors $c_1$ and $c_2$ are the cognitive and social coefficient, respectively. They modulate the magnitude of the steps taken by the particle in the direction of its personal best and global best. $R_1$ and $R_2$ are two diagonal matrices of random numbers generated from a uniform distribution in $[0, 1]$, so that both components have a stochastic influence on the velocity update. The iterative process is repeated until a termination or stop criteria is met.

### 2.4 Optimal operation in polymerization

Offline dynamic optimization searches for optimal policies that lead to polymers with desired final characteristics. The process modelling software gPROMS and more specifically its dynamic optimization tool gOPT has the capability to compute easily these policies. The gOPT function is convenient for real-time applications as it uses a piecewise control variable definition, permitting the selection of a time interval in which decision variables are constant, and later they are updated for the next time interval (Ghadipasha et al., 2016). To ensure optimality the method applies adaptive control vector parameterization (Schlengel et al., 2005), which translates the problem into a nonlinear programming problem by parametrizing the control profiles. The optimization algorithm determines the values of the controls over each interval, as well as the duration of the interval. The optimization strategy implements a single-shooting dynamic optimization algorithm consisting of the following subsequent steps:

1) The control interval length and the values during the interval are chosen by the optimizer;

2) Starting from the initial conditions, the dynamic system is solved for computing the time-variation of the states of the system;
3) Based on the solution, the values of the objective function and its sensitivity to the control variables and the constraints are determined, and

4) The optimizer revises the choices at the first step and the procedure is repeated until the convergence towards the optimum is attained.

Eq. (2.3) and Eq. (2.4) illustrate a general dynamic optimization problem suitable for a number of specific target polymers in which the first term targets a desired final conversion, the second a final weight-average molecular weight, the third a final chain length distribution and the last one optimizes the use of monomer.

\[
\min_{t_f,u(t),s(t)} \, w_1 \left( \frac{X_f}{X_t} - 1 \right)^2 + w_2 \left( \frac{M_{w,f}}{M_{w,t}} - 1 \right)^2 + w_3 \sum_{i=1}^{nc} \left( \frac{g_{i,f}}{g_{i,t}} - 1 \right)^2 + w_4 (N_{m,f,f}) \quad \text{(2.3)}
\]

Constrained to:

\[
\begin{align*}
  & j(t_0) - j_0 = 0 \\
  & t_f^{\text{min}} \leq t_f \leq t_f^{\text{max}} \\
  & u^{\text{min}} \leq u(t) \leq u^{\text{max}} \\
  & s^{\text{min}} \leq s(t) \leq s^{\text{max}}
\end{align*}
\quad \text{(2.4)}
\]

where, the subscript \( f \) stands for final value and \( t \) for the target value of the optimized variable. Notice that the first three terms in the objective function seek to achieve target properties while the fourth term searches the optimal use of monomer. The weighting factors \( w_i \) vary depending on the particular MWD of interest which is obtained by following specific \( M_w \) trajectories. In the constraints, \( j_0 \) symbolizes the initial conditions of the system, \( t_f \) represents the time-horizon, \( u(t) \) the control variables subjected to the pilot plant physical constraints, and \( s(t) \) represents the time variant parameters also constrained to the pilot plant characteristics, e.g., volume of the contents inside the reactor.
The objective of the dynamic optimization is to find the optimal policies for one or more control variables of the system which drives the process to desired final polymer property while minimizing the reaction time. The process control variables conform to their impact on the product quality and their capability for real time implementation.

Figure 2.4 illustrates a schematic representation or proposed framework for hierarchical optimization of polymerization operations. First, the mechanistic model is validated and its parameters fitted with the available experimental data. Once the model is reliable, the dynamic optimization searches optimal operational conditions (static or dynamic/trajectories) that lead to pre-established polymer properties defined as target characteristics. The proposed model-centric framework has adaptability to a number of desired policies, and it is meant to adapt to different polymerizations.

Figure 2.4. Schematic representation of a generic optimization problem for polymerization processes.
2.5 References


3 CONTROL STRATEGIES IN POLYMERIZATION

3.1 Introduction

The smart manufacturing of polymers relies on advance control strategies that guarantee the mass production of plastic materials with reliable quality and standardized properties. Uniformity between batches and desired end-characteristics are of preponderant importance for final manufacturers. For instance, thermal stability, strength, and capability of being processed are polymer properties of paramount importance that require consistency for determined applications. An extensive portfolio of advanced control strategies has been developed during the past decades (Lee & Sullivan, 1988; Eaton & Rawlings, 1990; Srinivasan et al., 1995; Alvarez, 1996; Allgöwer et al., 1999; Romagnoli & Palazoglu, 2005). Nevertheless, these advancements are less developed for polymerization systems mainly because of the non-availability of smart sensors capable of permitting the direct observability and the consequent controllability of vital polymer properties such as, the molecular weight distribution (MWD), the number-average molecular weight \(M_n\), and the weight-average molecular weight \(M_w\). In addition, polymerization processes hold complex dynamics and are difficult to represent mathematically due to the intrinsic nonlinearities arising during the reaction. Typical complexities include a significant exothermic behavior, radical changes in the kinetic coefficients of the system during reaction (propagation and termination rates), and the probability of gelation inside the reactor (Ray, 1985). The development of proper control strategies to regulate the underlying polymerization system are crucial for achieving products with desired characteristics. Therefore, the control of polymerizations remains as a major section of the chemical manufacturing industry that demands attention from managers, stakeholders, investors, and academia.
The molecular weight distribution is a key property of plastics and polymeric materials. It describes relevant physical and mechanical characteristic including the strength, toughness, elasticity modulus, glass transition temperature, and processability (Nguyen & Kausch, 1999; Gentekos et al., 2016; Gao et al., 2017). Nevertheless, operational disturbances (e.g., temperature variations, inlet flow rate fluctuations, or non-ideal mixing) and the presence of impurities in feedstock materials might compromise the desired final molecular structure. The MWD of polymers can shift from its desired target distribution due to the sensitive molecular structure, and other factors that include degree of mixing, concentration of reactants, and the reactor temperature (McKeen, 2014). In this sense, the control of polymerizations has focused on either establishing open-loop strategies (recipes) or controlling observable properties and process variables, such as the density and reactor temperature, which indirectly intends to influence the final characteristic properties.

Understating the needs of polymer reaction engineering, different control strategies were critically discussed by Yoon et al. (2004) and Kreft et al. (2009). Mathematical modeling demonstrated high competency as a powerful tool in advanced control applications for polymerization systems. Typically and with the help of a mechanistic model, the trajectories of manipulated variables are determined by some means. It is assumed that by tracking a selected trajectory, the control variable can achieve desired target properties. For instance, by controlling the temperature profile in a batch reactor, Crowley & Choi (1997) followed a desired chain length distribution when studying a free-radical polymerization. A sequence of discrete reactor temperature set points lead to the target distributions which were computed by solving an optimization problem. An online level controller followed the optimal temperature profiles by manipulating the coolant feed flow to the reactor’s jacket. Similarly, Gentric et al. (1999) proposed
a nonlinear control strategy tracking an optimal temperature profile to achieve a target final $M_n$ for a batch emulsion polymerization of styrene and $\alpha$-methyl-styrene. Temperature control is achieved through a fluid flowing in a double jacket at a constant flowrate. The fluid inlet temperature is controlled by using a three-way valve and two heat exchangers (hot and cold). Furthermore, Chang & Liao (1999) computed an ideal temperature path to achieve a target MWD in a batch polymerization applying a revised two-step method. The required temperature profile that leaded to the desired distribution was computed based on the instantaneous average chain length trajectory. For control purposes, a conventional proportional-integral (PI) controller was deployed to track the optimal temperature policy. As portrayed, the mentioned strategies highly depend on the ability of the model to accurately estimate the trajectories of manipulated variables (temperature in these cases). In contrast, Kiparissides et al. (2002) considered uncertainty in the model. An online estimator-optimization scheme was proposed to update the optimal control policy. At each iteration the controller forced the process to follow an updated optimal trajectory. Even though these approaches appear to be reasonable for achieving control objectives, they lack the ability to exert direct impact on the control objective, and the majority rely on a manipulated variable that has slow dynamics.

More promising control strategies are the ones that make direct use of mechanistic models such as model predictive control (MPC). Park et al. (2004) implemented a nonlinear model in the learning algorithm of an MPC. The proposed nonlinear MPC was developed for the semi-batch solution copolymerization of the methyl-methacrylate/methyl-acrylate system. Likewise, Alhamad et al. (2005) proposed a multi-layer control algorithm for real-time deployment applying optimal control policies for emulsion copolymerizations. A multi-input-multi-output (MIMO) formulation sought to maximize the average properties. To overcome the insufficiency of a sensor
to measure the MWD, a soft-sensor was applied using the underlying model to estimate an online distribution and $M_w$. Other contributions suggest the use of nonlinear MPC in polymerizations because of the characteristic nonlinearities of the system (Prasad et al., 2002; Bindlish, 2015). Nevertheless, direct observability on the control objective is required to assure robustness in closed-loop control while making an appropriate use of the control variables.

To close the loop in polymerization processes it is ideal to count with soft or smart sensors able to capture the online changes of relevant properties. The availability of such sensors should guarantee a better control action and ultimately the accomplishment of high quality polymeric materials. In this regard Wang et al. (2016) took advantage of available specific viscosity measurements to solve the Mark-Houwink equation for computing the $M_w$, resembling a sophisticated soft sensor for ultra-high molecular weight. In addition, over the past years, several investigation have been done for developing the state-of-the-art sensor Automatic Continuous Online Monitoring of Polymerization reactions (ACOMP) (Florenzano et al., 1998). In fact, the ACOMP system represents a major advancement in providing online measurements of important polymer properties, including $M_w$, monomer concentration ($C_m$) and polymer concentration ($C_p$) (Reed & Alb, 2014). This smart sensor has already demonstrated a proficient ability in monitoring polymer properties in different types of liquid-phase systems, such as synthesis of polyacrylamide (Giz et al., 2001), copolymerizations and homopolymerizations (Kreft & Reed, 2009a; 2009b). The ACOMP system extracts and dilutes continuously a small sample from the polymerization reactor. The analysis of the collected sample combines different detectors including, multi-angle laser light scattering, UV/visible spectrophotometry, viscometry, refractivity, and conductivity.
3.2 Exact linearizing control in polymerization

Even though conventional control approaches show adequate performance in various processes, in polymerization these techniques suffer from the disadvantage of relying on tangent model approximations or even linear black-box models. If a model is available, the intrinsic prior knowledge on the system dynamics is advantageous. Indeed, improved control performance can be expected from the exploitation of the nonlinear model structure when setting control objectives or analyzing the effective use of control variables (Soroush & Kravaris, 1992; Bindlish, 1999).

A renowned approach for control is the exact linearizing control strategy in which linearization is introduced into the problem. Figure 3.1 compares conventional control with linearizing control. As detailed, the conventional approach requires the calculation of a linearized approximation of the model to design a linear controller. However, the closed loop remains as nonlinear and lacks the ability to cover a broader range of operating conditions around the transient trajectory. On the other hand, the exact linearizing control method assesses a nonlinear controller which is designed in such a way that the closed loop remains linear, guaranteeing stability and operability in a broader range of operating conditions.

Figure 3.1. Schematic of the conventional control and linearizing control.
Linearizing control makes use of the nonlinear model to track an output signal identified as $y^*(t)$ which is controlled by regulating the selected control variable. A control law, $u(\theta, y^*)$, represents a multivariable nonlinear function of $\theta$ and $y^*$ such that the tracking error ($y^* - y$) is governed by a pre-stated stable linear differential equation as a reference model. Where, $\theta$ is a matrix of state variables and parameters which are either online measured or are obtained from observations (Bastin & Dochain, 1990).

The mechanistic model to be exploited using linearizing control is explained in detail in Chapter 6. However, for the sake of clarity some information regarding to the nonlinear model for polyacrylamide synthesis in aqueous solution using potassium persulfate as initiator is introduced in this section (Ghadipasha et al., 2016; Ghadipasha et al., 2017; Salas et al., 2018). The control response and tradeoff is evaluated in terms of the ability of achieving set point trajectories and other properties. For a complete explanation of the process variables, parameters, and operating conditions, the reader is encouraged to review Chapter 6.

The design of the nonlinear controller for linearizing control can be explained in three phases. First, the input-output model should be derived by the appropriate manipulation of the general dynamic model. Second, a stable linear reference model of the tracking error is selected as denoted in Eq. (3.1).

$$
\sum_{j=0}^{\delta} \lambda_{\delta-j} \frac{d^j}{dt^j} [y^*(t) - y(t)] = 0 \quad \lambda_0 = 1
$$

(3.1)

where, $\delta$ is the relative degree of the input-output model, $\lambda_{\delta-j}$ are the tuning coefficients which are chosen to maintain the differential equation stable. Finally, the control design calculates the
control action $u(t)$ such that the input-output model accurately matches with the reference model described in Eq. (3.1).

To test the performance of the proposed nonlinear controller, the validated model and control elements are implemented in MATLAB R2015a and run in a PC Intel Core™ i7-4790K CPU @ 4.00 GHz with 16.0 Gb of installed RAM. The differential equations of the model are dynamically solved using ode45 (Dormand & Prince, 1980; Shampine & Reichelt, 1997), and the selected control interval for updating the controlled variable is set to 2.5 min. The control action initializes after 5 min the reaction starts (this time arbitrary selected to let the reader observe the initial step change of the control action). Figure 3.2 illustrates the schematic representation of the approach for the computational experiments. It should be noticed that the initial recipes are obtained from the software gPROMS (as explained in Chapter 2), and the control objective is obtained from optimal policies. The manipulated inputs (controlled variables) are adjusted by the feedback control action while all other inputs remain fixed according to the formulated recipe. Uncertainty to the kinetic parameters of the closed-loop model is applied to mimic a real operation.

Figure 3.2. Schematic of the nonlinear controller implementation for computational testing.
When considering the experimental unit to be introduced in Chapter 6, three manipulated variables are foreseen, these include: the temperature of internal contents in the reactor \((T)\), monomer flow rate \((F_m)\), and initiator flow rate \((F_i)\). For the testing case scenarios, the total amount of monomer in the reactor \((N_m)\) is selected as the set point trajectory. In addition and because it is a property of interest, the weight-average molecular weight \((M_w)\) is tracked as well. Controllability is tested for all possible manipulated variables in different computational experiments, evaluating the control response and performance.

### 3.2.1 Case 1: control total amount of monomer by manipulating temperature

The input-output model for the total amount of monomer is written in Eq. (3.2) using the differential equation which describes its dynamics.

\[
\frac{dN_m}{dt} = -\left( k_p + k_{fm} \right) P_0 N_m + F_m C_{mf} - F_{out} C_m
\]  \hspace{1cm} (3.2)

The total amount of monomer at a given trajectory is defined as \(N_m^*\). A first order reference model to regulate the error is proposed in Eq. (3.3).

\[
\frac{d}{dt} (N_m^* - N_m) + \lambda_1 (N_m^* - N_m) + \lambda_2 \int_0^t (N_m^* - N_m) \, dt = 0
\]  \hspace{1cm} (3.3)

A pseudo-PI controller with a nonlinear term is considered for the structure of the error. With the help of Eq. (3.2) for the real variable and knowing the dynamics of the nominal trajectory, Eq. (3.3) can be solved for the controlled variable temperature. The temperature variable is found in the kinetic rates because they hold an Arrhenius equation form. Therefore, the referenced equation is nonlinear with respect to the temperature (no explicit solution) and has to be solved numerically.
Figure 3.3 portrays the results for Case 1, considering an increasing weight-average molecular weight trajectory.

![Graphs showing the results for Case 1.](image)

**Figure 3.3.** Control of $N_m$ by manipulating $T$. Open loop results (blue circles), closed loop results (red continuous lines), and optimal or set point trajectories (dashed lines).
The open-loop profile represents the computational experiment. It is modeled including uncertainty to the kinetic parameters of the model, and it follows the nominal trajectories defined as optimal policies. The closed loop profile refers to the response of the model with uncertainty when the temperature profile is regulated to follow the set point trajectory. Notice that when temperature is controlled, small variations of the controlled variable (less than 5 °C) occur to achieve the control objective. However, the $M_w$ shows a significant shift from its target value, which makes necessary to explore other possibilities of control.

3.2.2 Case 2: control total amount of monomer by manipulating monomer flow rate

For this case study, the previously introduced Eq. (3.3) is solved explicitly for the monomer flow rate by substituting Equation (3.2) into (3.3). The resultant Eq. (3.4) shows the nonlinear update of $F_m$.

$$F_m = \frac{dN^*_m}{dt} - \lambda_1 [N^*_m - N_m] - \lambda_2 [\int (N^*_m - N_m) dt] + F_{out}C_m + (k_p)C_pN_m$$

When designing the nonlinear controller for Case 2, the $F_m$ is constrained between a high flow and low flow rate. These lower and upper bounds are introduced to mimic real operations. Limitations of the experimental unit (explained in Chapter 6) indicate that the positive displacement have operational limitations. Therefore, the operative $F_m$ is expected to be between $5 \times 10^{-6}$, and $0.12 \times 10^{-6}$, $[mol. m^{-3}]$.

The simulation results for the nonlinear controller in Case 2 are presented in Figure 3.4. The controller tracks proficiently the total amount of monomer along the desired nominal trajectory, indicating a good response to disturbances, but it fails to achieve the desired $M_w$ trajectory. As occurred previously, small variations of the controlled variable take place to achieve
the control objective. Notice that the mismatch between the closed-loop $M_w$ and its desired set point shows less variation when compared with the previous one (portrayed in Figure 3.3).

**Figure 3.4.** Control of $N_m$ by manipulating $F_m$. Open loop results (blue circles), closed loop results (red continuous lines), and optimal or set point trajectories (dashed lines).
3.2.3 Case 3: control total amount of monomer by manipulating initiator flow rate

Eq. (3.2) is not suitable for deriving the linearizing control for the initiator flow rate because of the nonexistent explicit relationship among the initiator flow rate and the total amount of monomer. Nevertheless, when differentiating Eq. (3.2) and using the dynamic expression for the total amount of initiator presented in Eq. (3.5a), Eq. (3.6a) can be derived:

\[
\frac{dN_i}{dt} = -k_d N_i + F_i C_{if} - F_{out} C_i
\]  

(3.5a)

where,

\[
P_0 = \frac{2e_i C_i k_d}{\sqrt{k_{tc} + k_{td}}}
\]  

(3.5b)

\[
C_i = \frac{N_i}{V}
\]  

(3.5c)

Therefore, the manipulated variable \(F_i\) is obtained from the second derivation of the total amount of monomer. Straight forward calculations lead to the following linearizing control law.

\[
F_i = \left[ Z - \frac{A}{2\sqrt{C_i}} \left[ \frac{-k_d N_i - F_{out} C_i}{V} \right] \right]
\]

\[
\frac{A}{2\sqrt{C_i}} \left[ \frac{C_{if}}{V} - \frac{A}{2\sqrt{C_i}} \frac{N_i}{V^2} \right] - \frac{B}{V^2}
\]

(3.6a)

where A, B and Z are defined as:

\[
A = -\left(k_p N_m\right) \sqrt{\frac{2f_k d}{k_{td}}}
\]

(3.6b)

\[
B = -F_{out} N_m
\]

(3.6c)

\[
Z = \frac{d^2 N_m^*}{dt^2} - \lambda_1 [N_m^* - N_m] - \lambda_2 \int N_m^* - N_m
\]

(3.6d)
Because the input-output model is a second order differential equation the reference model
is also of second order form. The simulation results of the controller are presented in Figure 3.5.

**Figure 3.5.** Control of $N_m$ by manipulating $F_i$. Open loop results (blue circles), closed loop
results (red continuous lines), and optimal or set point trajectories (dashed lines).
Similarly as observed in Case 2, the $F_i$ is constrained between a high flow and low flow rate. The $F_i$ is expected to be between $2 \times 10^{-6}$ and $1 \times 10^{-7}$, [\textit{mol.m}^{-3}]. The flow rate of initiator shows poor controllability even with the maximum operational flow rate. The control objective is not achieved in this evaluation even when fine tuning the controller or increasing the concentration of initial in the controlled $F_i$. The reason is related to the low concentration of the initiator in the feed.

In our system, when the temperature or monomer flow rate are manipulated to control the total amount of monomer, the relationship holds a relative degree of 1. On the other hand, when manipulating the initiator flow rate to control the total amount of monomer or the weight-average molecular weight, the relative degree is 2. In this context, for controlling the weight-average molecular weight with the monomer flow rate using linearizing control, the relative degree will be very high, making this pair of controlled-manipulated variables unfeasible using the linearizing control approach.

In addition, as evidenced in Figure 3.3, Figure 3.4, and Figure 3.5 even when the control objective is accomplished, other properties are not achievable due to the intrinsic uncertainties of the system. In our practice, these uncertainties are introduced in the form of random variations of the kinetic rate constants, but in real practice there might be other operational disturbances. Recalling the main purpose of achieving target polymers, it is desirable to have direct observability on the ultimate control objective, and not only follow an indirect control action.

In the following section, a direct feedback control of weight-average molecular weight using the monomer flow rate as manipulated variable is discussed. This methodology is based on the regulation of the monomer flow rate using a linear proportional-integral-derivative (PID)
controller. Small changes from the original trajectory are expected as well as the achievement of target properties.

### 3.3 Feedback control of weight-average molecular weight

Considering the ACOMP system as an accessible smart sensor that permits the observability of the $M_w$ dynamic evolution with minimum time delays, an immediate benefit from this setup will be the capability of direct control of this variable. As mentioned before, the ACOMP system has been tested in aqueous solution polymerizations considering mainly three controlled variables: reactor temperature, flow rate of monomer and flow rate of initiator. Even though temperature appears to be a promising control variable (Section 3.2.1), in real-time operations it is preferable to maintain the process isothermal. As verified experimentally in aqueous polymerizations (Ghadipasha et al., 2017; Salas et al., 2018), sudden temperature changes can increase the viscosity of the solution causing heat transfer matters between the medium and the heating jacket which can be detrimental for to the pilot plant. In addition, the flow rate of monomer and initiator appear are feasible control variables for the purposed control objective ($M_w$).

Given a $M_w$ set point trajectory, a PID controller is designed where $M_w$ is controlled by manipulating the monomer flow rate. The choice of the manipulated variable for feedback control of $M_w$ is justified based on the typical input effects that this variable has in terms of gain and response time. Indeed, it is important to mention the ACOMP system has ~2 minutes delay in providing information on the measurements. From simulation analyses the monomer flow rate is more proficient in meeting the control requirements than the initiator flow rate. Figure 3.6 exhibits a block diagram for $M_w$ feedback control using the ACOMP system as smart sensor. Notice that
measurements might be contaminated by noise and further signal processing might be required (Chapter 4 addresses strategies for signal processing).

The PID control law consists of a three-term expression where the behavior of the controller can be modified by the choice of three parameters. The transfer function for a PID is expressed as:

$$\frac{\bar{u}(s)}{\bar{e}(s)} = g_c(s) = k_c \left(1 + \frac{1}{\tau_I s} + \tau_D s \right)$$  \(3.7\)

where $\bar{u}$ is the deviation variable, $\bar{e}$ is the error, $k_c$ represents the proportional gain, $\tau_I$ is the integral time constant and $\tau_D$ is the derivative time constant. The proportional gain stabilizes how sensitive is the controller to intrinsic errors of the system. The integral time constant or reset time recognizes the persistence of an error; thus, it permits a quick error elimination. Finally, the derivative time constant has the role of judging changes in the error, so if an error persists but does not change the control signal might decrease.
In industrial applications, the information flow might not be continuous, and it is necessary to hold a discrete form of the controller (Romagnoli & Palazoglu, 2005). For this reason it is mandatory to discretize the PID controller for deployment. Eq. (3.8) presents the velocity form of the PID algorithm, which offers advantages such as not requiring initialization, not being influenced by previous states, and focusing on immediate changes.

\[ u_i = u_{i-1} + k_p \cdot (e_i - e_{i-1}) + k_i \cdot \Delta t_\beta \cdot e_i + \frac{k_d}{\Delta t_\beta} \cdot (e_i - 2e_{i-1} + e_{i-2}) \]  

(3.8)

Similarly, in the velocity form each term represents the contribution of the individual control actions. For each control time interval \((\Delta t_\beta)\), the error between the measured or estimated value and its set point is represented by \(e\). The controller parameters \(k_p\), \(k_i\), and \(k_d\) are the proportional, integral and derivative gains.

For weight-average molecular weight control, the velocity form exhibits two main advantages. First, it contains provisions for anti-reset windup because the summation of errors is not explicitly computed and it could be high for \(M_w\) because the time constants of the process are larger than the response. Second, the initialization of the output is not needed permitting to straightforwardly switch from automatic to manual operation. This requirement is particularly important in this application because the ACOMP system requires \(~20\) minutes before measurements can be considered reliable due to disturbances (bubbles in the system).

In our practice, the tuning of the PID controller requires the use of a closed loop computational experiment which emulates real behavior and permits to tune properly the controller response. In summary, the principal aim of the strategy is to achieve a good tradeoff between the
control action (manipulated variables) and the control objective (controlled variable) towards the Smart Manufacturing of polymers.

### 3.4 References


4 NONLINEAR STATE ESTIMATION IN POLYMERIZATION

4.1 Introduction

During the operation of a chemical reactor, the complete state vector, which exerts direct impact on the final product properties, is seldom measured, and usually the number of observations is lower than the number of states (Leu & Baratti, 2000). Even if measurements are economically available for the system, they are often inaccurate or contaminated by noise. In this context, state estimation strategies can suffice the lack of genuine measurements that permit a complete reconstruction of the states (Romagnoli & Sanchez, 1999; Simon, 2006). A well-adjusted combination of both experimental measurements and mathematical models allow a better understanding of the system dynamics. In this sense, developed more than half a century ago, the Kalman filter (KF) (Kalman, 1960; Kalman & Bucy, 1961) provides an elegant basis for incorporating both the available experimental data and the mechanistic model of the process of interest (Qin, 2014). The KF addresses the problem of estimating states of a discrete-time controlled process governed by a linear stochastic difference equation. Assumptions on linearity of measurements and transitions are crucial for its correctness (Simon, 2006). However, due to the complex nature of mechanistic polymerization models, the estimation problem requires to be compatible with nonlinear systems. When this is the case, the extended Kalman filter (EKF) is one the most broadly utilized state estimation technique and has proven applicability in chemical processes (Hashemi et al., 2016).

Main purposes when implementing state observers embrace noise reduction for improving the control action, and the online estimation of polymer properties such as the molecular weight distribution, the weight-average molecular weight, and the number-average molecular weight. In
polymer synthesis, many authors have studied a variety of state estimation strategies. For example, Kozub & MacGregor (1992) considered different EKF configurations for semi-batch polymerizations. Ellis et al. (1994) implemented a molecular weight distribution estimator for the methyl-methacrylate system using measurements from the gel permeation chromatography (GPC) for experimental testing. Tatiraju & Soroush (1997) compared the performance of an EKF with a nonlinear observer for the methyl-methacrylate system in a continuous reactor. Gentic et al. (1999) proposed an optimal policy formulation integrated with a geometric controller and an EKF for a batch emulsion-polymerization reactor. Li et al. (2004) proposed a framework for online state estimation and parameter estimation. In addition, statistical methods such as the particle filter have achieved a robust performance in nonlinear state estimation (Hashemi et al., 2016). Due to the difficulty of measuring the internal reactor contents, other authors included the management of delayed and infrequent measurements (Galdeano et al., 2011; Gopalakrishnan, 2011). Finally, Beyer et al. (2008) presented a combined structure for control and state estimation using a sigma-point KF for improving the control action in a Chylla-Haase polymerization reactor.

The geometric observer (GO) initially proposed by Alvarez (2000) has proven applicability in chemical processes of nonlinear nature. The GO holds a robust local convergence, simple implementation due to its systematic construction procedure, and the possibility of different architectures (Tronci et al., 2005; Alvarez & Fernández, 2009; Fernández et al., 2012). In addition, the GO offers simple tuning guidelines and implementation, considering that performance depends on the nonlinear model and the observer structure rather than the algorithm (Porru & Özkan, 2017). As a first step towards the development of adjustable structures for robust state estimation in polymerization processes, López & Alvarez (2004) proposed and evaluated a GO for an exothermic free-radical continuous solution copolymerization. This work considered simple
measurements, and different structures were assessed. The best structure was implemented to estimate relevant unmeasured properties.

As previously explained, the majority of authors who address online estimation problems have focused on the development of strategies for reconstructing the state vector rather than the estimation of the kinetic parameters of the fundamental model. Typically, the kinetic parameters of a polymerization model require to be estimated before the model can be utilized. The maximum likelihood or least squares are common criteria that seeks to fit a semi-empirical or fundamental model using the available experimental data as explained previously in Chapter 2. Nevertheless, this fitting strategies do not consider that parameters might change along the reaction due to changes into the process that can bring uncertainties and disturbances including feedstock material impurities, experimental errors, and even changing environmental conditions. In this context, some authors have studied the implementation of nonlinear observers for parameter estimation, which are able to predict polymer properties while estimating the kinetic parameters of the polymerization. The first work on this matter corresponds to Sirohi & Choi (1996). An extended Kalman (EKF) filter was implemented to estimate kinetic parameters and heat transfer coefficients using a computational experiment. In addition, for estimating simultaneously state variables and parameters, Li et al. (2004) implemented an EKF for a continuous ethylene-propylene-diene polymerization system. Chen et al. (2005) studied a particle filtering strategy for a batch polymerization. Finally, Sheibat-Othman et al. (2008) performed a comparison among different online parameter estimation strategies including the minimization based approach, EKF, high gain, and adaptive observer. The results were evaluated qualitatively for the solution homopolymerization of acrylic acid using measurements from infrared spectroscopy. All mentioned methods require an adjoin model, or to rely on explicit knowledge of the parameters.
dependence, which implies that the mathematical model must be computable and know by the estimation algorithm (e.g., the EKF requires the Jacobian of the dynamics). In addition, initial information on the parameters is required; otherwise, the algorithm fails to converge.

4.2 The hybrid discrete-time extended Kalman filter

A particular configuration of the EKF is the discrete-time extended Kalman filter (DEKF) as explained by Simon (2006). This state estimation algorithm combines the nonlinear model and its linearization to compute state estimates. A hybrid variation of the discrete-time extended Kalman filter (h-DEKF) was formulated using a novel auto-tuned procedure based on searching model errors with a stochastic global optimization technique.

A model represented in a discrete compact form is considered for the formulation of the estimation problem:

\[
\begin{align*}
x_k &= f_{k-1}(x_{k-1}, u_{k-1}, w_{k-1}) \quad w_k \sim N[0, Q] \\
y_k &= h_k(x_k, v_k) \quad v_k \sim N[0, R]
\end{align*}
\] (4.1)

where, \( k \) is the discrete time, \( x \) represents the state vector, \( u \) denotes the manipulated variables vector, \( y \) is the measurements vector, and \( f(\cdot) \) and \( h(\cdot) \) are the nonlinear model and measurements, respectively. It is assumed that the model and the measurements have uncorrelated, zero mean and white Gaussian noise, \( w \) and \( v \), with covariance error \( Q \) and \( R \), respectively. The h-DEKF is purely recursive and initializes after reaching a threshold iteration \( (k_{\alpha}) \), defined by the initialization time,

\[ t_\alpha = (k_\alpha + 1) \Delta t_\alpha. \]

*First step for \( k < k_{\alpha} \): Model Initialization*, the model from Eq. (4.1) initializes with \( x_0 \), and the available initial measured control variables \( u_0 \).
Second step for \(k = k_a\): h-DEKF Initialization, the filter free-parameters are set based on model and measurement errors. Thus, matrix \(R\) contains the diagonal of the observations error vector \((\sigma_v^2)\), \(Q\) the diagonal of the model error vector \((\sigma_w^2)\) which is defined as the product between the current states and its relative errors \((\sigma_w = x_{k_a}e_w)\). The initial covariance error matrix \(P_0\) is the product of \(Q\) and an arbitrary constant.

Third step for \(k > k_a\): h-DEKF, the superscripts “+” and “−” denote a priori and a posteriori states, respectively. A priori refers when the calculation is done before \(y_k\) is considered, and a posteriori after \(y_k\) is considered. The following occurs:

- Derive the Jacobian matrix of partial derivatives for the nonlinear model, linearize it around its previous a posteriori estimate and approximate it into a discrete-time approach (Hashemi & Engell, 2016).

\[
F_{k-1} = \exp\left(\frac{\partial f}{\partial x}\bigg|_{\hat{x}_{k-1}^+} \cdot \Delta t_a\right)
\]  
(4.3)

- Calculate the time update of the a priori estimates and covariance error matrix.

\[
\hat{x}_{k}^- = f_{k-1}(\hat{x}_{k-1}^+, u_{k-1}, 0)
\]  
(4.4)

\[
P_{k}^- = F_{k-1} P_{k-1}^+ F_{k-1}^T + Q
\]  
(4.5)

- Compute the Jacobian matrix of partial derivatives for the measurements and linearize it around its current a priori states.

\[
H_k = \frac{\partial h_k}{\partial x}\bigg|_{\hat{x}_k^-}
\]  
(4.6)

- Calculate the measurement update (using the nonlinear model) of the estimates and the a posteriori covariance error matrix. The Kalman gain matrix \((K)\) computes the amount of correction to incorporate or take from the states on their a priori estimation, and the
stability of the $h$-DEKF is evaluated through the eigenvalues of the estimation error dynamics ($F - KH$) (Bonniwell, 2015).

\[
K_k = P_k^- H_k^T (H_k P_k^- H_k^T + R)^{-1}
\]

\[
\hat{x}_k^+ = \hat{x}_k^- + K_k [ y_k - h_k(\hat{x}_k^-, 0) ]
\]

\[
P_k^+ = (I - K_k H_k) P_k^-
\]

The nonlinear model integration in real-time for computing the state estimates, and its linear approximation for calculating the covariance error matrix and filter gain provides robustness in the nonlinear state estimation. The advantages of the $h$-DEKF encompass the nature of estimation and its predictive-corrective ability. The recursive characteristic allows rapid estimation in real-time operations, which is mandatory for online deployment. However, a disadvantage is that it lacks the ability of taking into account bounds on process variables and other related constraints (Haseltine & Rawlings, 2005).

To improve the filter action, an adequate tuning of its free-parameters is required. The tuning problem addresses the search of model errors ($e_w$) that minimize the squared difference between estimated and noise-reduced measurements ($\tilde{y}_k$) depending on the measurement covariance error matrix. In general, the tuning procedure follows a systematic methodology considering measurement errors (Leu & Baratti, 2000). The tuning cost function, introduced in Eq. (10), aims to minimize the errors between estimated and noised-reduced measured properties. In addition, to avoid unreal kinetics and unstable behavior, the problem is constrained to only positive values of the $a$ posteriori estimates as mentioned in Eq. (4.11a).

\[
\min \sum_{k=1}^{k} [\tilde{y}_k - h_k(e_w)] R^{-1} [\tilde{y}_k - h_k(e_w)]^T
\]
Constrained to:

\[ 0 < \xi_k^+ \quad (4.11a) \]
\[ 0 \leq e_w \leq 0.08 \quad (4.11b) \]

The algorithm to tune the \( h \)-DEKF (by searching optimal \( e_w \)) is the Parallel Local Metric Stochastic Radial Basis Function with Restart (ParLMSRBF-R) algorithm developed by Regis & Shoemaker (2007; 2009), following the implementation criteria from Salas et al. (2017).

The algorithm uses a surrogate model, e.g. radial basis function, and evaluates multiple points simultaneously (in parallel). When no improvement is confirmed, the algorithm restarts to avoid being trapped in local optima. In summary, the algorithm follows a master-worker criterion, assuming that \( \gamma \) processors are available and two function evaluations consume the same computational time. A set of initial points are generated by a space filling (or other similar) technique to evaluate a previously defined cost function. The surrogate model is initially fitted and then updated using the output(s) from each iteration. The ParLMSRBF-R performs exploitation on the solution domain by keeping track of the consecutive failed \( C_{\text{fail}} \), and successful \( C_{\text{success}} \), iterations. When \( C_{\text{fail}} \) or \( C_{\text{success}} \) exceed a predefined tolerance value, the step size is reduced by half or doubled, respectively. Later, the modified values of \( C_{\text{fail}} \) and \( C_{\text{success}} \) are reset to their initial values.

Figure 4.1 sketches the functionality of the ParLMSRBF-R algorithm and the interaction of its different components, including the interaction with the nonlinear model and \( h \)-DEKF for computing the cost function. Table 4.1 lists the ParLMSRBF-R algorithm parameters employed for tuning of the \( h \)-DEKF.
Figure 4.1. Schematic representation of the ParLMSRBF-R algorithm.

Table 4.1. Parameter values for ParLMSRBF-R for global optimization

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Omega_n$, number of candidate points for each parallel iteration.</td>
<td>500 $d$</td>
</tr>
<tr>
<td>$Y$, weight pattern.</td>
<td>$\langle 0.3, 0.5, 0.8, 0.95 \rangle$</td>
</tr>
<tr>
<td>$\kappa$, number of weights in $Y$.</td>
<td>4</td>
</tr>
<tr>
<td>$\sigma_n$, initial step size.</td>
<td>0.2 $\ell(\Omega)$</td>
</tr>
<tr>
<td>$\sigma_{min}$, minimum step size.</td>
<td>$(0.1) \left( \frac{1}{2} \right)^6 \ell(\Omega)$</td>
</tr>
<tr>
<td>$\delta_{tol}$, radius tolerance.</td>
<td>0.001 $\ell(\Omega)$</td>
</tr>
<tr>
<td>$\mathcal{T}_{success}$, threshold parameter for deciding when to</td>
<td>3</td>
</tr>
<tr>
<td>increase the step size.</td>
<td></td>
</tr>
<tr>
<td>$\mathcal{T}_{fail}$, tolerance parameter for deciding when to reduce</td>
<td>max $\left( \left[ \frac{d}{P} \right], \left[ \frac{</td>
</tr>
<tr>
<td>the step size.</td>
<td></td>
</tr>
<tr>
<td>$\mathcal{M}_{fail}$, maximum failure tolerance parameter.</td>
<td>5 $\mathcal{T}_{fail}$</td>
</tr>
</tbody>
</table>
4.3 The geometric observer

4.3.1 Observability and detectability

The effectiveness of the nonlinear geometric observer depends on basic properties of the system such as, the observability and detectability.

It is recognized that observability and detectability are fundamental notions in system analysis (Dragan et al., 2010). In general, observability refers to the measure of how well the internal states of a system can be inferred from the available external knowledge (outputs or observations). Therefore, a system is supposed to be observable if the current states of the underlying dynamic model can be determined in finite time by using only the outputs of the system. On the other hand, a system is not observable when the values of some of its state variables cannot be determined through observations. Detectability is a feebler concept than observability because it describes the fact that all unobservable states are asymptotically stable (Damm, 2007).

For the formulation, a model represented in a continuous compact form considers a nonlinear dynamic system where \( x \in \mathbb{R}^n \) is the state vector which is \( x_0 \) at initial time \( (t_0) \), \( u \in \mathbb{R}^q \) is the input vector (controlled variables), \( y \in \mathbb{R}^m \) is the output, \( f \) is the \( n \)-dimensional vector function and \( h \) is the \( m \)-dimensional nonlinear vector relating the outputs and the states.

\[
\dot{x} = f(x, u), \quad x(t_0) = x_0 \tag{4.12}
\]

\[
y = h(x) \tag{4.13}
\]

Consider the nonlinear map proposed by Alvarez & Fernández (2009) \( \phi(x, u) \) denoted in Eq. (4.14a-b).

\[
\phi(x, u) = [\phi_1, \phi_2, \ldots, \phi_m]^T \tag{4.14a}
\]
\[ \phi_i = (h_i, L_f^1 h_i, \ldots, L_f^{\kappa-1} h_i) \quad (4.14b) \]

where, the term \( L_f^j h_i \) is the recursive \( j^{th} \) Lie derivative of the time varying scalar field \( h_i \) along the vector \( f \), \( \kappa_i \) is the observability index of the \( i^{th} \) output, and \( \kappa \) is the estimator order. In Alvarez & Fernández (2009), it is stated that the motion of \( x \) is robustly exponentially observable if there exist \( m \) observability indexes \( \kappa_i \) (see Eq. (4.15)) such that the map \( \phi(x, u) \) is robustly invertible with respect to \( x \).

\[ \kappa_1 + \kappa_2 + \cdots + \kappa_m = \kappa = n \quad (4.15) \]

Ill-conditioning of the observability matrix implies the possibility that the observer gains could become large because of the low sensitivity of the outputs and their derivatives with respect to the states. In this case, the presence of measurement errors can seriously affect the estimator performance. Robust observability can be obtained maximizing the minimum singular value (\( \sigma \)) of the exponential observability matrix (\( \Omega \)), which seeks to satisfy the condition in Eq. (4.16b). The threshold value \( \varepsilon_0 \) is tuned by simulation, and it depends on the intensity of the measurement noise (Porru & Özkan, 2017). It is worth to notice that only local observability can be assessed because the matrix \( \Omega(x, u) \) is state dependent. In this work, the observability matrix was calculated for different trajectories, and an average \( \sigma \) value for a given trajectory has been considered.

\[ \text{rank}(\Omega(x, u)) = \text{rank}(\partial_x \phi(x, u)) = n \quad (4.16a) \]

\[ \text{avg} \sigma(t) \geq \varepsilon_0 \quad (4.16b) \]

If the conditions on observability hold, it is possible to reconstruct at each time the unmeasured states of the system \( x \), through the measured signals (\( y \) and \( u \)) and their time
derivatives. However, matrix $\mathbf{\Omega}(x,u)$ might be ill-conditioned, and, in this case, a full-order observer might be detrimental in practice.

If the condition does not hold and the rank of the observability matrix is $\kappa < n$, there are unobservable states and the system is RE-estimable if the unobservable motions are stable (Alvarez, 2000). In this case, it is possible to make a distinction between distinguishable ($x_i$) and undistinguishable states ($x_u$), with $x = [x_i, x_u]^T$.

### 4.3.2 Full-order geometric observer

The proposed nonlinear observer reconstructs the polymerization dynamics based on the geometric observer developed by Alvarez (2000). The observer is reported in Eq. (4.17a) for innovated and in Eq. (4.17b) for non-innovated states.

$$\dot{x}_i = \dot{f}_i(\hat{x},u) + (\partial_x \Phi(x,u))^{-1} K(y - h(\hat{x})) \quad (4.17a)$$

$$\dot{x}_u = \dot{f}_u(\hat{x},u) \quad (4.17b)$$

where, the inverse of the Jacobian of matrix $\Phi$ is evaluated, at each time step and $K$ is a block diagonal matrix.

$$K = \begin{pmatrix} B_1 & 0 & \cdots & 0 \\ 0 & B_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & B_m \end{pmatrix}, \quad B_1 = \begin{bmatrix} k_{11} \\ \vdots \\ k_{1v_1} \end{bmatrix}, \quad B_2 = \begin{bmatrix} k_{21} \\ \vdots \\ k_{2v_2} \end{bmatrix}, \quad B_m = \begin{bmatrix} k_{m1} \\ \vdots \\ k_{mv_m} \end{bmatrix} \quad (4.17c)$$

and $v_i = \kappa_{i-1}$

The gain $k_{i,j}$ is set in such a way that the error dynamics remain stable through the whole process (Alvarez, 2000). Tuning guidelines are provided in the work of Lopez & Alvarez (2004) and Porru & Özkan (2017), showing that a set of tuning parameters $k_{i,j}$ is required for every
measurement $i$. For observability indexes equal to 1 or 2 ($\kappa_i = 1, 2$), the proportional gains can be obtained following the guidelines from Eq. (4.18a-b).

\[
\begin{align*}
  k_{i1} &= 2\zeta \omega_0, & k_{i2} &= \omega_0^2 \\
  \omega_0 &\in [10\omega_c, 30\omega_c], & \zeta &= [1, 3] 
\end{align*}
\]

(4.18a) (4.18b)

where, $\omega_c$ is the characteristic frequency of the system (Alvarez, 2000). The inverse of the estimated run time has been proposed as an approximation of the characteristic frequency of the system by Porru & Özkan (2017).

### 4.3.3 The iLU geometric observer for parameter estimation

For the reconstruction of kinetic parameters, consider the geometric observer for parameter estimation in Eq. (4.19). The GO for parameter estimation follows a similar idea of the GO for state estimation, with the difference that instead of reconstructing states, it estimates parameters.

\[
\dot{\hat{z}} = \dot{\hat{z}} + \Omega_{\hat{z}}(\hat{x}, \hat{z})^{-1}K_{\hat{z}}(y_{\hat{z}} - h_{\hat{z}}(\hat{x}, \hat{z})) 
\]

(4.19)

where, $z \in \mathbb{R}^p$ is the vector of important kinetic parameters (to be estimated), $K_{\hat{z}}$ is a block diagonal matrix (similar to Eq. (4.17c)), and the exponential observability matrix ($\Omega_{\hat{z}}$) that aims to reconstruct parameters is obtained by defining a nonlinear map that updates the motion of $\hat{z}$ as depicted in Eq. (4.20).

\[
\Omega(x, z) = \frac{\partial \phi(x, z)}{\partial z} 
\]

(4.20)

Further, to overcome stability limitations, an incomplete LU factorization strategy is implemented (Saad, 2003) as a preconditioning technique to stabilize the observability matrix by reducing the condition number ($\tilde{\sigma}/\sigma$). The incomplete LU decomposition of the exponential
observability matrix gives a lower triangular ($L$), upper triangular ($U$) and a residual ($\mathcal{R}$) matrix as presented in Eq. (4.21a). The stability condition is foreseen when all the elements of the diagonal (or pivot) of the matrix $U$ are different from zero (Dopico et al., 2006), evidencing the absence of a singular matrix. The iLU GO is formulated and introduced in Eq. (4.21b).

$$\Omega(x, z) = LU + \mathcal{R}$$  \hspace{1cm} (4.21a)

$$\dot{\hat{z}} = \hat{z} + (L \Omega(\bar{x}, \bar{z})^{-1} U) K_{LU}(y_{z} - h_{z}(\bar{x}, \bar{z}))$$ \hspace{1cm} (4.21b)

### 4.4 Data-driven parameter estimation

Another method for online parameter estimation is the retrospective cost model refinement (RCMR) algorithm (Goel et al., 2016; Goel & Bernstein, 2018a; Goel & Bernstein, 2018b). This method is data-driven, and it does not require knowledge on the nonlinear model or the initial values of the estimated parameters. For polymerization processes, the method requires to be adapted in separate channels that estimate each parameter independently.

#### 4.4.1 Estimation problem

A polymerization model of interest can be written in compact discrete-time form as portrayed in Eq. (4.22).

$$\begin{cases} x_{k+1} = f(x_k, u_k, z) + v_k \\ y_k = h(x_k, u_k, z) + w_k \end{cases}$$ \hspace{1cm} (4.22)

where, $x \in \mathbb{R}^{l_x}$ is the state vector, $u \in \mathbb{R}^{l_u}$ is the vector of inputs, $z \in \mathbb{R}^{l_z}$ is the unknown parameter vector, $y \in \mathbb{R}^{l_y}$ is the vector of measurements, $v \in \mathbb{R}^{l_x}$ and $w \in \mathbb{R}^{l_y}$ are the model and measurement errors, respectively.
For estimation purposes, the compact model is considered as in Eq. (4.23).

\[
\begin{align*}
\tilde{x}_{k+1} &= f(\tilde{x}_k, u_k, \tilde{z}) + \nu_k \\
\tilde{y}_k &= h(\tilde{x}_k, u_k, \tilde{z}) + w_k 
\end{align*}
\] (4.23)

where, \( \tilde{x} \) is the estimated state vector, \( \tilde{y} \) is the vector of estimated measurements, and \( \tilde{z} \) is the output of the parameter estimator. The parameter estimator is updated by minimizing a cost function based on the performance variable (\( e \)).

Considering an ARMA model with a built-in integrator, \( \tilde{z} \) is given by:

\[
\tilde{z}_k = \sum_{l=1}^{n_c} P_{lk} \tilde{z}_{k-1} + \sum_{i=1}^{n_c} Q_{ik} e_{k-l} + R_k g_k 
\] (4.24)

where,

\[
g_k = g_{k-1} + e_{k-1}, e_k = \tilde{y}_k - y_k 
\] (4.25)

and \( P \in \mathbb{R}^{l_z \times l_z}, Q_i, R \in \mathbb{R}^{l_z \times l_y} \) are the coefficient matrices that are updated recursively by the algorithm. The integrator is combined with the estimator to guarantee that the performance variable approaches to zero as the iterations approach to infinity. Rewriting Eq. (4.25), the following is obtained:

\[
\tilde{z}_k = \Phi_k \theta_k 
\] (4.26)

where,

\[
\Phi_k = I_{l_z} \otimes \phi_k^T \in \mathbb{R}^{l_z \times l_\theta}, \\
\phi_k = [\tilde{z}_{k-1}^T \ldots \tilde{z}_{k-n_c}^T e_{k-1}^T \ldots e_{k-n_c}^T g_k^T]^T
\] (4.27a)

and

\[
\phi_k = [\tilde{z}_{k-1}^T \ldots \tilde{z}_{k-n_c}^T e_{k-1}^T \ldots e_{k-n_c}^T g_k^T]^T
\] (4.27b)
\[ \mathbf{\theta}_k = \text{vec} \left[ \mathbf{P}_{1k} \ldots \mathbf{P}_{n_c k} \mathbf{Q}_{1k} \ldots \mathbf{Q}_{n_c k} \mathbf{R}_k \right] \in \mathbb{R}^{l\theta}, \] (4.27c)

\[ l_\theta = l_z^2 n_c + l_z l_y (n_c + 1). \] (4.27d)

and, \( \Phi \) is the regressor matrix, \( \mathbf{\theta} \) contains the estimator coefficients computed by the RCMR algorithm. The operator “\( \otimes \)” is the Kronecker product, and \( \text{vec} \) represents the column-stacking operator.

It is assumed that \( z \) is identifiable, and that the input signal \( u_k \) is persistently exciting.

### 4.4.2 Retrospective cost model refinement (RCMR) algorithm

The retrospective performance variable is defined as follows:

\[ \hat{e}_k = e_k - G_f(q) \left( \Phi_k \hat{\mathbf{\theta}} - \hat{z}_k \right) \] (4.28)

where, \( q \) is the forward-shift operator, and \( \hat{\mathbf{\theta}} \) has the parameter estimation coefficients to be optimized.

\[ G_f(q) = \sum_{i=1}^{n_f} \frac{N_i}{q^i} \] (4.29)

For all \( i, N_i \in \mathbb{R}^{l_y \times l_z} \). \( G_f \) is a finite impulse response filter of order \( n_f \). Eq. (4.28) is then rewritten as follows:

\[ \hat{e}_k = e_k + N \Phi_{b_k} \hat{\mathbf{\theta}} - NZ_{b_k} \] (4.30a)

where,

\[ N = \begin{bmatrix} N_1 \ldots N_{n_f} \end{bmatrix} \in \mathbb{R}^{l_y \times l_z n_f}, \] (4.30b)

64
\[
\Phi_{b_k} = \begin{bmatrix} \phi_{k-1} \\ \vdots \\ \phi_{k-n_f} \end{bmatrix} \in \mathbb{R}^{l_k n_f \times l_0}, \quad (4.30c)
\]

\[
Z_{b_k} = \begin{bmatrix} \hat{z}_{k-1} \\ \vdots \\ \hat{z}_{k-n_f} \end{bmatrix} \in \mathbb{R}^{l_k n_f}. \quad (4.30d)
\]

The retrospective cost function, defined by Goel & Bernstein (2018a; 2018b) is minimized by making use of recursive least squares.

Let \( P_0 = R_\theta^{-1} \) and \( \theta_k = 0 \), the algorithm that updates the estimator coefficients is as follows:

\[
\theta_k = \theta_{k-1} - P_k \Phi_{b_{k-1}}^T N_k R_{e_{k-1}} (N \Phi_{b_{k-1}} \theta_{k-1} + e_{k-1} - N Z_{b_{k-1}})
\]

\[
P_k = \lambda^{-1} P_{k-1} - \lambda^{-1} P_{k-1} \Phi_{b_{k-1}}^T N_k \Gamma_k^{-1} N \Phi_{b_{k-1}} P_{k-1}
\]

\[
\Gamma_k = \lambda R_{e_{k-1}}^{-1} + N \Phi_{b_{k-1}} P_{k-1} \Phi_{b_{k-1}}^T N_k
\]

where, \( R_e \) and \( R_\theta \) are positive-definite matrices, and \( \lambda \leq 1 \) is the forgetting factor.

Figure 4.2 portrays the architecture of the proposed data-driven parameter estimation strategy. The experimental unit generates measurements \( y \), which are assumed to be driven by the inputs \( u \). The data-driven adaptive estimator consists of the nonlinear estimation model, which is also driven by the inputs \( u \), and the RCMR algorithm. Although the nonlinear estimation model is required to generate the estimated measurements \( \hat{y} \), it does not provide knowledge for the parameter updates. The estimated parameter \( \hat{z} \) is updated by the estimator, which seeks the minimization of the error signal \( e \).
Figure 4.2. Data-driven parameter estimation architecture.

4.5 References


5 FRAMEWORK DESIGN FOR THE SMART MANUFACTURING OF POLYMERS

5.1 Introduction

The concept of frameworks for the smart manufacturing of materials and goods is a relatively new concept which faces different challenges depending on the particular industrial application where these frameworks are employed. By integrating process data and high-fidelity models for decision support in real-time, better operating choices can be made along the production line. However, complete enterprise integration and analytical or technological tools might entail high investment and capital expenditures. Thus, smart manufacturing addresses the challenge of prevalent adoption of cost-effective infrastructure (smart sensors, soft sensors and software) across the entire production facility (Davis et al., 2012). Therefore, optimization is always and an ongoing task. Strategies such as a cloud-based workflow environment with customizable templates that collects, processes and analyses data for later distribution of outputs represents an innovative step towards integration (Korambath et al., 2014).

For chemical industry applications, the development of platforms can lower the cost of various operational and design expenditures including the information technology (IT) infrastructure, sensors selection, modelling and simulation deployment, which translates in a more efficient and economical operation. Kumar et al. (2015) proposed a smart manufacturing approach for tackling operation issues of industrial steam-methane reformers. In their approach, two key elements marked a difference. First, the inclusion of advanced temperature sensors and soft sensors to provide better observations of the internal parts of the furnace (reactor). Second, a rigorous model capable of precisely describing temperature profiles, which in combination with the first managed a better furnace balancing. The combination of a virtual factory and the real factory
besides acquainting redundancy, it improves the managerial decision-making process and the overall control of the facility. In addition, Li (2016) proposed a plan for smart factory in petrochemical industry projecting a complete integration by 2025, in which production and management are embedded, design and operation blended, and the whole supply chain projects to a cross-organization interaction. The whole integration concept takes participation in the global market. Therefore, various factors seem to be critical in advance manufacturing including not only the availability of smart sensors and the mechanistic model of the process, but also their integration, architecture, robustness and efficiency.

The integration of smart sensors, nonlinear models and state estimation techniques are part of the scope of Smart Manufacturing frameworks for polymer synthesis (Salas et al., 2017). A shortcoming of using advanced operating and control strategies in polymerization is mainly due to the unavailability of sensors capable of determining online process status. However, with the advent of the Automatic Continuous Online Monitoring of polymerization reactions (ACOMP) the gap towards the integration of monitoring, control and optimization tools for complex industrial polymerizations is being reduced (Alb et al., 2008). A trustworthy structure combining real-time measurements from the ACOMP system, advanced modelling and control principles (including nonlinear state estimation and parameter estimation) is of imperative necessity since it can accomplish unprecedented results during polymer synthesis. The ultimate goal, a self-contained intelligent system for the advanced operation of polymerization processes, foresees the combination and interaction of both state-of-the-art sensors and a software environment exchanging information seamlessly towards achieving high-quality target final products.
5.2 Integrated model-centric framework for polymer synthesis

The concept behind model-centric frameworks which integrate nonlinear modelling, parameter estimation, dynamic optimization and feedback control is illustrated in Figure 5.1. In this case, the chosen simulation environment is the gPROMS modelling platform, which provides a complete set of tools for analysis and modelling of complex and high nonlinear systems. Among gPROMS, the following benefits are evinced:

a) Computational efficiency and robustness;

b) Multi-tasking with a solely model;

c) Integrated dynamic and steady state simulation;

d) Parameter estimation capability;

e) Newfangled optimization tools, and

f) Information architecture for advanced process control applications.

First steps engage the parameter estimation tool (gEST) and the available experimental data. The mentioned tool has the ability of estimating an unlimited number of parameters while revealing different variance models between variables and sets of experimental data (different experimental runs). In addition and once the model is reliable (after parameter estimation), the optimization tool generates favorable operating conditions such that desired final properties or characteristics are achieved. This platform is flexible and capable of considering a continuous, semi-batch and batch operation for the generation of operating conditions as recipes. On top of the computational tools, another key aspect is connectivity. Indeed, the connectivity/communication
between the software platform and the sensor (the ACOMP system) underlies integration. In this particular application, the software gPROMS needs to be initiated from an external application and data will travel back and forth. Here, a useful strategy can be the gSERVER API, which transforms the ultimate application into a so-called gPROMS-based Application, or gBA or as an alternative via gO: RUN-xml (Ghadipasha et al., 2016).

**Figure 5.1.** Schematic of the integrated simulation, parameter estimation, and optimization for polymeric systems.

However, a more efficient integrated framework is possible when taking into account the advantages of other available modelling packages and tools, including open source environments and computational tools with a vast library. As discussed before, a framework for the smart manufacturing of polymers should embrace a validated/reliable nonlinear model of interest, optimal policies, nonlinear state estimation, feedback control and enhanced monitoring, all integrated and with seamless communications. The final aim is to achieve full polymer
characterization and subsequent enhanced monitoring while improving the control action in order to achieve target properties, including the MWD or average properties.

Figure 5.2 introduces a model-based framework for the smart manufacturing of polymers. Different components including experimental equipment, monitoring system, online and offline computational tools are embraced under a unified structure. Preliminary tasks include the generation of optimal recipes by minimizing a multi-objective dynamic optimization problem (as already introduced in Chapter 2), assessment and tuning of the selected state estimation strategy (from the proposed strategies in Chapter 4 or any other preferred technique), selection and implementation of feedback control, and finally testing running real-time experiments for the correspondent validations.

![Diagram of framework design for the smart manufacturing of polymers. Integration between experimental apparatus and computational in/offline tools.](image)

**Figure 5.2.** Framework design for the smart manufacturing of polymers. Integration between experimental apparatus and computational in/offline tools.
Once the experiment starts, the nonlinear model computes states until the nonlinear estimation and controller initialize. From our practice, the ACOMP system requires around 15-20 minutes to provide stable observations; thus, sufficient time is necessary to let the sensor settle down. However, in other applications it is required to give only a few seconds (or iterations) before initialization. Once the nonlinear state estimator is activated, estimated states from the nonlinear filter u observer are available and the control action starts. Finally, at the end of each experiment, a sample of the final product is taken to measure relevant polymer properties. This measurements cannot be accomplished during regular operation because they require some time (between 20 to 30 minutes) for providing results.

5.3 Module development, implementation and functionality

A tailor-made module is implemented for signal processing, enhanced monitoring and feedback control in Python 2.7 environment. Python is selected because it allows full connectivity with the ACOMP server guaranteeing seamless communications. The code in the background follows an object oriented architecture, where a graphic user interphase (GUI) permits a continuous monitoring of properties and to easily adjust the controller parameters and estimator parameters. In addition, the module keeps track of the measurements and when a measured value is not sensed, its previous iteration remains as the current measurement to help continuity and robustness of the systems in terms of error rejection. This particular feature seemed to be very useful since during polyacrylamide synthesis experiments (refer to Chapter 6) it is tedious to restart experiments that last for around 5-6 hours from preparation to disassembly.

Figure 5.3 explains the functionality of the tailor made module. As portrayed in the information flow diagram, the module is built in a cascade assembly because this architecture
improves the resolution of the filter/observer signal. A good resolution is of interest as it assures an adequate control action since the signal has been corrected more recurrently than the control action occurs. The filter remains in the inner loop at a higher frequency, and the control action is allocated in the outer loop at a lower frequency. The ACOMP system updates measurements every 1 sec; thus, the relation $1\;sec < \Delta t_\alpha < \Delta t_\beta$ must occur for a satisfactory operation of the module. Here, $\Delta t_\alpha$ represents the estimation time interval and $\Delta t_\beta$ the control action time interval. A time interval of 2.5 minutes is selected for control action (low frequency) in order to overcome the delay time hold by the measurements and the ACOMP system. The proposed module results will be evinced later in Chapter 6.

![Flow diagram of the functionality of the tailor made module.](image)

**Figure 5.3.** Flow diagram of the functionality of the tailor made module.
With the intention of providing a better understanding of deployment for real-time experiments, two additional illustrations are included. First, Figure 5.4 denotes an experimental unit where at the left (in green) a laboratory scale ACOMP system is exhibited. In addition, the two Erlenmeyer flasks correspond to the storage of monomer and initiator in aqueous solution. In the middle, the polymerization reactor with all the instrumentation (condenser, stirrer, thermometer and more) can be found. Moreover, Figure 5.5 shows the in-house GUI (bottom) in which as background the framework from Figure 5.2 runs, and the current monitoring system of the ACOMP system (top).

![Figure 5.4. Experimental apparatus and ACOMP system.](image-url)
Figure 5.5. ACOMP monitoring system and in-house GUI for the smart manufacturing of polymers.
5.4 References


6 CASE STUDY 1: ACRYLAMIDE-WATER-POTASSIUM PERSULFATE SYSTEM

6.1 Mechanistic model

The underlying mechanistic model evaluated in Case Study 1 is the free-radical polymerization of acrylamide using KPS as initiator. The model has the capability of describing the experimental system in a range of conditions and, after experimental validation and kinetic parameter fitting, has adaptability to various applications, e.g., dynamic optimization, nonlinear state estimation and control (Ghadipasha et al., 2016; 2017; Salas et al., 2018). In addition, the model considers the computation of the molecular weight distribution (MWD) in semi-batch following an analogous approach as proposed by Crowley & Choi (1997a; 1997b) where the method of finite molecular weight moments combined with the kinetic rate equations is chosen. The reaction mechanism consists of three main steps including initiation, propagation and termination. Chain transfer to monomer and solvent is incorporated, and the reaction mechanism is explained in Eq. (6.1)-(6.7).

Initiation:

\[ I \xrightarrow{k_d} 2R \]  \hspace{1cm} (6.1)
\[ R + M \xrightarrow{k_i} P_1 \]  \hspace{1cm} (6.2)

Propagation:

\[ P_n + M \xrightarrow{k_p} P_{n+1} \]  \hspace{1cm} (6.3)
Chain transfer to monomer and solvent:

\[ P_n + M \xrightarrow{k_{fm}} D_n + P_1 \]  \hspace{1cm} (6.4)

\[ P_n + S \xrightarrow{k_{fs}} D_n + P_1 \]  \hspace{1cm} (6.5)

Termination:

\[ P_n + P_m \xrightarrow{k_{tc}} D_{n+m} \]  \hspace{1cm} (6.6)

\[ P_n + P_m \xrightarrow{k_{td}} D_n + D_m \]  \hspace{1cm} (6.7)

where, \( I \) corresponds to the initiator, \( R \) represents the primary initiator radical, \( M \) is the monomer, \( S \) is the solvent and \( P_j \) and \( D_j \) are the growing live and dead polymer radical. Under assumptions such as well mixing, quasi steady state and long chain hypothesis, the following set of kinetic and dynamic equations describe the system:

\[
\frac{dN_m}{dt} = - (k_p + k_{fm})P_0N_m + F_mC_{mf} - F_{out}C_m
\]  \hspace{1cm} (6.8)

\[
\frac{dN_i}{dt} = - k_dN_i + F_iC_{if} - F_{out}C_i
\]  \hspace{1cm} (6.9)

\[
\frac{dN_s}{dt} = - k_{fs}N_sP_0 + F_iC_{isf} + F_mC_{smf} - F_{out}C_s
\]  \hspace{1cm} (6.10)

\[
\frac{d(\lambda_0V)}{dt} = (k_{fm}N_m + k_{td}P_0V + k_{fs}N_s)\alpha P_0 + \frac{1}{2}k_{tc}P_0^2V - F_{out}\lambda_0
\]  \hspace{1cm} (6.11)

\[
\frac{d(\lambda_1V)}{dt} = [(k_{fm}N_m + k_{td}P_0V + k_{fs}N_s)(2\alpha - \alpha^2) + k_{tc}P_0V] \frac{P_0}{(1 - \alpha)} - F_{out}\lambda_1
\]  \hspace{1cm} (6.12)

\[
\frac{d(\lambda_2V)}{dt} = [(k_{fm}N_m + k_{td}P_0V + k_{fs}N_s)(\alpha^3 - 3\alpha^2 + 4\alpha) + k_{tc}P_0V(\alpha + 2)] \frac{P_0}{(1 - \alpha)^2} - F_{out}\lambda_2
\]  \hspace{1cm} (6.13)

where,

\[ N_m = C_mV, N_i = C_iV, N_s = C_sV \]
\[
\alpha = \frac{k_p C_m}{k_p C_m + k_{f_m} C_m + k_{f_s} C_s + k_{t_c} P_0 + k_{t_d} P_0}
\]  
(6.14)

\[
P_0 = \sqrt{\frac{2 e_f C_i k_d}{k_{t_c} + k_{t_d}}}
\]  
(6.15)

\[
\rho_s = -0.0031 T^2 - 0.1467 T + 1003
\]  
(6.16)

\[
V = \frac{\lambda_1 V w_m}{\rho_p} + \frac{N_m w_m}{\rho_m} + \frac{N_s w_s}{\rho_s} + \frac{N_i w_i}{\rho_i}
\]  
(6.17)

\(C_m, C_i\) and \(C_s\) are the concentrations of monomer, initiator and solvent in the reactor, respectively. \(V\) represents the volume of the content inside the reactor, \(F_m\) and \(F_i\) are the volumetric flow rates of monomer and initiator respectively that are added into the reactor in semi-batch operation mode. \(F_{\text{out}}\) is the constant flow rate exiting the reactor and needed by the ACOMP system as extraction stream for analysis. \(C_{mf}, C_{if}, C_{sif},\) and \(C_{smf}\) are the concentration of monomer in the monomer feed stream, concentration of initiator in the initiator feed stream and concentration of solvent in the initiator and monomer flow stream, respectively. \(P_0\) represents the total concentration of live polymer considered because of the quasi steady state assumption. \(\lambda_0, \lambda_1,\) and \(\lambda_2\) are the corresponding moments for the dead polymers, \(\alpha\) is the probability of propagation, \(e_f\) is the initiator efficiency and \(\rho_m, \rho_i, \rho_s,\) and \(\rho_p\) are the densities of the monomer, initiator, solvent and polymer which are temperature dependent (except for the polymer that is kept constant). \(k_p, k_d, k_{f_m}, k_{f_s}, k_{t_c},\) and \(k_{t_d}\) are the propagation, initiation, chain transfer to monomer, chain transfer to solvent, termination by combination and termination by disproportionation kinetic rates.

The conversion of the monomer is defined as the number of moles of monomer reacted in the tank divided by the total amount of monomer that has been loaded into the reactor initially \(N_{m0}\) and through the semi-batch flow. The conversion is defined in Eq. (6.18).
\[
X = \frac{N_{m0} + \int_0^t F_m C_{mf} dt - C_m V - \int_0^t F_{out} C_m dt}{N_{m0} + \int_0^t F_m C_{mf} dt}
\]  
(6.18)

The number-average and weight-average molecular weight are computed considering the moment of dead polymers as written in Eq. (6.19) and Eq. (6.20), which is valid for low and medium conversion systems (when live polymer is negligible).

\[
M_n = \frac{w_m \lambda_1 V}{\lambda_0 V}
\]  
(6.19)

\[
M_w = \frac{w_m \lambda_2 V}{\lambda_1 V}
\]  
(6.20)

In this work, 20 chain lengths delimit the chain length intervals presented in Eq. (6.21). Here, \( m \) and \( n \) represent the upper and lower bound of the intervals and are calculated using the arbitrary formula from Crowley & Choi (1997a).

\[
\frac{dg(m,n)}{dt} = \frac{k_p N_m P_0}{\lambda_1 V} \left[ \left( \frac{\alpha + m(1 - \alpha)}{\alpha} \right)^{m-1} - \left( \frac{\alpha + (n + 1)(1 - \alpha)}{\alpha} \right)^{n} \right]
\]  
(6.21)

The kinetic rate constants are temperature dependent and follow an Arrhenius-type relationship (Pinto & Ray, 1995) as explained in Eq. (6.22).

\[
k_{(\cdot)} = A_{(\cdot)} e^{-\frac{E_{a_{(\cdot)}}}{R_{\text{gas}} T}}
\]  
(6.22)

where, \( k_{(\cdot)} \) is the kinetic parameter that follows Arrhenius law, \( A_{(\cdot)} \) is the pre-exponential factor, \( E_{a_{(\cdot)}} \) is the energy of activation and \( R_{\text{gas}} \) is the universal gas constant.

Table 6.1. shows the parameters utilized for the pre-exponential factor, activation energy as well as other relevant thermodynamic properties. In this system, chain transfer to monomer and solvent are negligible, and termination happens only by disproportionation. From these
parameters, the first four \((A_d, A_p, A_p\) and \(e_f\)) are estimated using gEST and following the guidelines from Chapter 2 Section 2.

**Table 6.1.** Kinetic and thermodynamic parameters of the mathematical model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_d)</td>
<td>7.154 \times 10^{12}</td>
<td>min(^{-1})</td>
</tr>
<tr>
<td>(A_p)</td>
<td>4.80 \times 10^{5}</td>
<td>m(^3) mol(^{-1}) min(^{-1})</td>
</tr>
<tr>
<td>(A_{td})</td>
<td>4.08 \times 10^{9}</td>
<td>m(^3) mol(^{-1}) min(^{-1})</td>
</tr>
<tr>
<td>(e_f)</td>
<td>0.196</td>
<td>-</td>
</tr>
<tr>
<td>(E_d)</td>
<td>-101123.182</td>
<td>J mol(^{-1})</td>
</tr>
<tr>
<td>(E_p)</td>
<td>-11700.0</td>
<td>J mol(^{-1})</td>
</tr>
<tr>
<td>(E_{td})</td>
<td>-11700.0</td>
<td>J mol(^{-1})</td>
</tr>
<tr>
<td>(R_{gas})</td>
<td>8.31451</td>
<td>J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>(\rho_i)</td>
<td>2480</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>(\rho_m)</td>
<td>1130</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>(\rho_p)</td>
<td>1302</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>(\rho_s)</td>
<td>Eq. (9)</td>
<td>kg m(^{-3})</td>
</tr>
</tbody>
</table>

The mathematical model is valid when the concentration of \(P_0\) is negligible, which is possible for diluted systems. For this case study, the mixture between reactants and products inside the reactor is in solution, meaning that a low concentration of reactants and products is expected. This operational policy is important in order to avoid the formation of gels and to uphold a safe operation for the pilot plant.

From dynamic optimization (see Chapter 2 Section 4), recipes for three optimal semi-batch experiments corresponding to the increasing, constant, and decreasing \(M_w\) time-evolution are generated to test the operational flexibility of the framework. Figure 6.1 illustrates target MWDs
for the different $M_w$ trajectories, and Table 6.2 provides details on the initial experimental set up as well as the concentration of monomer and initiator in the inlet flows.

![Figure 6.1](image.png)

**Figure 6.1.** Final chain length distribution of optimal trajectories.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Increasing, Constant $M_w$</th>
<th>Decreasing $M_w$</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_m(0)$</td>
<td>0.05</td>
<td>0.1</td>
<td>mol</td>
</tr>
<tr>
<td>$N_s(0)$</td>
<td>30</td>
<td>35</td>
<td>mol</td>
</tr>
<tr>
<td>$N_l(0)$</td>
<td>0.008</td>
<td>0.008</td>
<td>mol</td>
</tr>
<tr>
<td>$\lambda_0 V(0)$</td>
<td>$10^{-6} \times V(0)$</td>
<td>$10^{-6} \times V(0)$</td>
<td>mol</td>
</tr>
<tr>
<td>$\lambda_1 V(0)$</td>
<td>$10^{-6} \times V(0)$</td>
<td>$10^{-6} \times V(0)$</td>
<td>mol</td>
</tr>
<tr>
<td>$\lambda_2 V(0)$</td>
<td>$10^{-6} \times V(0)$</td>
<td>$10^{-6} \times V(0)$</td>
<td>mol</td>
</tr>
<tr>
<td>$C_{if}$</td>
<td>3.70</td>
<td>3.70</td>
<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>$C_{mf}$</td>
<td>1406.87</td>
<td>1406.87</td>
<td>mol m$^{-3}$</td>
</tr>
</tbody>
</table>

**Table 6.2.** Experiment initial conditions for different trajectories.
6.2 Metaheuristic parameter estimation

Pursuing additional improvement and with the help of the metaheuristic algorithms introduced in Chapter 2 Section 3, the aforementioned kinetic parameters $A_d$, $A_p$, $A_p$ and $e_f$ are re-estimated using additional experimental data from semi-batch operations. The need of further improvement is due to the type of foreseen operation and possible experimental errors during experimental setup. The initial estimation (gEST) uses batch and semi-batch experimental data. After a number of experiments, only semi-batch are carried out; thus, the data requires adjustment for this type of operation.

To determine the most effective metaheuristic technique for this optimization problem (parameter estimation), the Genetic algorithm (GA), differential evolution (DE), and particle swarm optimization (PSO) are compared under fair conditions. All methods run in a PC Intel Core™ i7-4790K CPU @ 4.00 GHz with 16.0 Gb of installed RAM. Each algorithm has 30 independent runs of 1500 fitness function evaluations each. These methods are population-based and require the generation of 50 generations with a population size of 30 each. After 1250 evaluations, all algorithms show poor improvement in most runs.

For the GA, the parameters are tuned manually until they show good performance. The chosen crossover fraction is 0.6, extra-range for crossover factor is 0.4, mutation fraction set to 0.4, mutation rate to 0.1, and the selection method fixed as random. Regarding the DE, the crossover rate is 0.7 and $\beta$ is randomly selected between $[0.2, 0.8]$. Finally, the PSO uses as parameters 1.0 for the initial inertia weight, 0.99 for the damping ratio, 1.5 for the cognitive coefficient, and 2.0 for the social coefficient. Eq. (6.23a) introduces the objective function utilized for parameter estimation. The considered measurements are concentration of monomer, weight-
average molecular weight and volume of contents in the reactor: \([C_m, M_w, V]\). The values of the covariance error matrix \((R)\) are the same to be used in the \(h\)-DEKF in the following section and where obtained from experimental data.

\[
\min_p \sum_{l=1}^{L} \left[ \frac{1}{N_k} \sum_{k=1}^{N_k} \left( y_{k,l} - h_{k,l}(p) \right) R^{-1} \left( y_{k,l} - h_{k,l}(p) \right)^T + \sum_{n=1}^{20} \left( g_{n,l} - g_{n,l}(p) \right)^2 \right]
\]

subject to \quad 0.01 \ p_0 \leq \ p \leq 10 \ p_0

\[
R = diag [5, 100, 10^{-12}]
\]

where, \(l\) represents each experiment taken into account \((L = 3)\). In our practice, three representative experiments, corresponding to the increasing, decreasing and constant \(M_w\) trajectories (as defined at the end of Section 1 and summarized in Table 6.2), are included. The vector of parameters \((p)\) is constrained between a lower bound of 1\% of its original value \((p_0)\) and upper bound of 10 times its original value.

Figure 6.2 shows the convergence profiles for all the metaheuristic algorithms evaluated. Clearly, the DE algorithm is the one that shows qualitatively the best result overall. It demonstrates a faster convergence towards optima and a higher certainty in achieving the minimum results as observed in the time-evolution of the standard deviation.

Table 6.3 displays the results of the minimum \((f t_{min})\), maximum \((f t_{max})\), average value \((f t_{mean})\) and the standard deviation \((\sigma_{ft})\) of the final fitness function defined in Eq. (6.23a) constrained to the conditions in Eq. (6.23b). The results in the table are in accordance to the ones in Figure 6.3. After recognizing qualitatively and quantitatively that the DE algorithm demonstrates the best performance overall, it is required to evaluate the statistical difference of the means to verify its correctness.
Figure 6.2. Convergence profile and standard deviation for DE, GA and PSO.

Table 6.3. GA, DE and PSO performance and CPU time

<table>
<thead>
<tr>
<th>Algorithm</th>
<th>$f_{t_{\text{min}}}$</th>
<th>$f_{t_{\text{max}}}$</th>
<th>$f_{t_{\text{mean}}}$</th>
<th>$\sigma_{f_t}$</th>
<th>CPU time per run, [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA</td>
<td>661.662</td>
<td>663.416</td>
<td>662.294</td>
<td>6.97E-01</td>
<td>198.07</td>
</tr>
<tr>
<td>DE</td>
<td>661.662</td>
<td>661.663</td>
<td>661.663</td>
<td>1.54E-04</td>
<td>195.67</td>
</tr>
<tr>
<td>PSO</td>
<td>661.663</td>
<td>663.153</td>
<td>662.628</td>
<td>6.79E-01</td>
<td>195.48</td>
</tr>
</tbody>
</table>
Table 6.4 presents the results when DE is contrasted with GA, and when DE is compared with PSO. The statistical difference evaluation consists on first determining if the variances are alike or different with the F-Test. Then, the t-Test permits to determine if the average results of two sets of data are significantly different from each other. The null hypothesis states that the difference between the compared means is equal to cero. If the obtained value is greater than a chosen p-value (at a selected percentage of confidence), the null hypothesis is accepted; otherwise, we fail to reject it. Failing to reject the null hypothesis means that the means are significantly different. In the following analysis a 99.99% of confidence was selected (p-value of 0.005). Based on the t-Test results, the means are significantly different in all cases which in other words signifies that the DE algorithm is overall the best performing because it achieves a significantly different minimum value in the cost function.

Finally, Table 6.5 displays the set of kinetic parameters obtained in the metaheuristic parameter re-estimation. The original values obtained in gEST are compared with the new values. In most of the cases small variation are observed with exception of the parameter $A_{td}$ which shows a variation of more than twice its original value. The reason of these changes even after the initial estimation can be related with the availability of new experiments and the broader solution domain when employing metaheuristic estimation.

<table>
<thead>
<tr>
<th></th>
<th>DE vs. GA</th>
<th>For p-value of 0.005</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-Test</td>
<td>8.05E-99</td>
<td>+</td>
</tr>
<tr>
<td>t-Test</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DE vs. PSO</td>
<td>For p-value of 0.005</td>
</tr>
<tr>
<td>F-Test</td>
<td>1.72E-98</td>
<td>+</td>
</tr>
<tr>
<td>t-Test</td>
<td>0.0000</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.5. Kinetic and thermodynamic parameters of the mathematical model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$p_0$, original value</th>
<th>$p_*$, new value</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_d$</td>
<td>$7.154 \times 10^{12}$</td>
<td>$7.326 \times 10^{12}$</td>
<td>min$^{-1}$</td>
</tr>
<tr>
<td>$A_p$</td>
<td>$4.08 \times 10^5$</td>
<td>$6.183 \times 10^5$</td>
<td>m$^3$ mol$^{-1}$ min$^{-1}$</td>
</tr>
<tr>
<td>$A_{td}$</td>
<td>$4.08 \times 10^9$</td>
<td>$1.453 \times 10^{10}$</td>
<td>m$^3$ mol$^{-1}$ min$^{-1}$</td>
</tr>
<tr>
<td>$e_f$</td>
<td>0.196</td>
<td>0.195977</td>
<td>-</td>
</tr>
</tbody>
</table>

6.3 Experimental equipment and setup

Figure 6.3 sketches a flow diagram of the polymerization pilot plant for this case study, in which its main components and functionality are explained. The experimental equipment consists of a 1.5 L reactor including auxiliary fittings and instrumentation, all monitored by the ACOMP system. Pumps driven by encoded stepper motors inject monomer and initiator solutions into the reactor. An external jacket keeps the inner temperature of the reactor at constant conditions (isothermal). From a high flow rate recirculation loop (~40 mL/min), the ACOMP system extracts a constant sample stream. In the case of pilot scale, a rate of 0.5 mL/min is sufficient. This setup allows minimal time delay from the time new materials are added into the reactor until they are detected by the sensor (less than 2.5 minutes). The ACOMP system analyzes the sample by diluting it 80 times with deionized water and homogenizing it in a mixing chamber. Ultraviolet visible absorption spectroscopy, viscometry and multi-angle laser light scattering detectors measure the sample. Spectroscopy at 245 nm determine the monomer and polymer concentrations. The $M_w$ is calculated from the static/multi-angle light scattering data. Air bubbles are purged from the ACOMP sensors to guarantee uncontaminated and stable measurements. Three main measurements are taken into account $C_m$, $M_w$ and $V$. In addition, other measurements are available as well, these are $T$, $F_m$ and $F_i$. 

90
Once the experiments finalize, the Gel Permeation Chromatography (GPC) method provides the final MWD using an in-house built system. It consists of a Shimadzu LC-10ADVp (Columbia, MD) high-pressure solvent delivery pump that provides a continuous flow of sodium chloride solution through the GPC column followed by a Shimadzu RID-10A differential refractometer. The sample injector is an IDEX/Rheodyne MX-II with a 50 μL sample loop volume. A series of polyethylene oxide standards ranging from 25,000 to 1 million g/mol are utilized to create a standard column calibration. The described method is referred as GPC standard calibration.

Figure 6.3. Laboratory pilot plant setup.
6.4 Results for open-loop experiments with $h$-DEKF

6.4.1 $h$-DEKF tuning

The filter defined and explained in Chapter 4 Section 2 (auto-tune error-driven $h$-DEKF) is tuned by searching a vector of optimal model errors ($e_w$) using the ParLMSRBF-R algorithm and real data from one open-loop (OL) experiment. The algorithm evaluates sixteen promising candidate points simultaneously, taking advantage of parallel computing in a total of 16 iteration which represents a total of 512 points. Figure 6.4 shows the convergence profile of the cost function. The eigenvalues of the error dynamics matrix allow us to analyze the filter stability. In addition and to guarantee operational flexibility, the stability analysis is performed to evaluate all proposed trajectories in order to generalize the validity of the method for all experiments.

![ParLMSRBF-R Convergence Profile](image)

Figure 6.4. ParLMSRBF-R algorithm convergence profile of one run when searching optimal $e_w$ for auto-tuned error-driven free-parameters.

Figure 6.5 shows the eigenvalues distribution for all trajectories in a real-imaginary plane. All eigenvalues fall inside the unitary circle showing stable behavior in all proposed operational trajectories making closed-loop experiments promising.
\[ \sigma_\nu^2 = [5, 100, 10^{-12}] \]

\[ e_w = [0.08, 0.08, 0.0356, 0.0, 0.0, 0.0056] \]

\[ P_0 = 100Q \]

Figure 6.5. Eigenvalues of the estimation error dynamics for different OL experiments, where ■ increasing, ● constant and ○ decreasing \( M_w \) trajectory.

6.4.2 Open-loop results with \( h \)-DEKF

OL experiments permit the verification of the \( h \)-DEKF performance using real data from the ACOMP system. The reported results were obtained using the original kinetic parameters reported in Table 6.1. During these experiments, the process behavior follows strictly the trajectories obtained by the offline dynamic optimization (optimal policies). Thus, for isothermal operation, \( F_m \) and \( F_i \) are set equal to the optimal profiles provided by gPROMS considering updates every 2.5 min. The nonlinear model initializes while the reaction starts in the pilot plant. After 20 minutes, nonlinear state estimation starts. For this verification, the validated model and \( h \)-DEKF is implemented in MATLAB R2015a. The differential equations of the model in
MATLAB® are solved using ode45 (Dormand & Prince, 1980; Shampine & Reichelt, 1997), and for solving the exponential matrix for the filter, as presented in Eq. (4.3), expm(·) is selected (Moler & Van Loan, 2003; Higham, 2005; Al-Mohy & Higham, 2009; Golub & Van Loan, 2012).

Figures 6.6 to 6.8 illustrate the h-DEKF response in all OL scenarios. Each figure includes estimated properties, experimental values and optimal trajectories. Particularly, Figures 6.6a, 6.7a, and 6.8a illustrate relevant information related to the filter ability for state estimation and signal processing. Estimated $M_w$ points show noise reduction when compared with raw measurements. The h-DEKF estimates the time-evolution of $M_n$ which is an unmeasured property. Both estimated $M_w$ and $M_n$ are drawn in parallel with respect to their optimal trajectories showing physical consistency. Figures 6.6b, 6.7b, and 6.8b as well as Figures 6.6c, 6.7c, and 6.8c show the signal processing ability of the filter for the other two measurements, $C_m$ and $V$ respectively. However, the signal processing for $C_m$ does not show the same proficiency as witnessed for the other two measurements. Further tuning is required to the filter for overcoming it, which maybe can be to adjust the set values of the covariance error matrix that influence this measurement within the filter (see Eq. (4.7)). In addition, Figures 6.6d, 6.7d, and 6.8d illustrate another important objective, the monitoring of the MWD during polymerization. The estimated and measured final MWD are compared as well as experimental measurements obtained using the standard calibration GPC approach. The estimates show adequate approximation even if they do not capture the initial low mass section and the estimated long high mass tail. The reasons might be the experimental equipment and column calibration limitations. The experimental MWD is acquired after the experiment finalizes, and it takes between 15 to 30 min to obtain the measured values. Finally, Figures 6.6e, 6.7e, and 6.8e illustrate the estimated MWD time-evolution, showing real-time monitoring capability.
Figure 6.6. Results for the increasing $M_w$ trajectory in OL. Experimental measurements (blue circles), nonlinear model (dashed lines), $h$-DEKF (continuous lines). (a) $M_w$: black and red lines, $M_n$: grey and purple lines, (b) Concentration of monomer, (c) Volume of internal contents, (d) Final chain length distribution, and (e) Chain length distribution along the reaction by $h$-DEKF.
Figure 6.7. Results for the constant $M_w$ trajectory in OL. Experimental measurements (blue circles), nonlinear model (dashed lines), $h$-DEKF (continuous lines). (a) $M_w$: black and red lines, $M_n$: grey and purple lines, (b) Concentration of monomer, (c) Volume of internal contents, (d) Final chain length distribution, and (e) Chain length distribution along the reaction by $h$-DEKF.
Figure 6.8. Results for the decreasing $M_w$ trajectory in OL. Experimental measurements (blue circles), nonlinear model (dashed lines), $h$-DEKF (continuous lines). (a) $M_w$: black and red lines, $M_n$: grey and purple lines, (b) Concentration of monomer, (c) Volume of internal contents, (d) Final chain length distribution, and (e) Chain length distribution along the reaction by $h$-DEKF.
In summary, all the evaluated trajectories show good performance in both state estimation and signal processing. Once the filter switches on (after 20 min), the estimated properties move from the nonlinear model towards the measurements, providing a smoother projection of a given polymer property while reducing measurements noise. In regard to the online prediction ability of the MWD, the results are good in predicting the trends of this critical property. Finally, the implemented noise reduction is important towards enhancing the control action, which is the scope of the following section.

### 6.5 Results for closed-loop experiments with h-DEKF

After validating and verifying the h-DEKF performance in different OL experiments, the weight-average molecular weight control action, already explained in Chapter 3 Section 3, is tested in two sets of closed-loop experiments defined as follows: using only PID control, and using PID integrated with the filter. Similarly than OL experiments, the reported results for closed-loop were obtained using the initial kinetic parameters reported in Table 6.1. The control objective is to follow a given $M_w$ optimal set point trajectory by manipulating the $F_m$. Hence, $F_i$ and $T$ are set equal to its optimal profile trajectories, in all cases. The hypothesis is that only small variations of $F_m$ along the optimal input trajectory should be necessary to achieve the target trajectory. In the first set of experiments (PID), the controller collects raw $M_w$ measurements and computes an average value for a 30 sec time interval. The mentioned procedure intents to reduce noise from the data by using a simple average technique. In the second set of experiments (PID + h-DEKF), proceed using the in-house module and framework introduced in Chapter 5 Section 2. The reader should notice that the module was built in Python. Moreover, the estimated $M_w$ are the controller inputs and nonlinear state estimation and control action initialize 20 min after the reaction starts.
Figures 6.9 to 6.11 contrast the performance of OL, PID, and PID + h-DEKF closed-loop experiments under equal intended operational conditions. Results show the qualitative performance of three operating philosophies towards the synthesis of target polymers. These setups include OL optimal operation (following a recipe), direct PID control, and PID control combined with a nonlinear state estimator. Figures 6.9a, 6.10a, and 6.11a exhibit raw measurements of $M_w$, estimated $M_w$ and $M_n$ (computed by the filter during PID + h-DEKF experiments), and set-point trajectories. In terms of performance, the PID + h-DEKF shows a better response than the PID solely. The improvement is not only confirmed by the achievement of the desired $M_w$ trajectory, but also in providing a smoother response of the manipulated variable ($F_m$). The control variable profiles denoted in Figures 6.9b, 6.10b, and 6.11b evidence the aforementioned response behavior, in which small variation are required to achieve the desired set point trajectory.

Figures 6.9c, 6.10c, and 6.11c illustrate the estimated, measured and calculated $C_m$. Likewise in the open-loop experiments, signal processing is proficiently performed but further improvement could be achieved. Figures 6.9d, 6.10d, and 6.11d compare the target MWD or chain length distribution with the distribution estimated by the h-DEKF and the measured using the GPC standard calibration. In all evaluations, the nonlinear filter demonstrates a good prediction ability.

The $h$-DEKF provides extra information on the MWD time-evolution. Figure 6.12 provides a perspective of the estimated changes occurred to the MWD along the reaction in the three studied trajectories, demonstrating broader monitoring capabilities of this property at different times. In summary, signal processing or noise reduction represents a main benefit in terms of control performance while nonlinear state estimation offers the opportunity of achieving full polymer characterization when applying real-time model-based strategies.
Figure 6.9. Results for increasing $M_w$ trajectory closed-loop showing measurements for OL (grey), PID (orange) and $h$-DEKF (blue) experiments. (a) Experimental values (circles), set point(s) (dashed), $h$-DEKF (continuous), $M_w$: black and red lines, $M_n$: grey and purple lines, (b) Measured flow rate of monomer, (c) $C_m$, experimental measurements (blue circles), nonlinear model (dashed), $h$-DEKF (continuous), (d) Final chain length distribution, experimental measurements (circles), set-point (dashed), $h$-DEKF (continuous).
Figure 6.10. Results for constant $M_w$ trajectory closed-loop showing measurements for OL (grey), PID (orange) and $h$-DEKF (blue) experiments. (a) Experimental values (circles), set point(s) (dashed), $h$-DEKF (continuous), $M_w$: black and red lines, $M_n$: grey and purple lines, (b) Measured flow rate of monomer, (c) $C_m$, experimental measurements (blue circles), nonlinear model (dashed), $h$-DEKF (continuous), (d) Final chain length distribution, experimental measurements (circles), set-point (dashed), $h$-DEKF (continuous).
Figure 6.11. Results for decreasing $M_w$ trajectory closed-loop showing measurements for OL (grey), PID (orange) and $h$-DEKF (blue) experiments. (a) Experimental values (circles), set point(s) (dashed), $h$-DEKF (continuous), $M_w$: black and red lines, $M_n$: grey and purple lines, (b) Measured flow rate of monomer, (c) $C_m$, experimental measurements (blue circles), nonlinear model (dashed), $h$-DEKF (continuous), (d) Final chain length distribution, experimental measurements (circles), set-point (dashed), $h$-DEKF (continuous).
Figure 6.12. Evolution of the chain length distribution during closed-loop experiments. (a) Increasing $M_w$ trajectory, (b) Constant $M_w$ trajectory, (c) Decreasing $M_w$ trajectory.
In the antecedent Figures, the qualitative benefits of including a nonlinear state estimator were corroborated. Nevertheless, it is important to verify quantitatively the overall advantages. The sum of the absolute difference between the set point and raw measurements computed every one second permits to quantify the control action improvement of the PID + $h$-DEKF.

Table 6.6 denotes the percentages of improvement considering three different time intervals: after initialization (after 20 min), for the second half of the experiment (after 90 min) and for the last third of the experiment (after 120 min). The objective of this categorization is to evince the presence of overall improvement, at the middle of the reaction and the end of the polymerization. Clearly, the integration of the filter ($h$-DEKF) with control improves significantly the control action towards achieving the control objective, in this case a weight-average molecular weight trajectory determined as the result of a dynamic optimization.

<table>
<thead>
<tr>
<th>Trajectory Description</th>
<th>Improvement, [%] after:</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 min</td>
<td>90 min</td>
<td>120 min</td>
</tr>
<tr>
<td>Increasing $M_w$</td>
<td>50.5</td>
<td>69.2</td>
<td>74.0</td>
</tr>
<tr>
<td>Constant $M_w$</td>
<td>44.6</td>
<td>11.2</td>
<td>25.1</td>
</tr>
<tr>
<td>Decreasing $M_w$</td>
<td>56.5</td>
<td>24.9</td>
<td>18.2</td>
</tr>
</tbody>
</table>

6.6 Results: GO design and implementation

The nonlinear state estimation of the polymerization model under study can also be performed using the algorithm described in Chapter 4, Eq. (4.17). The initial observability and detectably assessment concluded that a complete observability is not possible because the state $\lambda_0 V$ cannot be determined from the information contained in the measured outputs and their Lie
derivatives. The maximum rank of the observability index is indeed five, because the zero-moment of the distribution does not affect the dynamics of the states related to the measurements.

Considering the observer algorithm, different combinations of structures can be selected. In the following sections, the construction of the observer structure is discussed. Different architectures in terms of observability indices, and choice of the innovated states are evaluated and discussed (Alvarez & Fernández, 2009).

6.6.1 Full-order observer

With the three available measurements ($C_m$, $M_w$ and $V$), five states are distinguishable and one state ($\lambda_0V$) is not. Using the notation of the estimation algorithm (see Eq. (4.17) in Chapter 4), the following partition is first considered.

$$\mathbf{x}_1 = [N_m, N_l, N_s, \lambda_1V, \lambda_2V], \quad \mathbf{x}_u = [\lambda_0V]$$

This structure corresponds to the full-order observer because the maximum number of innovated states is considered. Depending on the choice of the observability indexes ($\kappa_i$), three different observer structures are possible as introduced in Eq. (6.24a-c). Even though structures with indices of three or more are theoretically possible, their inclusion and evaluation were left apart because Lie derivatives of higher order reduce the robustness of the observer.

$$(\kappa_1, \kappa_2, \kappa_3) = (2,2,1); \quad (\kappa_1, \kappa_2, \kappa_3) = (2,1,2); \quad (\kappa_1, \kappa_2, \kappa_3) = (1,2,2) \quad (6.24a-c)$$

The subscripts of the observability indexes $\kappa_i$ are the monomer concentration ($i = 1$), weight-average molecular weight ($i = 2$), and volume of internal contents ($i = 3$). The best structure is the one that achieves a given estimation task with appropriate tradeoff between state reconstruction, speed and robustness. As detectability measures, the singular value and the
condition number of the observability matrix are computed (Hermann & Krener, 1977). The first
detectability index measures the sensitivity of a given measure with respect to the changes in a
particular state. The latter index gives information on the conditioning of the observer, e.g. when
it increases, the observer becomes more sensitive to measurement noise and modelling errors.

For selecting the best observer structure, detectability indices are initially computed for an
increasing weight-average molecular weight trajectory (as explained previously). This trajectory
is selected because it is more sensitive to errors. If the proposed methodology demonstrates
robustness for this operating condition, it should be robust for the other cases as well.

Table 6.7 reports the resultant average minimum singular value and condition number for
every full-order structure. Results indicate that the configurations which contain the Lie derivative
of the measured weight-average molecular weight have the higher minimum singular value. This
is expected because the function relating the output and the states \( h_2 \) is the only one that explains
\( \lambda_2 V \) dynamics; thus, by using its Lie derivative, it is possible to gain more information and
knowledge on the system dynamics. Among configurations (2,2,1) and (1,2,2), the former shows
better detectability indices, indicating that the incidence of the volume’s Lie derivative does not
lead to a prime understanding of the system from an observability point of view.

Following the tuning guidelines, and considering an estimated run time of 180 minutes, the
range of tuned gains are \( k_{i1} = [0.11, 1.00] \), \( k_{i2} = [0.0031, 0.0278] \) for all measurements.
However, the full-order observer showed robustness when low values of \( k_{i2} \) were included. This
response could be due to the high condition number observed.

It is important to underline that both \( M_w \) and \( C_m \) measurements are strongly affected by
noise, while the volume has more consistent data. Considering that both structures characterize for
having a high condition number, the full-order estimation is expected to be sensitive to model and measurement uncertainties. In such conditions, the choice of a configuration which uses the Lie derivative of the smoothest measurements is preferable. Based on these reflections configuration (1, 2, 2) is selected.

Results for the full-order GO (1, 2, 2), including a sensitivity evaluation of high, medium and low frequency tuning, are illustrated in Figure 6.13. The portrayed measurements show an adequate functioning of the GO for data reconciliation. However, after testing under a number of conditions, it was observed that the structure is very sensitive, careful tuning is required (for $k_{12}$), and poor predictions can be obtained for the unmeasured properties. This type of behavior is expected, even for the best structure, because the condition number of the system is very high, and the inclusion of the Lie derivatives make the structure sensitive to noise (as in the case of the monomer concentration and weight-average molecular weight), which deteriorates the observer performance. These matters motivated the investigation of a more robust observer which is explained in the following section.

Table 6.7. Average minimum singular values and condition number for full-order observer calculated along increasing $M_w$ trajectory

<table>
<thead>
<tr>
<th>Structure</th>
<th>(2,2,1)</th>
<th>(2,1,2)</th>
<th>(1,2,2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
<td>$1.8 \times 10^{-7}$</td>
<td>$6.5 \times 10^{-23}$</td>
<td>$3.12 \times 10^{-12}$</td>
</tr>
<tr>
<td>$\bar{\sigma}/\sigma$</td>
<td>$2.05 \times 10^{10}$</td>
<td>$3.6 \times 10^{28}$</td>
<td>$1.4 \times 10^{15}$</td>
</tr>
</tbody>
</table>
Figure 6.13. Comparison between experimental data (blue circles), full-order (1,2,2) GO (continuous line: purple low characteristic frequency, red average characteristic frequency and gold high characteristic frequency), and the nonlinear model (dashed line) for an increasing $M_w$ trajectory: (a) weight-average molecular weight; (b) monomer concentration; (c) volume of contents inside the reactor.
6.6.2 Low-order observers and passive structures

An enhanced observer performance is possible by implementing a different observer structure (Tronci et al., 2005; Fernandez et al., 2012), which can be inferred by analyzing the detectability report from Table 4. Even if the full-order structure (1,2,2) shows accuracy in estimating some properties, it is still characterized by a lower minimum singular value with respect to (2,2,1), indicating that the volume Lie derivative is less informative than the $C_m$ Lie derivative. This fact is also explained when taking into account that the volume is mainly affected by the moles of solvent in the reactor ($N_s$). In this context, a passive structure as proposed by Fernandez et al. (2012) appears to be useful for a robust estimation where the dynamics of the total number of moles of solvent are governed only by the volume output.

The other two remaining measurements can be used to correct all the other states, except $N_s$, but as discussed above, the results obtained for the full-order observer evidence that the application of Lie derivatives to measurements highly corrupted by noise is unfavorable for the estimator. This issue can be addressed by decreasing the number of innovated states, which implies the elimination of one or two Lie derivatives.

Being $M_w$ the measurement more affected by noise, the use of $L_f h_1$ ($h_1 = C_m$) is preferred to $L_f h_2$ ($h_2 = M_w$). The choice of the innovated states was accomplished by analyzing again the detectability indexes reported in Table 6.8. Clearly, important improvements can be observed in terms of both the condition number and the minimum singular values. Based on these considerations the observer reported in Eqs. (6.25a-c) is proposed.
\[ \dot{x}_{in} = \hat{f}_{in}(\hat{x}, u) + G_n^{-1}K_n(y_n - h_n(\hat{x})) \]  
(6.25a)

\[ \dot{x}_{ip} = \hat{f}_{ip}(\hat{x}, u) + G_p^{-1}K_p(y_p - h_p(\hat{x})) \]  
(6.25b)

\[ \dot{x}_{v} = \hat{f}_{v}(\hat{x}, u) \]  
(6.25c)

where,

\[ \hat{x}_{in} = [\hat{N}_m, \hat{N}_i, \hat{\lambda}_1V]^T, \quad y_n = [C_m, M_w]^T, \quad h_n = [h_1, h_2]^T = [\hat{c}_m, \hat{M}_w]^T \]

\[ G_n = \frac{\partial \phi_n}{\partial \hat{x}_{in}}, \quad \phi_n = [h_1, L_f h_1, h_2]^T, \quad K_n = \begin{pmatrix} B_1 & 0 \\ 0 & B_2 \end{pmatrix} \]

\[ B_1 = \begin{bmatrix} k_{11} & 0 \\ k_{12} & 0 \end{bmatrix}, \quad B_2 = \begin{bmatrix} k_{22} \\ 0 \end{bmatrix}, \quad \hat{x}_{ip} = [\hat{N}_s], \quad y_p = [V], \quad h_p = [h_3] = [\hat{V}] \]

\[ G_p = \frac{\partial h_3}{\partial \hat{x}_{ip}}, \quad K_p = k_{33}, \quad \hat{x}_{v} = [\hat{\lambda}_0V, \hat{\lambda}_2V]^T \]

Table 6.8. Average minimum singular values and condition number: 4 innovated states with passive structure calculated along an increasing \( M_w \) trajectory

<table>
<thead>
<tr>
<th>Innovated states variables (( \hat{x}_{in} ))</th>
<th>( N_m, N_i, \lambda_1V )</th>
<th>( N_m, N_i, \lambda_2V )</th>
<th>( N_m, \lambda_1V, \lambda_2V )</th>
<th>( N_i, \lambda_1V, \lambda_2V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma )</td>
<td>( 1.44 \times 10^2 )</td>
<td>( 7.3 \times 10^{-1} )</td>
<td>( 1.75 \times 10^{-5} )</td>
<td>( 2.0 \times 10^{-3} )</td>
</tr>
<tr>
<td>( \sigma / \bar{\sigma} )</td>
<td>( 2.5 \times 10 )</td>
<td>( 2.52 \times 10^3 )</td>
<td>( 2.3 \times 10^8 )</td>
<td>( 1.7 \times 10^6 )</td>
</tr>
</tbody>
</table>

The observer robustness can be further improved by also eliminating the \( C_m \) Lie derivative; thus, implementing a 3-state estimator. The following partition between the innovated and non-innovated states is then proposed and reported in Eq. (6.26a-b), using the same previous symbols as in Eq. (6.25a-c). The performance of the 3-state estimator is calculated again considering the increasing \( M_w \) trajectory.

\[ \hat{x}_{in} = [\hat{N}_m, \hat{\lambda}_1V] \]  
(6.26a)

\[ \hat{x}_v = [\hat{N}_i, \hat{\lambda}_0V, \hat{\lambda}_2V], \quad \phi_n = [h_1, h_2], \quad K_n = \begin{pmatrix} k_{11} & 0 \\ 0 & k_{22} \end{pmatrix} \]  
(6.26b-d)
The ability of predicting the $M_n$, and the final chain length distribution is compared among
the proposed GO structures and another estimation method, the $h$-DEKF (Salas et al., 2018).
Because there is no experimental data on $M_n$, this comparison is only qualitative, and it is
illustrated in Figure 6.14. The chain length distribution and $M_n$ are function of the state $\lambda_1 V$.
Therefore, the final experimental distribution permits to also evaluate the confidence on the
estimated $M_n$. Results on the final distribution, exhibited in Figure 6.15, indicate that the 4-state
GO with passive structure predicts more accurately the chain length distribution when compared
with the $h$-DEKF, full-order structure, and the 3-state GO with passive structure. When computing
the sum of the squared errors between the experimental and estimated final distributions, the full-
order GO underperforms when compared with the $h$-DEKF; however, the 4-state GO with passive
structure improves 52% the final distribution estimation while the 3-state GO with passive
structure improves 51%.

Figure 6.14. Number-average molecular weight comparison for: nonlinear model (blue continuous line); $h$-DEKF (gold dots); full-order GO (black dashed line); 4-order GO with passive structure (red continuous line); 3-order GO with passive structure (green dot-dashed line).
The signal processing ability of the $h$-DEKF is compared with the 4-order GO with passive structure. Figure 6.16 provides a comparison of both signals. The estimated values calculated by the 4-order GO with passive structure (tuned at medium frequency, $k_{i1} = 0.5$, $k_{i2} = 0.008$) have a smoother response, which is favorable and preferred for advanced control applications.

![Comparison between the experimental chain length distribution by GPC standard calibration (blue circles) and the estimated by: $h$-DEKF (gold dots); full-order GO (black dashed line); 4-order GO with passive structure (red continuous line); 3-order GO with passive structure (green dot-dashed line).](image)

**Figure 6.15.** Comparison between the experimental chain length distribution by GPC standard calibration (blue circles) and the estimated by: $h$-DEKF (gold dots); full-order GO (black dashed line); 4-order GO with passive structure (red continuous line); 3-order GO with passive structure (green dot-dashed line).

Additionally, the signal processing response of the $h$-DEKF is compared with the response when using the 4-order GO with passive structure. Figure 6.16 provides a comparison between the results obtained by the 4-order GO with passive structure and the $h$-DEKF in an arbitrary [15, 60] min time interval. In all cases, the estimated values calculated by the 4-order GO with passive structure have a smoother response (more noticeably during initialization at minute 20), which is favorable and preferred for control applications. Notice that in the case of monomer concentration (exhibited in Figure 6.16b) the 4-order GO with passive structure shows a superior noise rejection.
Figure 6.16. Comparison between experimental data (blue circles), 4-order GO with passive structure (red continuous line), $h$-DEKF (gold continuous line) and nonlinear model (dashed line) for increasing $M_w$ trajectory: (a) weight-average molecular weight; (b) monomer concentration; (c) volume of contents inside the reactor.
A better performance of the $h$-DEKF might be possible after a better tuning, but fine tuning can be a tedious task even when the approach is simplified (auto-tuned error-driven).

To prove flexibility and robustness, it is important to verify if the best performing observer (4-order GO with passive structure) is able to properly reconstruct the polymerization system in a range of operating conditions. Therefore, its performance is evaluated and compared with the $h$-DEKF considering two different decreasing $M_w$ trajectories. It is worth to mention that the same previous tuning parameters of both, GO and $h$-DEKF, are used in the runs for testing the system under different conditions.

Figure 6.17 and Figure 6.18 illustrate the dynamic response of the estimators for the two aforementioned weight-average molecular weight trajectories in terms of $M_w$, $M_n$ and $C_m$, along with the distribution measured at the end of the batch. In all cases, results appear to be acceptable for signal processing and property estimation. In the case of the estimated final chain length distribution, the 4-state GO with passive structure demonstrates a 40% improvement in terms of the sum of the squared errors when compared with the $h$-DEKF. The improvement is consistent in both evaluations. These results are in accordance with the results explained in Figure 6.15.

Clearly, a systematic construction using the GO method permits the selection of a structure capable of not only improving the quality of the estimates, but also achieving a proper signal processing of all measurements. Even though the number-average molecular weight remains as an unmeasured property, the fact that the final distribution achieved with the 4-state GO with passive structure is closer to the experimental values indirectly states that the reconstruction of this property ($M_n$) might be better performed by the GO in contrast with the $h$-DEKF. However, all $M_n$ (from the model and the estimated ones) hold a short distance through the reaction.
Figure 6.17. Comparison between experimental data (blue circles), 4-order GO with passive structure (red), h-DEKF (gold), and nonlinear model (black dashed line) for the first decreasing $M_w$ trajectory: (a) weight-average molecular weight (continuous line), and number-average molecular weight (continuous dots); (c) monomer concentration (continuous lines); (d) final chain length distribution.
Figure 6.18. Comparison between experimental data (blue circles), 4-order GO with passive structure (red), $h$-DEKF (gold), and nonlinear model (black dashed line) for the second decreasing $M_w$ trajectory: (a) weight-average molecular weight (continuous line) and number-average molecular weight (continuous dots); (c) monomer concentration (continuous lines); (d) final chain length distribution.
6.7 References


7 CASE STUDY 2: COPOLYMERIZATION OF ETHYLENE WITH 1,9-DECADIENE

7.1 Fundamental model

Polyolefins, mainly polypropylene and polyethylene, are the most abundantly produced plastics worldwide. The annual growth rate projected for such materials is estimated to be around 3-5% (Liu et al., 2016), which makes polyolefin synthesis a continuously growing and attractive market. Metallocene catalysts such as Dow Chemical’s constrained-geometry catalyst (CGC), produce polyolefins with narrow molecular weight distributions while allowing a noteworthy addition of α-olefins, dienes, and macromonomers into the growing chains (Stadler, 2006). The incorporation of macromonomers generates copolymers with long-chain branches (LCB), which besides enhancing physical and mechanical properties, improves the processability of the final plastic materials (Soares & Hamielec, 1996; Wang et al., 1998; Chum et al., 2000).

The reaction pathways that lead to the formation of LCBs in ethylene/α-olefins/diene copolymers are complex. Various experimental investigations have studied their kinetics during synthesis (Choo & Waymouth, 2002; Naga & Toyota, 2004; Mehdiabadi & Soares, 2011), while others have focused on the development of mechanistic models to explain their microstructures and to predict properties of interest (Soares, 2002; Ferreira et al., 2010; Mogilcharla et al., 2014).

Brandão et al. (2017a) proposed a mechanistic model for the semi-batch copolymerization of 1,9-decadiene with ethylene, and validated it with experimental measurements including ethylene flow rate ($F_m$), number-average ($M_n$) and weight-average ($M_w$) molecular weights. The model assumed that LCBs were formed by incorporating macromonomers through pendant unsaturations resulting from the copolymerization of 1,9-decadiene. In addition, two methodologies to calculate the polyolefin MWD including the adaptive orthogonal collocation...
method, and a Monte-Carlo based simulation, were evaluated (Brandão et al., 2017b). Both methodologies were able to describe the MWD under different experimental conditions such as temperature and catalyst concentration. For verification, the computed distributions were contrasted with experimental measurements obtained from a Polymer Char High-Temperature Gel Permeation Chromatographer (GPC) (Soares & McKenna, 2013).

The reaction mechanisms adopted for the copolymerization of ethylene and 1,9-decadiene with dimethylsilyl (N-tert-butlamido) (tetramethylcyclopentadienyl) titanium dichloride (CGC)/MAO as proposed by Brandão et al. (2017a, 2017b) is detailed as follows:

Catalyst activation

\[ C \xrightarrow{k_a} C^* \quad (7.1) \]

Initiation

\[ C^* + M \xrightarrow{k_{p1j}} P_1^* (+m) \quad (7.2) \]

Propagation (ethylene)

\[ P_i^* + M \xrightarrow{k_{p1i}} P_{i+1}^* (+m) \quad (7.3) \]

Propagation (diene)

\[ P_i^* + D \xrightarrow{k_{p12}} P_{i+1}^* (+d) \quad (7.4) \]

Transfer to monomer and β-hydride elimination

\[ P_i^* \xrightarrow{k_t} L_i^z + C^* \quad (7.5) \]
Living chain deactivation

\[ P_i^* + P_j^* \xrightarrow{k_{dp}} L_i + L_j + 2 \text{DC} \quad (7.6) \]

Macromonomer reincorporation

\[ P_i^* + L_j^* \xrightarrow{k_b K} P_{i+j}^* (+2 \text{lcb}) \quad (7.7) \]

where, \( C \) is the catalyst precursor, \( C^* \) is an active catalyst site, \( M \) is ethylene, \( D \) is the diene (1,9-decadiene), \( DC \) is a dead catalyst site, \( m \) and \( d \) are the total amounts of ethylene and diene inserted into the growing polymer chains, \( lcb \) is the long chain branching, \( P_i^* \) is a living polymer chain with chain size \( i \), \( L_i^* \) is a dead polymer chain of size \( i \) containing a terminal unsaturation, \( L_i \) is a dead polymer chain of size \( i \) without a terminal unsaturation, \( K \) is the total number of pendant unsaturation’s present in the dead chains, \( k_a \) is the catalyst activation constant, \( k_b \) is the macromonomer reincorporation rate constant, \( k_{dp} \) is the living chain deactivation rate constant, \( k_{p_{11}} \) is the propagation rate constant for ethylene, \( k_{p_{12}} \) is the propagation rate constant for diene, and \( k_t \) is the termination rate constant.

Under assumptions such as constant ethylene concentration throughout the polymerization, excess cocatalyst concentration, well-mixed reactor, initiation rate equal to propagation rate for ethylene (\( k_{p_{11}} \)), and propagation controlled by the chemical nature of the monomer species, the following set of differential equations describes the system:

\[ \frac{dC}{dt} = -k_a \left( \frac{C}{V} \right) V \quad (7.8) \]

\[ \frac{dC^*}{dt} = k_a \left( \frac{C}{V} \right) V - k_{p_{11}} \left( \frac{C^*}{V} \right) \left( \frac{M}{V} \right) V + k_t \left( \frac{\mu_0}{V} \right) V \quad (7.9) \]

\[ \frac{dDC}{dt} = k_{dp} \left( \frac{\mu_0}{V} \right)^2 V \quad (7.10) \]
\[
\frac{dD}{dt} = -k_{p_{12}} \left( \frac{\mu_0}{V} \right) \left( \frac{D}{V} \right) V \\
\frac{d(m)}{dt} = k_{p_{11}} \left[ \left( \frac{C^*}{V} \right) + \left( \frac{\mu_0}{V} \right) \left( \frac{M}{V} \right) \right] V \\
\frac{d(d)}{dt} = k_{p_{12}} \left( \frac{\mu_0}{V} \right) \left( \frac{D}{V} \right) V \\
\frac{d(lcb)}{dt} = 2k_b \varphi \left( \frac{\mu_0}{V} \right) \left( \frac{\lambda_1}{V} \right) V \\
\frac{d\mu_0}{dt} = -k_t \left( \frac{\mu_0}{V} \right) V - k_{dp} \left( \frac{\mu_0}{V} \right)^2 V + k_{p_{11}} \left[ \left( \frac{C^*}{V} \right) + \left( \frac{\mu_0}{V} \right) \left( \frac{M}{V} \right) \right] V \\
\frac{d\mu_1}{dt} = -k_t \left( \frac{\mu_1}{V} \right) V - k_{dp} \left( \frac{\mu_0}{V} \right) \left( \frac{\mu_1}{V} \right) V + k_{p_{11}} \left[ \left( \frac{C^*}{V} \right) + \left( \frac{\mu_0}{V} \right) + 2 \left( \frac{\mu_1}{V} \right) \right] \left( \frac{M}{V} \right) V \\
\frac{d\mu_2}{dt} = -k_t \left( \frac{\mu_2}{V} \right) V - k_{dp} \left( \frac{\mu_0}{V} \right) \left( \frac{\mu_2}{V} \right) V + k_{p_{11}} \left[ \left( \frac{C^*}{V} \right) + \left( \frac{\mu_0}{V} \right) + 2 \left( \frac{\mu_1}{V} \right) \right] \left( \frac{M}{V} \right) V \\
\frac{d\lambda_0}{dt} = k_t \left( \frac{\mu_0}{V} \right) V + k_{dp} \left( \frac{\mu_0}{V} \right)^2 V - k_b \varphi \left( \frac{\mu_0}{V} \right) \left( \frac{\lambda_1}{V} \right) V \\
\frac{d\lambda_1}{dt} = k_t \left( \frac{\mu_1}{V} \right) V + k_{dp} \left( \frac{\mu_0}{V} \right) \left( \frac{\mu_1}{V} \right) V - k_b \varphi \left( \frac{\mu_0}{V} \right) \left( \frac{\lambda_2}{V} \right) V \\
\frac{d\lambda_2}{dt} = k_t \left( \frac{\mu_2}{V} \right) V + k_{dp} \left( \frac{\mu_0}{V} \right) \left( \frac{\mu_2}{V} \right) V - k_b \varphi \left( \frac{\mu_0}{V} \right) \left( \frac{\lambda_3}{V} \right) V \\
\frac{dV}{dt} = \left( \frac{d\lambda_1}{dt} + \frac{d\mu_1}{dt} \right) \frac{MM}{\rho_{PE}} \\
\frac{d\lambda_3}{dt} = \frac{\lambda_2}{\lambda_0 \lambda_1} \left( 2 \lambda_2 \lambda_0 - \lambda_1^2 \right) \\
MM = \varphi MM_D + (1 - \varphi) MM_M
\]

where,

\[
\varphi = \frac{d}{d + m} \\
\lambda_3 = \frac{\lambda_2}{\lambda_0 \lambda_1} \left( 2 \lambda_2 \lambda_0 - \lambda_1^2 \right) \\
MM = \varphi MM_D + (1 - \varphi) MM_M
\]

here, \( \varphi \) is the average frequency of pendant double bonds in the polymer chains, \( \lambda_k \) are the \( k^{th} \) moment for the dead chain, \( \mu_k \) are the \( k^{th} \) moment of living chain, \( \rho_{PE} \) is the polyethylene density, \( MM \) is the average molar mass of the repeating unit, \( MM_M \) is the molar mass of ethylene, and \( MM_D \) is the molar mass of diene.
Because the concentration of ethylene is kept constant, \( \frac{dM}{dt} = 0 \), the inlet flow rate of ethylene \( (F_M) \), which represents the continuous demand of ethylene during the polymerization, is approximated as follows:

\[
F_M \approx k_{p11} \left( \frac{C^*}{V} \right) \left( \frac{M}{V} \right) V + k_{p11} \left( \frac{\mu_0}{V} \right) \left( \frac{M}{V} \right) V
\]  (7.25)

The average properties, which describe the characteristics of the polymeric products, are computed as described:

\[
M_n = \frac{\lambda_1 + \mu_1}{\lambda_0 + \mu_0} MM
\]  (7.26)

\[
M_w = \frac{\lambda_2 + \mu_2}{\lambda_1 + \mu_1} MM
\]  (7.27)

\[
PDI = \frac{M_w}{M_n} = \frac{\lambda_2 + \mu_2}{\lambda_0 + \mu_0}
\]  (7.28)

where, \( M_n \) is the number-average molecular weight, \( M_w \) is the weight-average molecular weight and \( PDI \) is the polydispersity index.

Table 7.1 lists the model rate constants in reparametrized and classical Arrhenius fashion. In general, the kinetic constants follow a reparametrized form of the Arrhenius equation in all cases, with exception of the propagation rate constant, which is in the classical form.

**Table 7.1.** Kinetic rate constants for the copolymerization of ethylene with 1,9-decadiene.

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Arrhenius Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst activation</td>
<td>( k_a = \exp \left[ k_1 + k_2 \left( \frac{T - T_r}{T} \right) \right] )</td>
</tr>
<tr>
<td>Propagation</td>
<td>( k_{p11} = k_{0p} \exp \left( -\frac{E_{ap}}{RT} \right) ), ( k_{0p} = 10^{k_p} )</td>
</tr>
<tr>
<td>Monomer transfer &amp; ( \beta )-hydride elimination</td>
<td>( k_t = \exp \left[ k_3 + k_4 \left( \frac{T - T_r}{T} \right) \right] )</td>
</tr>
<tr>
<td>Living chain deactivation</td>
<td>( k_{dp} = \exp \left[ k_5 + k_6 \left( \frac{T - T_r}{T} \right) \right] )</td>
</tr>
</tbody>
</table>
where, $T$ is the temperature inside the reactor, $T_r$ is a reference temperature (set to 130 °C), $E_{ap}$ is the activation energy for the ethylene propagation rate, $R$ is the ideal gas constant, and $k_{1-7}$ are trivial kinetic parameters that explain rate constants as denoted in Table 7.1.

Table 7.2 lists the nonlinear model parameters including the parameters predefined in the reparametrized Arrhenius equations, pre-exponential constants, activation energies, as well as other relevant thermodynamic properties and constants. It is important to remind the reader that the trivial kinetic parameters ($k_{1-7}$) permit to describe the actual rate constants.

Table 7.2. Kinetic and thermodynamic parameters for the copolymerization of ethylene with 1,9-decadiene using dimethylsilyl (N-tert-butylamido) (tetramethylcyclopentadienyl) titanium dichloride (CGC)/MAO.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Original rate constants (^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>-2.92</td>
<td>-</td>
<td>$k_a = \alpha(k_1, k_2)$</td>
</tr>
<tr>
<td>$k_2$</td>
<td>25.2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$k_3$</td>
<td>2.58 ± 0.08</td>
<td>-</td>
<td>$k_t = \alpha(k_3, k_4)$</td>
</tr>
<tr>
<td>$k_4$</td>
<td>17.2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$k_5$</td>
<td>10.91 ± 0.95</td>
<td>-</td>
<td>$k_{dp} = \alpha(k_5, k_6)$</td>
</tr>
<tr>
<td>$k_6$</td>
<td>30.12 ± 2.10</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$k_7$</td>
<td>7.56 ± 0.07</td>
<td>-</td>
<td>$k_{p_{1_1}} = \alpha(k_7)$</td>
</tr>
<tr>
<td>$k_{p_{12}}$</td>
<td>2039.8 ± 54.7</td>
<td>L mol(^{-1}) s(^{-1})</td>
<td></td>
</tr>
<tr>
<td>$k_b$</td>
<td>908.7 ± 69.0</td>
<td>L mol(^{-1}) s(^{-1})</td>
<td></td>
</tr>
<tr>
<td>$E_{ap}$</td>
<td>20520.0</td>
<td>J mol(^{-1})</td>
<td></td>
</tr>
<tr>
<td>$MM_M$</td>
<td>28.05</td>
<td>g mol(^{-1})</td>
<td></td>
</tr>
<tr>
<td>$MM_D$</td>
<td>138.254</td>
<td>g mol(^{-1})</td>
<td></td>
</tr>
<tr>
<td>$\rho_{PE}$</td>
<td>940</td>
<td>g L(^{-1})</td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>8.31451</td>
<td>J mol(^{-1}) K(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) $k_i = \alpha(k_j, k_y)$ represents $k_i$ as a function of $k_j$ and $k_y$.  

124
7.2 Experimental equipment and setup

Materials

Methylaluminoxane (MAO, 10 wt % in toluene), anhydrous ethyl alcohol (≥ 99.5 %), toluene anhydrous (99.8 %), 1,9-Decadiene (98 %), triisobutylaluminum (TIBA) (25 wt % in toluene), n-butyllithium solution (2.5 M in hexane), sodium (≥ 99 %, stored in mineral oil) were provided by Sigma-Aldrich (USA). Dimethylsilyl (n-tert-butylamido) (tetramethylcyclopentadienyl) titanium dichloride (CGC) (85.0-99.8 %) was acquired from Boulder Scientific (USA). Nitrogen (> 99.998 %) and ethylene were provided by Praxair (USA).

Polymer Synthesis

Prior polymerization, six cycles of nitrogen venting and vacuuming at 125 °C were applied in the reactor to remove oxygen. Then, the reactor received 150 mL of toluene and 0.5 g of triisobutylaluminum (impurity scavenger), and the temperature increased to 120 °C and kept constant for 20 minutes.

For homopolymerization, after reactor purging, 150 mL of toluene was charged into the reactor at ambient temperature. A solution of MAO was added to the reactor through a cannula under nitrogen pressure. The reactor was then heated until the reaction temperature was achieved (120, 130 or 140 °C). Then, ethylene was injected into the reactor until the solvent get saturated. After stabilizing the reactor temperature, the catalyst solution was added into reactor under nitrogen pressure. During polymerization, the reactor temperature remained constant, it only varied ± 0.15 °C from the given set point. Ethylene was supplied on demand, keeping a constant reactor pressure (at 120 psig). When the final reaction time was achieved, the ethylene supply valve was closed, and immediately the reactor contents were blowing out into a 1 L beaker with
100-250 mL of ethanol. Afterwards, the polymer was kept overnight under constant stirring, then filtered and dried in an oven. The copolymerization procedure was analogous to the homopolymerization procedure. The unique difference regards the fact that, after adding MAO to the reactor, the co-monomer solution was injected into the reactor following the same procedure used to feed MAO. Figure 7.1 presents a schematic of the experimental unit.

It is noteworthy to comment that average properties and the molecular weight distributions of the polymer samples were measured using a Polymer Char High-Temperature Gel Permeation Chromatographer (GPC) calibrated with polystyrene narrow standards and using a universal calibration curve in accordance with the methodology described by Soares & McKenna (2013). The GPC was operated at 140 °C, using 1,2,4-trichlorobenzene as solvent, with a flow rate of 1 mL.min⁻¹.

![Figure 7.1. Experimental unit for polyolefin synthesis, schematic. Adapted from Brandão (2017).](image-url)
The molar concentration and total amount of monomer, obtained using Peng-Robinson to calculate fugacity and UNIQUAC to determine the activity coefficients in liquid phase, are presented in Table 7.3. In addition, Table 7.4 enlists the initial polymerization conditions considered in the current investigation. The interested reader is encouraged to consult the original publication for more details in regard to the experimental setup, experimental apparatus and description of the process (Brandão et al., 2017a).

**Table 7.3.** Ethylene concentration and total moles of ethylene in toluene at different temperatures.

<table>
<thead>
<tr>
<th>T, [°C]</th>
<th>[C₂H₄], [mol L⁻¹]</th>
<th>[M], [mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>0.49472</td>
<td>0.07420</td>
</tr>
<tr>
<td>130</td>
<td>0.43732</td>
<td>0.06560</td>
</tr>
<tr>
<td>140</td>
<td>0.38141</td>
<td>0.05721</td>
</tr>
</tbody>
</table>

**Table 7.4.** Initial conditions for simulations and experiments.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Homopolymerization</th>
<th>Copolymerization</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(0)</td>
<td>0.767 × 10⁻⁶ × V(0)</td>
<td>0.271 × 10⁻⁶ × V(0)</td>
<td>0.271 × 10⁻⁶ × V(0)</td>
</tr>
<tr>
<td>C*(0)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>DC(0)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>D(0)</td>
<td>0</td>
<td>0.3 ÷ MM₉</td>
<td>0.4 ÷ MM₉</td>
</tr>
<tr>
<td>(m)(0)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(d)(0)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(lcb)(0)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>μ₀(0)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>μ₁(0)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>μ₂(0)</td>
<td>0</td>
<td>0</td>
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<td>V(0)</td>
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7.3 Online estimation of significant kinetic parameters

The assembly of the implemented strategies is summarized in Figure 7.2. Initially, the global sensitivity analysis provides information on the most important parameters of the polymerization system. Once these parameters are identified, the proposed framework seeks to estimate their values asynchronously, updating/estimating the parameters whenever measurements are available. Different types of estimators are considered. In addition, monitoring and signal processing are other challenges to be resolved by the proposed methodology. The estimated properties are expected to be close to experimental and theoretical values, and noise reduction of measurements is anticipated to occur.

![Flowchart](image)

**Figure 7.2.** Framework for the online estimation of significant kinetic parameters.
7.3.1 Parameter selection: global sensitivity analysis

From the global sensitivity analysis (explained in Appendix A1) of seven kinetic parameters ($k_{1-7}$), the fifth and seventh parameters show the highest sensitivity overall as portrayed in Figure 7.2. This result is consistent because $k_7$ is the exponent in the pre-exponential propagation rate constant ($k_{0p} = 10^{k_7}$) of the Arrhenius equation. The propagation rate constant determines the monomer consumption rate; thus, it has a high influence on the $F_M$ demand in order to maintain the concentration of ethylene constant as previously stated. The rate constant for the living chain (catalyst) deactivation ($k_{dP}$) is a function of $k_5$ (as defined in Table 7.2), because $k_{dP}$ has influence in the moment equations of the model, it is expected that this parameter is influential as well. Moreover, these results are in accordance with the work of Brandão et al. (2017a), since $k_5$ and $k_7$ belong to the parameters set classified by the authors as significant parameters when an identifiability analysis was applied over the seven parameters. Figure 7.3a illustrates the first-order sensitivity indices, and Figure 7.3b the total sensitivity. The total evaluation considered for the global sensitivity analysis were 100 samples.

![Figure 7.3](image-url)

**Figure 7.3.** Global sensitivity indices: (a) first-order sensitivity index; (b) total sensitivity index.
7.3.2 Homopolymerization

The identified significant kinetic parameters are estimated online using an extended Kalman filter (EKF) based on the EKF proposed by Tatiraju & Soroush (1997), a variation of the geometric observer (GO) for parameter estimation that uses a preconditioner (incomplete LU factorization) for normalization as explained in Chapter 4 Section 3.3, and the data-driven strategy referred as the retrospective cost model refinement (RCMR) algorithm explained in Chapter 4 Section 4. In the case of the iLU-GO and RCMR, both estimation strategies require the predefinition of some features previous their implementation. These particular set-ups are discussed next:

*iLU-GO for parameter estimation*

The objective of combining the GO with a preconditioner is to reduce the condition number of the system. The observer is implemented following the algorithm proposed in Eq. (4.21a-b), and its structure is as follows:

\[ \hat{z} = [\hat{k}_7, \hat{k}_5], \text{ } h_z = [h_1], \text{ } \Phi = [h_1, L_f h_1], \text{ } K_z = \begin{bmatrix} B_1 \\ 0 \end{bmatrix}, \text{ } B_1 = [k_{11} \text{ } k_{12}] \]

\[ \Omega = \frac{\partial \Phi}{\partial z} = \begin{bmatrix} \frac{\partial h_1}{\partial k_7} & \frac{\partial h_1}{\partial k_5} \\ \frac{\partial L_f h_1}{\partial k_7} & \frac{\partial L_f h_1}{\partial k_5} \end{bmatrix} \]

Similarly as evaluated in Chapter 6 Sections 6.1 and 6.2, observability indices are required to verify the robustness of the system. To confirm the impact of the preconditioner to the observability indices, the condition number for both the GO and the iLU-GO are compared. For the GO only, these calculations are applied to the exponential observability matrix, and for the
iLU-GO for the inverse of the product of the preconditioner and the inverse of the exponential observability matrix to evaluate the performance under fair conditions. The condition number measures the sensitivity of the structure to measurement and modelling errors.

The evolution of the condition number is computed for both observers using the homopolymerization experimental data at different temperatures (120 °C, 130 °C and 140 °C). Figure 7.4 illustrates the time evolution of the condition number for the GO and iLU-GO. Clearly, the inclusion of the preconditioner improves the stability of the system.

![Condition number evolution](image)

**Figure 7.4.** Condition number of the observability matrix for homopolymerizations at 120 °C (dashed line), 130 °C (dot-dashed line), 140 °C (continuous line) for: (a) GO, and (b) iLU-GO.

The condition number of the iLU-GO shows initially a peak but later converges to a condition number ~ 7-8 in all cases. The condition number evaluation leads to the conclusion that the iLU-GO might be more robust than the GO only.

*RCMR algorithm for parameter estimation*

The implementation of the RCMR algorithm relies on the estimation algorithm introduced in Chapter 4 Section 4. Similarly, the homopolymerization experiments at different reaction
temperatures permit the initial assessment and evaluation of the RCMR algorithm, which is implemented as follows:

\[ P_0 = R_\theta^{-1}, \theta_0 = 0, \text{ and } n_c = 0. \]

For the RCMR algorithm two configurations are evaluated, the estimation of only \( k_7 \) and both \( k_5 \) and \( k_7 \) simultaneously. For the proposed comparison under fair conditions, the second configuration is compared with the EKF and iLU-GO.

In the first configuration for estimating the parameter \( k_7 \) and consequently \( k_{p11} \), a fast initial convergence is required because in this case the parameter is assumed to be unknown and it starts at 0 initial value. It is assumed that \( l_x = 2 \), which means that two parameters are estimated rather than one. For the unestimated parameter, a constant value of \( \hat{z} = 11.3 \) provides a satisfactory response and tradeoff during the estimation. With these considerations, the implemented architecture uses \( n_f = 2 \) so that \( l_\theta = 2, \lambda = 0.999, \) and

\[ G_f(q) = \left[ \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right] \frac{q}{q^2} + \left[ \begin{array}{cc} 0 & 1 \\ q & 0 \end{array} \right] \]

For estimating a single parameter, \( R_\theta = 0.01I_{l_\theta} \), and \( R_e = 0.1 \). Furthermore, for estimating \( k_5 \) and \( k_7 \), and consequently \( k_{dP} \) and \( k_{p11} \) the same architecture implemented during the single parameter estimation is utilized with the distinction that the parameters are estimated in separate channels using the same error signal. Nevertheless, the arbitrary unestimated parameters are different and are as follows: \( \hat{z}_{k_5} = 23.5 \), and \( \hat{z}_{k_7} = 15.0 \) while everything else remains the same.
**Comparison between EKF, iLU-GO, and RCMR algorithm**

For the comparison of the three different estimation strategies, the validated nonlinear model, EKF, iLU-GO and RCMR are implemented in MATLAB R2015a. The differential equations of the model in MATLAB® are solved using ode23s (Shampine & Reichelt, 1997), which is based on a modified Rosenbrock formula of order 2.

Among the implemented parameter estimation strategies, the RCMR algorithm is the only one that has the ability of estimating unknown parameters from an initial value of 0. The other strategies (EKF and iLU-GO) require to initiate close to the real value of the parameter; otherwise, they fail to converge. Moreover, Figure 7.5, Figure 7.6, and Figure 7.7 illustrate the results of the homopolymerization experiments. Results on signal processing of $F_M$, portrayed in literal (a), demonstrate the ability of the algorithms in dynamic data reconciliation. An observed correlation of $F_M$ is that as the temperature increases, the oscillations of the measured signal increase as well, which is particularly captured by the RCMR algorithm. Following this idea, as uncertainty increases with temperature the iLU-GO shows a better competence on estimating properties at a higher uncertainty (140 °C). As mentioned previously, the RCMR algorithm has a better convergence of the estimated parameters as demonstrated in litterals (b) and (c). Finally, in terms of the estimation of other properties that are not measured online ($M_w$ and $M_n$) the results are divided. At lower temperatures, the RCMR algorithm shows adequate ability for estimating $M_w$ and $M_n$, and at higher temperatures, the iLU-GO has better ability for estimating $M_w$ and $M_n$; nevertheless, the inclusion of the estimators appears to be detrimental and to underperform when compared with the validated nonlinear model. In this sense, the most interesting characteristic is the ability observed in the RCMR algorithm for estimating completely unknown parameters. For this reason, the RCMR is explored more in detail next.
Figure 7.5. Homopolymerization at 120 °C. Experimental measurements (blue circles), nonlinear model (dashed lines), estimated (continuous line) by EKF (red), iLU-GO (gold), and RCMR (green). (a) $F_M$, (b) $k_5$, (c) $k_7$, (d) $M_w$, and (e) $M_n$. 
Figure 7.6. Homopolymerization at 130 °C. Experimental measurements (blue circles), nonlinear model (dashed lines), estimated (continuous line) by EKF (red), iLU-GO (gold), and RCMR (green).
(a) $F_M$, (b) $k_5$, (c) $k_7$, (d) $M_w$, and (e) $M_n$. 
Figure 7.7. Homopolymerization at 140 °C. Experimental measurements (blue circles), nonlinear model (dashed lines), estimated (continuous line) by EKF (red), iLU-GO (gold), and RCMR (green). (a) $F_M$, (b) $k_5$, (c) $k_7$, (d) $M_w$, and (e) $M_n$. 
RCMR algorithm for homopolymerizations

The RCMR algorithm is tested for homopolymerization experiments estimating $k_7$ only, and $k_5$ and $k_7$ simultaneously. Figure 7.8 shows the results of the estimated $k_7$ and $k_{p_{11}}$ at different reaction temperatures. The estimated parameters converge in all cases close to theoretical values.

**Figure 7.8.** Estimation of a single significant parameter. Comparison between theoretical (dashed line), and estimated kinetic parameters (continuous line) at 120 °C (blue), 130 °C (green), 140 °C (orange): (a) Dynamic estimation of $k_7$; (b) Dynamic estimation of $k_{p_{11}}$.

Figure 7.9 shows the results of the estimated $k_5$, $k_{dP}$, $k_7$, and $k_{p_{11}}$ at different reaction temperatures. In all cases the estimated parameters ($k_5$, $k_7$) arise close to theoretical values, converging from an initial value of 0 in both cases. A noisy performance is observed similar to Figure 7.8, which can be attributed to the presence of impurities that could not be removed during the experiment preparation, or to the occurrence of side reactions not contemplated within the fundamental model. In addition, as the reaction temperature increases, the estimated parameters get more sensitive to noise, which provides the insight that temperature is proportional to the noise/uncertainty of the experimental data.
Figure 7.9. Estimation of two significant parameters. Comparison between theoretical (dashed line), and estimated kinetic parameters (continuous line) at 120 °C (blue), 130 °C (green) 140 °C (orange): (a) Dynamic estimation of $k_5$; (b) Dynamic estimation of $k_{dP}$; (c) Dynamic estimation of $k_7$, (d) Dynamic estimation of $k_{p_{11}}$.

Figure 7.10 illustrates the ability of the RCMR for both estimating the $\hat{F}_M$, and reducing the measurement’s noise. The reader should notice that it takes some time to the estimated $\hat{F}_M$ to achieve its expected value. Goel & Bernstein (2018a; 2018b) explain that the unknown parameter moves toward different subspaces until it tends toward the subspace spanned by $N_1^T$. In addition, there is a delay time difference between the estimated $\hat{F}_M$ with a single and two significant parameters mostly related to the tuning conditions. Finally and as stated before, the $\hat{F}_M$ in the highest evaluated temperature (140 °C) shows oscillatory response.
Figure 7.10. Comparison of the monomer flow rate ($F_M$) between the experimental values (circles), fundamental model (dashed line), estimated with a single parameter (continuous red line), and estimated with two parameters (continuous green line) at: (a) 120 °C, (b) 130 °C, (c) 140 °C.
Figure 7.11 provides a comparison between calculated, measured and estimated average properties at different polymerization temperatures. Results at 120 °C of both estimated properties ($M_w$ and $M_n$) are very close to theoretical and experimental values, but as temperature increases the uncertainty increases as well. Nevertheless, the estimation of two parameters simultaneously appears to provoke less reliable results when compared to the estimated properties with a single parameter, especially at higher temperatures.

![Figure 7.11](image)

**Figure 7.11.** Comparison of the final average properties at different temperatures for experimental values (circles), fundamental model (squares – dashed line), estimated with a single parameter (triangles – continuous line), and estimated with two parameters (diamonds – continuous line): (a) weight-average molecular weight ($M_w$); (b) number-average molecular weight ($M_n$).

### 7.3.3 Copolymerization of ethylene with 1,9-decadiene (RCMR)

Following the same criterion as in the homopolymerization experiments, the copolymerizations use the same RCMR architecture for the estimation of significant kinetic parameters and important polymer properties. Indeed, the criterion extends to the application of the same channels for estimating one and two significant kinetic parameters and their resulting properties.
The copolymerization experiments consider only one temperature condition. Initially, \( k_7 \) and consequently \( k_{p_{11}} \) are estimated for the copolymerizations described in Table 7.4 (A & B). Figure 7.12 illustrates the results of the estimated \( k_7 \) and \( k_{p_{11}} \) at 120 °C and different initial diene concentrations. The unknown parameter converges towards the theoretical value without requiring prior knowledge at both initial diene concentrations.

**Figure 7.12.** Estimation of a single significant parameter. Comparison between theoretical (dashed line), and estimated kinetic parameters (continuous line) at different initial diene concentrations for the copolymerization experiment A (purple), and copolymerization experiment B (gold): (a) Dynamic estimation of \( k_7 \); (b) Dynamic estimation of \( k_{p_{11}} \).

Moreover, the parameters \( k_5 \) and \( k_7 \), and, consequently, \( k_{dP} \) and \( k_{p_{11}} \) are estimated simultaneously. The same architecture and tuning used during the homopolymerizations is applied. Figure 7.13 shows the results of the estimated \( k_5 \), \( k_{dP} \), \( k_7 \), and \( k_{p_{11}} \) at different initial diene concentration and 120 °C. Clearly, in all cases, the unknown parameters \( k_5 \) and \( k_7 \) achieve close to theoretical values, converging from an initial value of 0. An interesting observation in these experiments is a slight decrease trend (negative slope) of the parameters, evinced clearer in the dynamic evolution of \( k_{dP} \) and \( k_{p_{11}} \). The reason of this behavior might be related to LCBs formation during the copolymerization. The presence of LCBs in the living chains might cause a
steric hindrance to the incorporation of ethylene molecules, which disfavors the deactivation and propagation reactions. However, this hypothesis must be proved by additional experiments and further simulations.

![Figure 7.13. Estimation of two significant parameters. Comparison between theoretical (dashed line), and estimated kinetic parameters (continuous line) at different initial diene concentrations for the copolymerization experiment A (purple), and copolymerization experiment B (gold): (a) Dynamic estimation of $k_7$; (b) Dynamic estimation of $k_{p_{11}}$; (c) Dynamic estimation of $k_5$; (d) Dynamic estimation of $k_{d_P}$.](image)

Figure 7.14 demonstrates the ability of the RCMR for estimating the $F_M$ and reducing the measurement’s noise. Likewise before, it takes some time to the estimated $F_M$ to achieve values close to experimental and theoretical. There are not visible differences to point when the initial concentration of diene varies, which permits to observe that temperature is more influential to the reaction behavior. In contrast to the homopolymerization results (Figure 7.10), the estimated $F_M$
in the copolymerization experiments shows a higher delay time of convergence. It could be argued that it should be influenced by the increase of the complexity of modelling, but because the RCMR algorithm is purely a data-driven strategy, that does not require information on the nonlinear model, the reasons must be totally related to the nature of the experiment.

**Figure 7.14.** Comparison of the monomer flow rate \( F_M \) during copolymerization between the experimental values (circles), fundamental model (dashed line), estimated with a single parameter (continuous red line), and estimated with two parameters (continuous green line) at different initial diene concentrations: (a) copolymerization experiment A, (b) copolymerization experiment B.

Finally, Figure 11 portrays a comparison between calculated, measured and estimated average properties of the copolymerization experiments at different initial diene concentrations. Data on the average properties was obtained during the reaction. Results show the RCMR algorithm,
besides computing the unknown parameters, it is capable of estimating $M_n$ satisfactorily using the error signal obtained as the difference between estimated and measured $F_M$. This only signal permits the estimator to gain enough knowledge on the system to estimate $M_n$. On the other hand, $M_w$ achieves a similar dynamic when compared to the fundamental model, but the estimates fail to attain perfect values close to the experimental measurements.

**Figure 7.15.** Comparison of average polymer properties at different initial diene concentrations between experimental values (circles), fundamental model (dashed line), estimated with a single parameter (red continuous line), and estimated with two parameters (green continuous line). (a) weight-average molecular weight ($M_w$) for copolymerization A; (b) number-average molecular weight ($M_n$) for copolymerization A; (c) weight-average molecular weight ($M_w$) for copolymerization B; (d) number-average molecular weight ($M_n$) for copolymerization B.
7.4 References


8 CONCLUSIONS AND FUTURE PERSPECTIVES

8.1 Conclusions

Different model-centric smart manufacturing strategies were designed, adapted, and evaluated using experimental data from two different polymerization systems. The combination of various computational tools provided redundancy, flexibility, and high adaptability while making the underlying mechanistic model more reliable. Once the model was consistent, different optimal policies were designed, advance control elements were developed, and nonlinear observers constructed for signal processing and property estimation.

The first system under study was the synthesis of polyacrylamide in aqueous solution using potassium persulfate as initiator in a semi-batch free-radical polymerization reactor. In this system, the proposed framework integrated nonlinear modelling, dynamic optimization, advanced control strategies, and nonlinear state estimation. The main aims included the achievement of target polymer characteristics through control while reaching a complete polymer monitoring. Overall, the estimated properties provided by the state observers were closer to experimental measurements, and there is a visible noise reduction in all measurements. Initially, a hybrid discrete-time extended Kalman (h-DEKF) filter was assessed and implemented to improve the control action. Thereafter, closed-loop response was tested, and experimental results provided satisfactory outcomes. The control action (as explained in Chapter 6) showed an improvement of 42% of set-point achievement in average, indicating that to include a nonlinear observer for signal processing combined with feedback control is beneficial. In addition, other state estimation strategies where studied. The best identified geometric observer (GO) structure (4-state GO with passive structure) demonstrated a superior nonlinear estimation ability of the final polymer
distribution. It showed an improvement of 52% when compared with the previously implemented $h$-DEKF.

The second evaluated system was the copolymerization of ethylene with 1,9-decadiene using dimethylsilyl (N-tert-butylamido) (tetramethylcyclopentadienyl) titanium dichloride (CGC)/MAO as catalyst in semi-batch operation. For this system, initial steps included the validation of the nonlinear model, and a global sensitivity analysis to identify the most important kinetic parameters of the system with respect to the available measurement (flow rate of monomer). Afterwards, three different parameter estimators were implemented and contrasted on their ability of estimating online the significant kinetic parameters of the system, and the ability of estimating other properties of interest. The implemented strategies were an extended Kalman filter (EKF), a variation of the GO that uses a preconditioner (incomplete LU factorization), and the retrospective cost model refinement (RCMR) algorithm. From these methodologies, the RCMR algorithm demonstrated very interesting capabilities of estimating unknown kinetic parameters which started from an initial value of 0. The RCMR was evaluated more in detail and tested for the estimation of one and two kinetic parameters.

8.1.1 Control strategies in polymerization

In Chapter 3, advanced control strategies were studied for polymerization systems. Particularly, linearizing control and the consequent design of nonlinear controllers relying on the previous knowledge of a mechanistic model was addressed. For the evaluated system it was observed that when manipulating the reactor temperature or the monomer flow rate to control the total amount of monomer the relationship holds a relative degree of 1. Moreover, when manipulating the initiator flow rate to control the total amount of monomer or the weight-average molecular weight, the relative degree is 2. However, a more promising pairing that considers the
monomer flow rate as manipulated variable and the weight-average molecular weight as control objective appears to be unfeasible using direct feedback due to the expected high relative degree on the nonlinear controller. In addition, even when the control objective is accomplished, other properties of interest were not achieved due to the uncertainties of the system, which were modeled in this case by incorporating randomness to the kinetic parameters.

To overcome this obstacles and taking advantage of the availability of the ACOMP system as smart sensor, a linear feedback controller (PID control) was incorporated. The controller was coupled with a nonlinear observer that performs signal processing of the measured control objective which follows a type of model-based strategy that makes use of a linear controller. This setup represents a simple solution of a complex control problem (supported by the Ockham Razor's perspective) (Hoffmann et al., 1996). All in all, results demonstrate effectiveness in achieving the control objectives as well as good performance.

8.1.2 Nonlinear state estimation in polymerization

During the operation of polymerization reactors, the complete state vector as well as other polymer properties are sporadically measured. Most of the time, the number of possible observations is lower than the number of states (or parameters), and the available measurements are often contaminated by noise. Thus, state (or parameter) estimation becomes a critical task that seeks the improvement of the quality of the actual observations by reducing their noise as well as for predicting unmeasured properties during operation. Nonlinear observers, take into account disturbances from the experimental data (e.g., impurities, experimental errors, and less frequent side reactions) that might not be captured by the mechanistic model alone. In this sense, observers contribute in using the available data to correct the underlying mathematical model which is crucial in model-based strategies. In this doctoral dissertation four types of nonlinear estimators were
incorporated into smart manufacturing frameworks, representing innovative contributions to the existing literature in this matter.

A hybrid discrete-time extended Kalman (h-DEKF) filter was proposed. The particularity of this filter is that the initialization relies on an auto-tuned error-driven strategy which in other words signifies that the filter free-parameters (diagonal values of the covariance error matrix of the model and the measurements, and the initial covariance error matrix) are established from the model and measurement errors. The measured errors are set while the model errors are obtained through the tuning of the filter using a stochastic global optimization algorithm that seeks optimal model errors. The h-DEKF demonstrated a robust performance and high ability in filtering the noise of the measurements, but manifests difficulties in estimating unmeasured properties of interest. This particularity motivated the search of another type of nonlinear state estimation strategy.

Different structures of the geometric observer (GO) by Alvarez & Fernández (2009) were assessed and evaluated under a set of different operating conditions. High to low order structures and variations of innovated states were analyzed using the criteria of observability indices: the minimum singular value and the condition number. In this case, the selection of the observer focused on guaranteeing a good tradeoff between performance and accuracy of the final polymer distribution (estimated values contrasted with measured values). Adequate tools for structure analysis in conjunction with physical insight provided valuable information to identify the most promising observer architecture. It was concluded that the 4-state GO with passive structure is the best performing GO overall. It is important to mention that the measurement errors bring instability to the systems, which was overcome by reducing the order of the observer and incorporating the passive assembly.
The GO in conjunction with a pre-conditioner (incomplete LU decomposition) was assessed for the online estimation of significant parameters. The iLU decomposition is observed in numerical simulation of oil reservoirs (Forsyth & Sammon, 1986). The incorporation of this preconditioning strategy contributed to reduce the condition number of the system, and showed competent performance in uncertain systems that have high noise in the measurements. In terms of the tuning of the iLU-GO, it is interesting to notice that high frequency tuning has the same (or very similar) response. Also, in all cases the iLU-GO has a smooth performance.

Finally, the RCMR algorithm, a strategy never implemented in polymerizations or chemical engineering problems, permitted the estimation of the significant kinetic, which were assumed to be unknown. After verifying consistency, the proposed strategy was tested in the copolymerization of ethylene with 1,9-decadiene at different diene concentrations. Overall, results were satisfactory, showing not only adequacy in signal processing but also in property estimation. The usage of data-driven algorithms such as the RCMR represents a paramount that could permit an easier estimation of parameters of nonlinear systems, as those observed in polymer synthesis. Disturbances from the experimental data (e.g., impurities, experimental errors, and less frequent side reactions) that might not be captured by the fundamental model could be overcome by applying this strategy.

8.1.3 Model-centric smart manufacturing frameworks

Smart manufacturing frameworks governed by mechanistic models depend on a proficient and continuous connectivity of the different components. In the case of polymerization processes by integrating process data (measurements) and high-fidelity models through nonlinear state observers not only better estimates are expected, but also a more adequate control action. The final goal is that target polymers are feasible during synthesis while complete understanding of polymer
characterization is possible (monitoring). In our practice, two frameworks were developed generally speaking and the conclusions of each one are explained in the following paragraphs.

The first framework was the most complete one (Figure 5.2). It integrates dynamic optimization, an auto-tuned error-driven h-DEKF as nonlinear state estimator, and feedback control. It used the online measurements of the ACOMP system (smart sensor), and it was integrated in two levels, online and offline. In the offline layer different design and optimization tools were utilized. For instance, gPROMS and its components gEST and gOPT allowed a profound manipulation of the model seeking reliability and optimality. Moreover, the software MATLAB® allowed the easy incorporation of metaheuristic algorithms for further optimization, filter tuning, and extra manipulations of the nonlinear model (e.g., control action). In the online layer, the platform Python permitted the development of an in-house module to connect the smart sensor (and through it the pilot plant) with the module providing full functionality and connectivity as well as expanding the sensor capabilities. These initial steps comply with the advent of smart manufacturing super structures that will require seamless connectivity towards the production of high quality plastic materials.

The second framework (Figure 7.2) focuses on improving the monitoring capabilities of polyolefin polymerization processes. In this case the framework incorporates a global sensitivity analysis of kinetic parameters, and the estimation of the selected parameters using three strategies an EKF, iLU-GO, and the RCMR algorithm. It is interesting to observer the response of the estimates, especially when using the RCMR algorithm, with only one online measurement. The framework aimed to improve monitoring through the integration of an observer and the validated fundamental model.
8.2 Future directions

Future directions in this field include the incorporation of more detailed mechanistic polymerization models (as virtual plants, probably modelled in Aspen Plus® or similar environments) able to run simultaneously with the actual plant in real-time, and provide support at different levels (resembling hierarchical control) embracing optimization of operating conditions, detection of outliers (operational deviations), and to serve as bridge with higher decision making levels. However, a crucial threshold that requires particular attention is the communication between all sensors (including smart and soft sensors), the mechanistic model and other tools such as nonlinear observers, controllers, and optimizers. On top of that, and following up with the IoT concept, a library of different polymerization models will be useful for polymer manufacturers. This knowledge sharing might bring higher efficiency among the industry. Finally, another important paradigm shift is the use of big data analytics. Indeed, data-driven strategies (Corbett & Mhaskar, 2016) have high potential in polymer synthesis because they have the power of understanding deeply different hidden correlations that have not been observed yet in production facilities.

8.2.1 Data-driven smart manufacturing frameworks

Data-driven strategies have the capability of making adequate use of all the data from the DCS (measurements or observations) collected in polymer manufacturing towards the production of target materials efficiently while contributing in fault detection, property shift recognition and energy efficiency. With the advent of smart sensors such as the ACOMP system, the task of generating high-quality polymeric materials might not even require the formal understanding of mechanistic modelling. However, a mathematical model that describes the underlying process will
always represent an advantage as it permits the exploration of various operating conditions or resultant properties without the need of an experimental setup.

8.3 References


APPENDIX: ADDITIONAL INFORMATION

A.1 Significant parameter selection: global sensitivity analysis

A global sensitivity analysis shows how significant input values (parameters or state variables) are with respect to one or various output values. A robust and widely utilized variance-based sensitivity analysis technique is the Sobol method (Sobol, 1993). This method proposes the expansion of a function \( G = g(z_1, \ldots, z_q, \ldots, z_Q) \) into terms of increasing dimensions with mutually independent input parameters, defined as a \( Q \)-dimensional cube, such that all summands are mutually orthogonal, as explained in Eq. (A1.1).

\[
G = g_0 + \sum_{q=1}^{Q} g_q(z_q) + \sum_{1 \leq q < b \leq Q} g_{qb}(z_q, z_b) + \cdots + g_{1,2,\ldots,Q}(z_1, \ldots, z_Q) \tag{A1.1}
\]

where, the index \( q \) denotes an individual parameter of interest, \( b \) another parameter, and \( Q \) is the total number of evaluated parameters. Each term in Eq. (A1.1) has quadratic integrability over the domain of existence, where \( g_0 \) is a constant, \( g_q = g_q(z_q) \), \( g_{qb} = g_{qb}(z_q, z_b) \), and so forth.

Eq. (A1.2) shows the decomposition of the variance of \( G \).

\[
V(G) = \sum_{q=1}^{Q} V_q + \sum_{1 \leq q < b \leq Q} V_{qb} + \cdots + V_{1,2,\ldots,Q} \tag{A1.2}
\]

where, \( V_q, V_{qb}, V_{1,\ldots,q,\ldots,Q} \) are the individual variances of functions \( g_q, g_{qb}, g_{1,\ldots,q,\ldots,Q} \).

Sensitivity indices help understand the variance decomposition from Eq. (A1.2). First-order sensitivity indices \( \hat{S}_q \) permit the selection and classification of the most sensitive parameters, depending on the individual importance of their contribution in changing the variance of the function of interest. The main effect of varying parameter \( z_q \) on the output value \( G \) is measured by
\( \hat{S}_q \), as presented in Eq. (A1.3). In addition, the total sensitivity index (\( \hat{S}_{Tq} \)) incorporates the sum of all the effects that involve the parameter \( z_q \). The total sensitivity index for parameter \( z_q \) is computed as indicated in Eq. (A1.4).

\[
\hat{S}_q = \frac{\hat{V}_q}{V} \tag{A1.3}
\]
\[
\hat{S}_{Tq} = 1 - \frac{\hat{V}_{-q}}{V} \tag{A1.4}
\]

where, \( \hat{V}_{-q} \) is the sum of all variance terms that exclude \( z_q \).

\( \hat{S}_q \) and \( \hat{S}_{Tq} \) can be compared to evaluate whether a model is additive or not. For non-additive models \( \hat{S}_q < \hat{S}_{Tq} \); for additive models \( \hat{S}_q = \hat{S}_{Tq} \). Additive models are those in which no interactions between evaluated parameters occur (Cosenza et al., 2014).

The Sobol standard method can be improved by introducing sampling and resampling matrices (Saltelli, 2002; Saltelli et al., 2008), and even better performance is achieved when the results of the evaluated functions are averaged, creating extra data points (Wu et al., 2012). In this study, we used an improved version of Sobol’s method, as implemented by Salas et al. (2017), including a third sampling matrix to avoid unfeasible scenarios. The method follows the steps below:

1) Define an objective function, and the dimension \( (N) \) for a sample of input parameters. For each parameter, define an uncertainty index. In this case, we adopted 4% of change with respect to the mean value.

2) Build three random matrices, \( M_1 \), \( M_2 \) and \( M_3 \), Eq. (A1.5a) to Eq. (A1.5c) respectively, of dimension \( N \times Q \) based on the defined uncertainty: \( M_1 \) is the sampling matrix, \( M_2 \) is the
resampling matrix, $M_3$ is the backup matrix, and $Q$ is the total number of parameters to be evaluated.

\[
M_1 = \begin{bmatrix} z_{11} & \cdots & z_{1q} & \cdots & z_{1Q} \\ \vdots & \ddots & \vdots \\ z_{N1} & \cdots & z_{Nq} & \cdots & z_{NQ} \end{bmatrix} \quad (A1.5a)
\]

\[
M_2 = \begin{bmatrix} z_{11}' & \cdots & z_{1q}' & \cdots & z_{1Q}' \\ \vdots & \ddots & \vdots \\ z_{N1}' & \cdots & z_{Nq}' & \cdots & z_{NQ}' \end{bmatrix} \quad (A1.5b)
\]

\[
M_3 = \begin{bmatrix} z_{11}'' & \cdots & z_{1q}'' & \cdots & z_{1Q}'' \\ \vdots & \ddots & \vdots \\ z_{N1}'' & \cdots & z_{Nq}'' & \cdots & z_{NQ}'' \end{bmatrix} \quad (A1.5c)
\]

3) Evaluate the row vectors of matrices $M_1$ and $M_2$. If the output is unfeasible, use the next available feasible row of the matrix $M_3$, and update the matrices to $M_1'$ and $M_2'$, which are the improved sampling and resampling matrices, respectively. Then, calculate the total average ($\hat{g}_0$) of both evaluations as described in Eq. (A1.6).

\[
g_S = g(M_1'), \quad g_R = g(M_2')
\]

\[
\hat{g}_0 = \frac{1}{2N} \sum_{n=1}^{N} (g_S + g_R) \quad (A1.6)
\]

where, $h$ represents the output vector of $M_1'$ and $g_R$ is the output vector of $M_2'$.

4) Generate a matrix $N_q$ formed by all columns of matrix $M_2'$, except the column of the $z_q$ parameter, which is pulled from $M_1'$ as explained in Eq. (A1.7a). Consecutively, generate another matrix $N_{Tq}$ formed with all columns of $M_1'$ and with the column of the $z_q'$ parameter, pulled from $M_2'$ as denoted in Eq. (A1.7b).
\[ N_q = \begin{bmatrix} z_{11} & \cdots & z_{1q} & \cdots & z_{1Q} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ z_{N1} & \cdots & z_{Nq} & \cdots & z_{NQ} \end{bmatrix} \]  
(A1.7a)

\[ N_{Tq} = \begin{bmatrix} z_{11} & \cdots & z_{1q} & \cdots & z_{1Q} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ z_{N1} & \cdots & z_{Nq} & \cdots & z_{NQ} \end{bmatrix} \]  
(A1.7b)

5) Evaluate the row vectors of matrices \( N_q \) and \( N_{Tq} \). If an evaluated function is unfeasible, the output is replaced by \( \hat{g}_0 \). The outputs are obtained in column vectors.

\[ g'_q = g(N_q), \quad g'_{Rq} = g(N_{Tq}) \]

where, \( g'_q \) is the output vector of matrix \( N_q \), and \( g'_{Rq} \) is the output vector of matrix \( N_{Tq} \).

6) A sample generates the following estimates, which are calculated based on scalar products of the vectors from above.

\[ \gamma_q^2 = \frac{1}{2N} \sum_{n=1}^{N} (g_S \cdot g_R + g'_q \cdot g'_{Rq}) \]  
(A1.8)

\[ \hat{V} = \frac{1}{2N} \sum_{n=1}^{N} (g_S^2 + g_R^2) - \hat{g}_0^2 \]  
(A1.9)

\[ \hat{V}_q = \frac{1}{2N} \sum_{n=1}^{N} (g_S \cdot g'_{Rq} + g_R \cdot g'_{Rq}) - \gamma_q^2 \]  
(A1.10)

\[ \hat{V}_{-q} = \frac{1}{2N} \sum_{n=1}^{N} (g_S \cdot g'_q + g_R \cdot g'_{Rq}) - \gamma_q^2 \]  
(A1.11)

where, \( \gamma_q^2 \) the squared mean value of the outputs for each parameter \( z_q \).

The selection of sensitive parameters relies on the first and total sensitivity indices.

Eq. (A1.12) introduces the objective function, defined in this case as:
\[ G = \sum_{k=1}^{k} \frac{y_k - h_k(z)}{\sigma_{y_k}^2} \]  

where, \( y_k \) is the measurement at each interval, \( h_k(z) \) is the calculated measurement, and \( \sigma_{y_k}^2 \) is the variance of the experimental fluctuations. Because \( F_M \) is the only measurement calculated continuously, the global sensitivity analysis is performed to test the sensitivity of the set of kinetic parameters towards \( F_M \).

A.2 References


AUTHOR PUBLICATIONS

The journal paper publications of the author are listed below:


The presentations in national and international conferences of the author are listed below:


VITA

Santiago D. Salas was born in Quito (Ecuador). He graduated from San Gabriel high school and received his Bachelor degree in Chemical Engineering from Universidad Central del Ecuador in 2012. During college, he was active in various student associations, including secretary of the Latin-American Chemical Engineering Students’ Association, president of the Ecuadorian Chemical Engineering Students’ Association, president of the Universidad Central’s Chemical Engineering Student Council, and founder and first president of the AIChe-FIQ-UCE Student Chapter.

He initiated his professional career working as a technical assistant for Petroamazonas EP for one year; thereafter, as a process engineer in TECNA del Ecuador for one and a half years and as a process engineer for GDP at Petroamazonas EP for one year. He has participated in conceptual, basic and detailed engineering for oil & gas projects, including the conceptual and basic engineering of Block 43 (ITT). As a parenthesis, he attended in between to the course of History of European Civilization “Notre Dame de la Clarière” in Creutzwald (France).

After receiving a Fulbright scholarship, he started graduate studies in the Cain Department of Chemical Engineering at Louisiana State University where he joined the Process Systems Engineering group under the supervision of Prof. José A. Romagnoli. In May 2016, he received a Master of Science degree in Chemical Engineering from Louisiana State University, and he expects to receive the Doctor of Philosophy degree in Chemical Engineering with a minor in Industrial Engineering in August 2019. To date, he has been a visiting scholar at the University of Cagliari (Italy), is author of eight journal articles, and his research has been presented at eight major national and international conferences. His motto “be more to better serve”.

162