An approximation to the scale-up of batch processes using phenomenological-based models

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To my family and friends ...

A mi familia y amigos ...
To begin with, I would like to thank the most important persons in my life: my father, my mother, my sister and Tebo. They have always been there for me, supporting and motivating me to progress.

I would also like to express my gratitude to my advisor Professor Hernán Alvarez, for giving me the opportunity of working with him, for his wise words, and for allowing me to grow integrally during these years of working together.

Marce, Sebas and Vivi, thanks for your friendship. Your insightful opinions motivated me to bring out the best of me to accomplish this goal. I feel fortunate to rely on friends like you.

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Abstract

An approximation to the scale-up of batch processes using phenomenological-based models

This work presents a methodology for scaling up Batch Processes (BPs) using a Phenomenological-Based Semophysical Model (PBSM) and the Hankel matrix as tools for maintaining the Operating Regime (OR) at each stage of the process when scaling it up. To do this, a review on the scale-up methods differentiating batch from continuous processing is made, finding that: traditional scale-up approaches do not consider BPs characteristics; many particular successful cases of BPs scale-up have been reported, but no formal procedure has been developed for scaling up these processes; traditional scale-up approaches do not guarantee a good commercial unit design; and a phenomenological-based model of the process is a fundamental tool for carrying out the scale-up task. Taking into account these facts, the proposed scale-up methodology is presented in which a PBSM of the process and an extension of the discrete form of the Hankel matrix to BPs are used for analyzing the dynamic behavior of the process and scaling it up, including the effect of the design variables as a whole over each state variable by computing the State Impactability Index (SII). The latter allows determining the most impacted dynamics (the main dynamics) by scale changes at each stage of the batch and, by means of its calculation, the establishment of the critical point of the Operating Trajectory (OT) at which the batch must be scaled-up. Finally, the methodology is applied to a non-isothermal batch suspension polymerization reactor, finding the scale factors for keeping the same polymer molecular weight when increasing the scale. It is also shown that by means of the SII calculation, it is possible to identify if a process unit is over or under sized.

Keywords: Hankel matrix, scale-up methodology, batch process, operating trajectory, dynamics hierarchy, phenomenological-based model.
En este trabajo se presenta una metodología para escalar Procesos por Lotes (PpL) usando un Modelo Semifísico de Base Fenomenológica (MSBF) y la matriz de Hankel como herramientas para mantener el Régimen de Operación (RdeO) en cada una de las etapas que atraviesa un proceso por lotes. Para ello, se hace una revisión de literatura acerca de los métodos de escalado diferenciando los procesos discontinuos de los continuos, encontrando que: los métodos tradicionales de escalado no consideran las características de los PpL; se han reportado diversos casos particulares de éxito en el escalado de PpL pero no se ha desarrollado un procedimiento formal para escalar estos procesos; los métodos tradicionales de escalado no garantizan que el diseño a escala industrial tenga un buen desempeño; y un modelo de base fenomenológica del proceso es una herramienta fundamental para llevar a cabo la tarea de escalado. Teniendo en cuenta esto, se presenta la metodología de escalado propuesta en la que un MSBF del proceso y la extensión de la forma discreta de la matriz de Hankel a PpL se utilizan para analizar el comportamiento dinámico del proceso y escalarlo, incluyendo el efecto de las variables de diseño como un todo sobre cada una de las variables de estado a partir del cálculo del Índice de Estado Impactable (IEI). Este último permite determinar la dinámica más impactada (la dinámica principal) por los cambios de escala en cada etapa del lote y, por medio de su cálculo, establecer el punto crítico de la Trayectoria de Operación (TdeO) en el cual se debe escalar el lote. Finalmente, la metodología propuesta se aplica a un reactor no isotérmico de polimerización en suspensión por lotes, encontrando los factores de escala para mantener el mismo peso molecular del polímero al aumentar la escala. Se muestra, adicionalmente, que mediante el cálculo IEI es posible identificar si una unidad de proceso tiene tamaño mayor o menor al requerido.

Palabras clave: Matriz de Hankel, metodología de escalado, proceso por lotes, trayectoria de operación, jerarquía de dinámicas, modelo de base fenomenológica.
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<tr>
<td>A</td>
<td>System matrix</td>
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<tr>
<td>B</td>
<td>Input matrix</td>
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<tr>
<td>C</td>
<td>Output matrix</td>
</tr>
<tr>
<td>C</td>
<td>Controllability matrix</td>
</tr>
<tr>
<td>(\mathbf{F})</td>
<td>State variables function vector</td>
</tr>
<tr>
<td>(\mathbf{G})</td>
<td>Output variables function vector</td>
</tr>
<tr>
<td>(\mathbf{H})</td>
<td>Hankel matrix</td>
</tr>
<tr>
<td>III</td>
<td>Input impactability index</td>
</tr>
<tr>
<td>m</td>
<td>Output variables vector dimension</td>
</tr>
<tr>
<td>n</td>
<td>State variables vector dimension</td>
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<td>(\mathcal{O})</td>
<td>Observability matrix</td>
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<td>Output impactability index</td>
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<td>p</td>
<td>Synthesis parameters vector</td>
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<td>(\mathbf{p})</td>
<td>Input variables vector dimension</td>
</tr>
<tr>
<td>r</td>
<td>Matrix rank</td>
</tr>
<tr>
<td>SII</td>
<td>State impactability index</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>(\mathbf{u})</td>
<td>Manipulated variables vector</td>
</tr>
<tr>
<td>U</td>
<td>SVD matrix composed by the left singular vectors</td>
</tr>
<tr>
<td>(u_i)</td>
<td>(l)-th manipulated variable</td>
</tr>
<tr>
<td>(\mathbf{V})</td>
<td>SVD matrix composed by the right singular vectors</td>
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<tr>
<td>(\mathbf{w})</td>
<td>Design-variable-dependent parameters vector</td>
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<tr>
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<td>State variables vector</td>
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<td>(x_k)</td>
<td>(k)-th state variable</td>
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<td>(y_k)</td>
<td>(k)-th output variable</td>
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<tr>
<td>(\mathbf{z})</td>
<td>Design variables vector</td>
</tr>
<tr>
<td>(z_l)</td>
<td>(l)-th design variable</td>
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## Greek letters

<table>
<thead>
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<tr>
<td>(\Sigma)</td>
<td>Singular values matrix</td>
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<tr>
<td>(\sigma_{ii})</td>
<td>(i)-th singular value</td>
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## Subscripts

<table>
<thead>
<tr>
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<tr>
<td>$c$</td>
<td>Continuous system</td>
</tr>
<tr>
<td>$d$</td>
<td>Discrete system</td>
</tr>
<tr>
<td>$f$</td>
<td>Final condition</td>
</tr>
<tr>
<td>$\text{max}$</td>
<td>Maximum value</td>
</tr>
<tr>
<td>$\text{min}$</td>
<td>Minimum value</td>
</tr>
<tr>
<td>$N$</td>
<td>Nominal value</td>
</tr>
<tr>
<td>$o$</td>
<td>Initial condition</td>
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## Superscripts

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$T$</td>
<td>Matrix transpose</td>
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## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>$BP$</td>
<td>Batch Process</td>
</tr>
<tr>
<td>$BPs$</td>
<td>Batch Processes</td>
</tr>
<tr>
<td>$CP$</td>
<td>Continuous Process</td>
</tr>
<tr>
<td>$CPs$</td>
<td>Continuous Processes</td>
</tr>
<tr>
<td>$cs$</td>
<td>Current scale</td>
</tr>
<tr>
<td>$CV$</td>
<td>Capacity Variable</td>
</tr>
<tr>
<td>$ns$</td>
<td>New scale</td>
</tr>
<tr>
<td>$OR$</td>
<td>Operating Regime</td>
</tr>
<tr>
<td>$OT$</td>
<td>Operating Trajectory</td>
</tr>
<tr>
<td>$PBSM$</td>
<td>Phenomenological-Based Semiphysical Model</td>
</tr>
<tr>
<td>$RP$</td>
<td>Reference Point</td>
</tr>
<tr>
<td>$SVD$</td>
<td>Singular Value Decomposition</td>
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CHAPTER 1
Introduction

Process scale-up is an essential task in any industrial activity. It is not possible to build a plant without supporting calculations, studies, and demonstrations of its functioning at a smaller operating scale [1]. In this chapter an introduction to the research addressed in this thesis is presented, highlighting the significance of the scale-up and its main inconveniences when chemical processes are developed at an industrial scale. The chapter is organized as follows: Section 1.1 exposes the motivation toward this research is guided. In Sections 1.2 and 1.3, the research problem and the objectives for conducting this thesis are presented. Also, in Section 1.4, the main accomplishments and publications achieved during the development of the thesis are quoted. Finally, Section 1.5 gathers the thesis outline.

1.1. Motivation

Batch processing is considered to be important in the chemical industry, mainly when low production volumes or a great variety of products within a single process unit are required [2]. Although this kind of processing represents the natural way to increase process capacity from the laboratory to a commercial process unit [3; 4], continuous processing has dominated research works in the scale-up field [5; 6; 7; 8; 9].

Neither particular nor generalizable progress has been reported in the field of chemical processes scale-up. Such processes are still scaled-up using traditional methods that have not changed significantly since the 1960s [10; 11; 12; 13; 14]. Industrial scale-up is dominated by empirical rules, requiring geometrical similarity fulfillment with criteria such as equal tip speed or equal mass transfer coefficients, leading to drawbacks from keeping a single parameter constant [4; 13; 15; 16]. Here, given that some parameters are fixed, the rest ones could change substantially in unforeseen ways [8; 17], resulting in an erroneous commercial unit design requiring additional costs and time to be corrected [10; 18].

Whereas there is no particular literature about how to scale-up Batch Processes (BPs), the same scale-up methods are used for either batch or continuous processes [11; 13; 19; 20]. For batch processing, usually employed by biotechnological [4], pharmaceutical, polymer, food, and specialty chemical industries [21], the combination of scale-up methods such as similarity criteria, dimensional analysis, and rules of thumb are traditionally used to obtain an acceptable unit design at a new operating scale [6; 17; 18; 22]. This fact shows that it does not exist a general rule for scaling up BPs, and that a huge effort and proficiency is required to achieve an adequate outcome of the process at an industrial scale [8; 13; 15], making attractive the study of this thematic.

Finally, an additional prominent motivation for carrying out this thesis is the existence of a work on Continuous Processes (CPs) scale-up, developed by Ruiz and Alvarez [10]. That approach uses a Phenomenological-Based Semiphysical Model (PBSM) as a tool to comprehend the
behavior the process susceptible to be scaled-up, and the Hankel matrix as a tool for analyzing
the process dynamic behavior and increasing its scale by holding the Operating Regime (OR)
through scale changes. The present thesis exploits the potential of this previous approximation,
expanding its field of application to BPs and overcoming its limitations.

1.2. Research problem

During the research and development of a new chemical process, one of the problems that
merits close attention, and often proves to be problematic, is the scale-up of any process unit
[23]. The scale-up risks encountered by an engineer vary depending on the nature of the
system that is being investigated. In practice, no single design protocol can be universally
applied to all process units [14; 24]. This fact illustrates that no general rule exists for scaling
up chemical processes, and that a huge effort and a great level of skill is required to achieve
the same conversion, selectivity, and product distribution at an industrial scale as reached at
the laboratory scale [8; 13].

For years, scale-up has been a sort of art in which expertise, rules of thumb, trial and error, and
particular solutions have been implemented to obtain a proper result at a new operating scale
[13; 25]. Within the drawbacks of these scale-up approaches, the main problem is to make a
complete list of the relevant independent variables [26; 27]. Here science meets art: the choice
of these variables is highly subjective, disregarding any rigor [11; 12]. For instance, despite
four similarity criteria must be considered in chemical engineering (geometrical, mechanical,
thermal and chemical), where each criterion requires the fulfillment of the others, in real
engineering problems it is impossible to satisfy the similarity criteria (as a whole), resulting in
the fact that not all the characteristic parameters and not all the dimensionless numbers can
be kept constant during the scale-up [13; 28].

Although the use of phenomenological-based models has increased in the scale-up field in
the past few years [15; 19; 22; 23; 29; 30], it carries a big inconvenient when validating it
at several operating scales; especially because model parameters such as transfer coefficients
(mass, heat and momentum) vary when scale changes [1; 8; 10; 31; 32]. In addition, when the
studied system is considered to be complex (see Definition 1.1), the designer is forced to use
optimization algorithms to find optimal parameters, which results in an impractical, arduous
and boundless task [1; 15; 18; 20; 33] evidencing the lack of a procedure that facilitates finding
these parameters. Within this thesis a complex system is defined as:

**Definition 1.1.** A system is considered to be complex if it is described by a PBSM
that consists of more than two dynamics with any interaction, i.e. it is described by
more than two coupled differential equations.

On the other hand, three major characteristics of BPs must be considered in order to scale-up a
batch unit: (i) dynamic operating point, (ii) nonlinear behavior and (iii) constrained operation
[3; 34]. In this way, as a consequence of BPs characteristics, transport phenomena change
significantly during the batch [9]. These changes are usually not considered when scaling up
discontinuous processes, forcing the designer to determine by expertise which mechanism is
governing the process on each stage of it [4; 17]. Here, the establishment of the rate-limiting
step is critical for determining the process scale factors.

All these facts illustrate that there is no agreement on how to proceed when scaling up BPs,
and that an explicit differentiation between batch and continuous processes must be done,
considering discontinuous processes particular characteristics and the Operating Regime (OR) along the batch. Thus, the research question that guides this work is:

**Is it possible to propose a methodology for scaling up batch processes using a Phenomenological-Based Semiphysical Model (PBSM) and considering the Operating Regime (OR) along each stage of the batch?**

### 1.3. Objectives

The objectives that conduct this thesis are:

**General objective:**

Propose a methodology for scaling-up batch processes using a Phenomenological-Based Semiphysical Model (PBSM), and considering the Operating Regime (OR) along each stage of the batch, using Hankel matrix singular value decomposition as a tool for finding the Operating Regimes of the process.

**Specific objectives:**

1. Identify the most popular methods for scaling chemical processes.
2. Differentiate the principles underlying traditional scale-up methods and their limitations.
3. Extend the usage of the Hankel matrix singular value decomposition to the scale-up of batch processes.
4. Validate the proposed methodology by scaling up a specific batch process.

### 1.4. Major findings and dissemination of results

The main outcome of this work is the incorporation of the State Impactability Index (SII) to the scale-up of BPs. This index provides a quantitative measure of the significance of each state variable in the process (a dynamics hierarchy) and, hence, the most impacted state variable by the scale increments. In this sense, the *SII* allows determining the real scale factors of a given process holding the same dynamics hierarchy, i.e. maintaining the Operating Regime (OR) when changing the scale. Here, the use of the discrete form of the Hankel matrix to analyze system dynamics, and determine the effect of the design variables as a whole over each state variable, is the key for carrying out a successful scale-up.

The publications related to this work are:

**Conference papers:**


Journal papers:


1.5. Thesis outline

Given that the purpose of this work is to develop a methodology for scaling up BPs using the Hankel matrix as a tool for holding the same OR at each stage the batch, the thesis is organized as follows:

- In Chapter 2, a review on the methods for scaling up chemical processes is done, with these purposes:
  - Summarizing the most popular methods for scaling up chemical processes and analyzing their current limitations.
  - Establishing the differences related to the scale-up of discontinuous and continuous processes and determining which of them are the most important from this thesis perspective.

- Chapter 3 comprises the mathematical tools used for developing the scale-up methodology, with these intentions:
  - Introducing the most used models on chemical processes representation and analysis, particularly Phenomenological-Based Semiphysical Models that are the keystone of this thesis.
  - Defining the Hankel matrix through discrete observability and controllability concepts, including its interpretation and importance from this work viewpoint.
  - Familiarizing the reader with the Singular Value Decomposition (SVD) as a tool to analyze chemical processes, emphasizing in SVD of Hankel matrix, its interpretation and significance in this thesis.
Presenting a route to quantify the dynamic effect of each input and output over the process, by means of singular values and vectors of the Hankel matrix.

In Chapter 4, the proposed scale-up methodology is presented, focusing on the next points:

- Defining the concepts of: state variables, design variables, synthesis parameters, design-variable-dependent parameters, and operating trajectory from the thesis perspective.
- Presenting the Hankel matrix and a PBSM employment when scaling up batch processes.
- Introducing the State Impactability Index (SII) and dynamics hierarchy concepts to the scale-up of batch processes.
- Implementing the proposed methodology to a general simple batch reactor.

In Chapter 5, the methodology presented in Chapter 4 is applied to a batch suspension polymerization reactor, seeking for the following ideas:

- Modeling a batch suspension polymerization reactor.
- Evaluating the methodology usefulness by applying it on a complex batch reactor.
- Determining the dynamics hierarchy at the current and new scale through the SII calculation of a batch polymerization.
- Finding the scale factors of a batch suspension polymerization reactor.
- Comparing the OT and designed equipment at the current and new scale by using the proposed methodology and a traditional scale-up method.
CHAPTER 2

Scale-up of chemical processes

The purpose of this chapter is to summarize the theoretical framework on chemical processes scale-up, including batch processes characteristics. To do this, in Section 2.1, the basis of the most used methods for scaling up chemical processes are described, analyzing their limitations in each case. Then, in Section 2.2, batch and continuous processing are compared, highlighting the importance of including batch processes characteristics during its scale-up. Afterwards, Section 2.3 presents some concluding remarks.

2.1. General scale-up approximations

**Definition 2.1.** Scale-up is the successful start-up and operation of a commercial unit size whose design and operation procedures are in part based upon experimentation and demonstration at a smaller operating scale [1].

The word *successful* must include product attainment at the planned rates, at the projected fabrication cost, and with the desired quality standards [1; 31]. Here, the most important objective is to design a commercial scale unit that achieves the targets set at low scale, while minimizing the investment of resources and elapsed time [24; 35].

Although the scale-up activity is one of the major tasks for chemical engineers and represents a fundamental step in the design and optimization of industrial plants [36], as mentioned in the introduction, since the 1960s there has not been significant progress in the methods for scaling up chemical processes (rules of thumb, trial and error, similarity criteria and dimensional analysis) [10; 11; 12; 13; 14; 25; 29]. In this empirical scale-up approach, the choice of critical variables has proved to be an arduous and problematic task, since issues such as the agitation, system geometry, fluid properties, and operating parameters have a significant effect on the process transport phenomena [18], and there is no direct way to determine their optimal values [4; 16; 33].

It is possible to distinguish three basic approaches in the scale-up procedure: (i) experimental, (ii) physical, and (iii) fundamental [13; 22; 37; 38]. In Fig. 2.1, a classification of the most popular methods for scaling up chemical processes is presented, according to previous mentioned approaches. The first two approaches (experimental and physical) are known as traditional scale-up methods [6; 28; 38]. On the other hand, despite researchers such as Bisio and Kabel [1]; Johnstone and Thring [39] mentioned the importance of the third approach (fundamental), it has only be explored in the past few years due to past limitations for solving complex models.

The following subsections briefly explain each method basis and their limitations.
2.1.1. Experimental approximation

This approach is also known as empirical approach. Here, the designer knowledge (expertise) of a particular process is used for carrying out its scale-up [1; 10; 37]. Usually, the empirical approach involves sequential scale-up studies, each increment building upon the knowledge gained in the previous increment [14; 36; 40]. The experimental approach offers a low scale-up ratio, which results in a large number of experiments, highly expensive if a large scale must be achieved [1; 37]. Two different methods can be followed in the context of the experimental approach [22; 29; 38]: (i) trial and error and (ii) the usage of rules of thumb.

2.1.1.1. Trial and error

In this method, a carefully planned test campaign is needed to collect data that adequately covers a wide range of the most important operating variables [37]. Usually, the design data for scaling up chemical processes can be provided from various sources: (a) past experience, (b) laboratory reports or results, and (c) literature [38; 39]. In general, the data is used for determining an explicit relation between measured variables and the scale-dependent variables with the aim of predicting the latter ones at a new operating scale [41].

The experimentation necessary to scale-up a given process unit is divided into three complementary parts [23]:

**Laboratory studies:** allow determining the reaction mechanism and operating variables such as space velocity, temperature, pressure, composition, among others [37]. The laboratory-scale experiments should be held in a wide range of conditions that cover those expected in the commercial unit, including key operating variables measurements, such as those mentioned before, which must be independent from the scale [23; 42]. This type of unit usually is not necessarily similar to the industrial one [36].

**Pilot-plant studies:** are carried out at a scale that has wide variations, but including all industrial constraints [42]. During the design of a pilot plant, the most important question is
how large to build it, unfortunately there is no single answer to this question. The plant must be large enough so it represents precisely the industrial scale phenomena, and small enough so the cost is not too high [37]. This type of unit is usually expensive and therefore the decision of building it is always a hard one [36].

**Mock-up studies:** are used to analyze the physical phenomena that are more sensitive to scale changes [1; 23]. They are also called cold models due to the absence of chemical reaction. This type of unit simulates physical processes by adapting mild operating conditions (temperature, pressure, velocity, etc.) and by using inexpensive and inert fluids with physical properties approaching to those of the reaction fluids [37].

Examples of the employment of trial and error for scaling up chemical processes can be seen from works of Gasparini et al. [14]; Nikakhtari et al. [40]; Yang et al. [43], in which various reactors were scaled-up from laboratory to pilot-plant or industrial scale performing sequential experiments, in combination with rules of thumb or similarity criteria (see also Subsections 2.1.1.2 and 2.1.2.1 respectively).

### 2.1.1.2. Rules of thumb

Rules of thumb are numerical values, suggestions and mathematical expressions that are reasonable to assume or use in engineering based on experience [44]. They have been used for years in order to enrich the use of fundamentals for solving practical engineering problems [45] and as a method for scaling up chemical processes [28].

Traditionally, when scaling up chemical processes, a constant value of a particular operating parameter is used as a general rule [6; 14; 15; 46]. The literature provides many rules of thumb for this purpose. For instance, criteria such as constant power per volume ratio, constant impeller tip speed, or equal mixing times can be applied in almost every scale-up problem [13; 47]. Here, the geometrical similarity is always implicit within the use of this method [22; 29] even though it is hardly ever possible to achieve in practice [18].

The use of rules of thumb is valuable in the sense that the operating parameter selected for scaling up the process must have significant influence on the process governing phenomenon [22]. However, scale-up problems arise precisely from keeping a single parameter constant, mainly because as a specific parameter remain constant during the scale-up, the rest ones cannot be fixed altering the process behavior [15; 18; 28].

Examples of the use of rules of thumb as a scale-up method can be mostly seen from biological applications, where criteria such as constant power per volume, constant oxygen mass transfer coefficient at the liquid phase \(k_L a\), constant impeller tip speed, and equal mixing times are frequently employed as scale-up criteria [22]. The works of Ju and Chase [28]; Nikakhtari et al. [40]; Meyer [46]; Hansen [47] also show the application of this method in combination with geometrical similarity (see Subsection 2.1.2.1) for scaling up either biological and chemical processes.

### 2.1.2. Physical approximation

This approach involves the usage of dimensionless numbers, variables and relationships to relate the same process at different scales [7; 11; 42]. These dimensionless numbers or groups of parameters form the basis for scaling up from one size to another [12; 26; 30]. Bearing this in mind, a simple definition of a *dimensionless number* is provided as follows:
**Definition 2.2.** A dimensionless number is a group of physical quantities with each quantity elevated to a power such that all the units associated with the physical quantities cancel, i.e. dimensionless [37].

For relatively simple systems, the physical approach has proved to be an appropriate scale-up method, mainly because the number of dimensionless quantities involved is limited and easy to establish. On the other hand, for complex systems (see Definition 1.1), a large set of dimensionless quantities describe the problem. Given that these quantities are required to be similar at both scales and that it is impossible to fix all of them, the designer is forced to determine by expertise which are the key ones. Here, if key dimensionless numbers are not properly chosen, the resulting scaled-up design is susceptible to be adjusted [15; 42].

Two different methods can be followed in the context of the physical approach [16; 38; 42]: (i) similarity criteria and (ii) dimensional analysis. However, in practice, these two methods are combined into one [37].

### 2.1.2.1. Similarity criteria

The similarity criteria method covers the relations between physical systems of different sizes [39]. In essence, dimensionless ratios of physical and chemical parameters describing the process are used to design the scaled-up process unit [48].

The philosophy within this method establishes that dimensionless groups describing two or more process units at different operating scales must be similar [49]. Several similarity criteria have been defined to guide the engineer during the scale-up of a given unit. The most important ones are: (a) geometrical, (b) mechanical (c) thermal and (d) chemical similarities [30; 39; 50], discussed as follows.

**Geometrical similarity:** concerns the dimensional proportionality between the systems of interest [50]. Two bodies are geometrically similar when to every point in the one body there exists a corresponding point in the other [39]. Hence, between two pieces of equipment of different sizes, geometrical similarity exists only when they both have the same shape [37].

Thus, for any two geometric systems that can be described by a group of geometric parameters, they are similar if their parameters are respectively proportional to each other with the same proportionality constant [51].

**Mechanical similarity:** is composed by static, kinematic and dynamic similarity criteria [50]. Each of these criteria can be regarded as an extension of the concept of geometrical similarity to stationary or moving systems subjected to forces [39].

- **Static similarity:** concerns the deformation proportionality between the systems under study [50]. Geometrically similar bodies are statically similar when under constant stress their relative deformations are such that they remain geometrically similar [39].

- **Kinematic similarity:** concerns the time for moving proportionality between the systems of interest [50]. Geometrically similar systems are kinematically similar when corresponding particles trace out geometrically similar paths in corresponding intervals of time [37; 39]. According to this, kinematic similarity involves keeping the same dimensionless numbers based on velocities [16].
Dynamic similarity: concerns the force proportionality between the systems under consideration [50]. Geometrically similar moving systems are dynamically similar when ratios of all corresponding forces are equal [39].

Thermal similarity: concerns the temperature proportionality between systems that are being investigated [50]. Geometrically similar systems are thermally similar when corresponding temperature differences bear a constant ratio to one another and when the systems, if they are moving, are kinematically similar [39; 48]. This criterion implies matching the temperatures in corresponding portions of the process units under comparison [49]. In this sense, thermal similarity involves maintaining the same heat transfer dimensionless numbers [16].

Chemical similarity: concerns the concentration proportionality between the systems in question [50]. Geometrically and thermally similar systems are chemically similar when corresponding concentration differences bear a constant ratio to one another and when the systems, if they are moving, are kinematically similar [39]. Here, the corresponding concentration differences are defined in the same manner as corresponding temperature differences, which means that these differences are measured at corresponding geometrical points and at corresponding times [48].

Each of these four criteria is dependent on the other three [48]. However, in practice, a complete similarity cannot be accomplished between two process units at different scales [15], making this method limited to simple systems [42]. A plethora of works involving the use of similarity criteria as scale-up method can be found in the literature, some examples are the works of Leckner et al. [30]; Landin et al. [52]; Litster et al. [53], where constant values of key dimensionless numbers are used to obtain the scaled-up unit design.

2.1.2.2. Dimensional analysis

Dimensional analysis is a technique for expressing the behavior of a physical system in terms of the minimum number of independent variables and in a form that is unaffected by changes in the magnitude of measurements units [39]. It is based upon the recognition that a mathematical formulation of a physical problem can be of general validity only when process equations are dimensionally homogeneous [26; 54]. Here, the physical groups are arranged in dimensionless groups consisting of the ratios of quantities such as lengths, velocities, forces, densities, among others [39].

Within this method, the number of variables on which a physical problem depends on can be reduced to a few (the independent ones) [27]. The main inconvenient when performing this reduction is the establishment of the list of relevant independent variables, which is actually unknown and its selection depends on the designer a priori knowledge of the process [11]. Two different methods can be followed in the context of the dimensional analysis [12; 27; 37; 39]: (a) Buckingham \( \pi \)-theorem based method, and (b) inspectional analysis.

Buckingham \( \pi \)-theorem based method: is also known as empirical dimensional analysis [37] because it uses expertise for the selection of the list of relevant independent variables [11]. This method is highly useful when the differential equations that governs the system behavior are unknown [27].

In brief, the Buckingham \( \pi \)-theorem intends to express the dependence of one specific parameter as a function of relevant independent variables to its simplest dimensionless form [11]. The theorem states the following two parts [33; 39; 55]:
1. The solution to every dimensionally homogeneous physical equation has the form:

\[ \phi(\pi_1, \pi_2, \pi_3, \cdots) = 0 \]  

where \( \pi_1, \pi_2, \pi_3, \cdots \) represent a complete set of dimensionless groups of the variables and the dimensional constants of the equation.

2. If an equation contains \( n \) separate variables and dimensional constants and these are given dimensional formulas in terms of \( m \) primary quantities (dimensions), the number of dimensionless groups in a complete set is \( n - m \).

The aim of empirical dimensional analysis is to check if a given equation is dimensionally homogeneous, i.e. verify if each one of its additive terms has the same dimensions [27]. To do this, two steps should be followed [26; 54]: (a) identify the complete set of dimensional independent variables, and (b) check the dimensional homogeneity of the physical content by transforming it to a dimensionless form. Although all relevant variables are required to be known to succeed, the Buckingham \( \pi \)-theorem does not explicitly provide information about the completeness of the list of relevant variables [11]. This fact represents the biggest disadvantage of this method.

A countless number of publications show that empirical dimensional analysis has been widely used over the years. Some examples of the application of this method to chemical processes scale-up can be seen from works of Ruzicka [12]; Glicksman et al. [27]; Inglezakis and Poulopoulos [37].

**Inspectional analysis**: is also known as scaling of equations method [12] given the use of dimensionless equations for describing the behavior of the system of interest [7]. This method is useful when the differential equations that govern the process are known and they can be made dimensionless to yield a set of dimensionless numbers which completely describe the system [11].

The objective of this method is to derive the dimensionless groups from the governing equations of the process, assuming that these equations are dimensionally homogeneous. Bearing this in mind, dimensionless numbers associated with a given process can be obtained by following three basic steps [27; 37]: (a) identify the scales of the problem (i.e. length, time and velocity), (b) use the scales of the problem for making dimensionless each term in the governing equations, and (c) choose one of the terms in each governing equation and divide each term in the equation by it. The resulting dimensionless terms in the normalized equations are the relevant dimensionless independent numbers or quantities.

Although inspectional analysis is a simple and transparent procedure for obtaining the list of relevant dimensionless numbers, it does not provide the relation among dimensionless numbers. The establishment of this relation must be done by applying empirical dimensional analysis (previously described), and so find similarity laws that govern the process and then scale it up [12]. Here, it must be considered that it is often impossible to keep all the dimensionless groups constant when changing the scale [15], so the choice of the key variables falls back over to the designer previous knowledge.

Inspectional analysis has also been extensively applied in a wide number of applications, some examples of chemical processes scale-up can be seen from works of: Ruzicka [12]; Glicksman et al. [27]; Inglezakis and Poulopoulos [37]; Worstell [56].
2.1.3. Fundamental approximation

This approach involves proper modeling of the process under consideration [1; 22; 31], it is based in the development of a phenomenological-based model for the description of the process behavior [15; 19; 32; 37], generating an excellent process understanding and allowing for a process to be scaled-up by more than 1000 times, quickly and reliably [1; 10].

Two different methods can be followed in the context of the fundamental approach: (i) simulations with variation of parameters [15; 29; 37] and (ii) the usage of the dynamics hierarchy (Hankel matrix) [10; 38]. The extension of the latter to the scale-up of batch processes is the focus of this thesis.

2.1.3.1. Simulations with variation of parameters

This method implies the solution of momentum, mass, and energy balances in the system that is being investigated [22; 31]. Its main drawback arises from the determination of the most sensitive parameters of the model when changing the scale [1; 15].

Nevertheless, an alternative tool for finding these parameters is the regime analysis introduced by Johnstone and Thring [39]. This approach provides information about process rate-limiting steps [13; 22] from the quantification of the process variables, derivation of rate constants (time constants) and comparison of these values for establishing the slowest rate (largest time) that governs the process (rate-limiting step) [25].

Once regime analysis provides the rate-limiting step, this method inconveniences seem solved. However, when using this tool, it is impossible to know if the established rate-limiting step at one scale will be the same at a new one [13]. So, although regime analysis reduces the effort in the determination of the most sensitive parameters related to the scale-up, it is hardly ever possible to anticipate if the rate-limiting step has changed when increasing the operating scale [25].

It is worth highlighting that despite there is no general rule or procedure about how to scale-up a process using this approach, the development of fundamental models able to describe key characteristics of the system is perhaps the most helpful tool for successfully scaling up processes and for attaining the optimal conditions at an industrial scale [15]. In recent years, Computational Fluid Dynamics (CFD) has shown to be an effective tool to study the hydrodynamics of reactors and scale-up of chemical processes. Some examples of the use of this method including CFD as a tool for scaling up the system in question can be seen from works of Gavi et al. [32]; Letellier et al. [57].

2.1.3.2. Usage of the dynamics hierarchy

The dynamics hierarchy method was first introduced by Ruiz [38]. In this approximation, a methodology for scaling up continuous processes was developed, employing a PBSM as a tool to comprehend the behavior of the process and the Hankel matrix as a tool for analyzing process dynamics and scaling it up, maintaining the same OR through scales changes. Some years later, as a way to overcome the methodology limitations, various modifications were introduced in [58] to the original proposal of Ruiz [38]. This thesis extends the modified methodology to batch processes applications (see Chapter 4).
Also, it is important to define the operating regime concept from this thesis viewpoint, given the difference with the concept introduced by Johnstone and Thring [39] related to the rate-limiting step. In this work the OR must be understood as stated:

**Definition 2.3.** The Operating Regime (OR) is a quantitative hierarchical relation between the state variables of the process at a given point of the Operating Trajectory (OT). This relation is established from the calculation of the State Impactability Index (SII) of each state variable, which includes the effect of the design variables as a whole over each state variable at each point of the OT.

The previous statement is based on the definition provided by Ruiz and Alvarez [10], but including the relation of the SII with the dynamics hierarchy and its extension to batch processes.

### 2.2. Batch processing and the scale-up task

In discontinuous processes (batch and fed-batch type) raw materials are loaded in predefined amounts and they are transformed through a specific sequence of activities (known as recipe) by a given period [59]. In this way, a determinate amount of a specific product is obtained after a given time [34; 60]. Typically, this type of processing includes loading the materials into the equipment, processing them, discharging the final product and preparing the next batch [61; 62].

In contrast, in continuous processes, materials are transported in a continuous flow through the equipment. After reaching the desired operating point (steady state) the process is independent of time [63]. In this type of process, starts, stops, and transitions usually do not contribute to achieve the desired characteristics of the product [34; 64].

Although batch processing is an antique, flexible and versatile operating mode [5; 65], widely used to obtain high-value products [2], it is still scaled-up using traditional methods (described in previous sections) [9; 13; 17; 18], leading to unforeseen problems (equipment and operating conditions adjustment) and additional production costs [66]. Three major differences between batch and continuous processes must be considered in order to successfully scale-up a batch unit.

The first difference is related to the operating point. CPs have a single operating point, which means that they have time-constant characteristics. On the contrary, BPs have a dynamic operating point, which means that they have time-varying characteristics [3; 17].

Given that BPs involve chemical transformations that proceed from an initial state to a highly different final state [67], there is not a unique operating point around which the process can be scaled-up as is the case of CPs [34]. In this way, as a consequence of BPs time-varying characteristics, kinetic reaction and transfer coefficients change significantly during a batch, forcing the designer to determine by expertise which mechanism is governing on each stage of the batch in order to scale-up the process [4; 17].

The second difference is related to the nonlinear behavior. Both BPs and CPs can exhibit this behavior that can be attributed to various sources, the two major ones being: (i) the nonlinear relation between the reaction rates with concentrations (often) and with temperature (always), and (ii) the nonlinear relationship between the transport-phenomena-dependent parameters and the inside-reactor properties [3]. However, in CPs there is a unique rate-limiting stage since they have a single operating point, so their inside-reactor properties remain constant during
the process time [17]. Instead, in BPs the inside-reactor properties change significantly during the batch time, causing changes in the transfer coefficients and, hence, the existence of various rate-limiting stages. The dominant of these stages must be established in order to scale-up this type of process. Here, it is considered as rate-limiting stage a given phenomenon that governs the process dynamics during a finite period of time.

Finally, the third difference is related to the presence of constraints. Although in BPs and CPs all manipulated variables are physically constrained, BPs also exhibit operating constraints [2; 5; 34] that must be considered when scaling up the process. Here, the dynamic nature of BPs is the source of internal disturbances and, hence, the need to be constrained for safety, quality or stability reasons [67]. For instance, in exothermic batch polymerization reactors, a common industrial practice is to keep an isothermal operation (at low temperature) for the batch safety. Although higher temperatures can reduce the reaction time by speeding up the polymerization reaction rates, a temperature increase produces an excess of heat that raises the risk of a thermal runaway as well as producing polymer of lower molecular weight [68]. Therefore, there must be an equilibrium point between productivity on one hand, and safety, stability and quality on the other one, for the selection of the reactor temperature [34]. Furthermore, due to the wide operating range of BPs, it is rarely possible to design and operate this type of process away from constraints, as is typically done for CPs [3].

As a way to include these differences to BPs scale-up and taking advantage of the information that a phenomenological-based model can offer, this work includes the previously mentioned characteristics (dynamic operating point, nonlinear behavior and constrained operation) and the use of a phenomenological-based model of the process to the scale-up of discontinuous processes.

### 2.3. Concluding remarks

This chapter has focused on the theoretical aspects of the most popular methods for scaling up chemical processes. Here, it is worth highlighting:

- Traditional scale-up methods do not consider that process phenomena (kinetic reaction and mass, energy, momentum transfer) can be altered when changing the scale, this fact represents a reduced vision of the problem, and hence a partial solution of it.

- There is no general rule or procedure for successfully scale-up chemical processes, so combinations of the scale-up methods mentioned in this chapter are used to obtain an acceptable outcome of the process at an industrial scale.

- There is no general criterion for the selection of the list of the relevant variables when scaling up chemical processes, so the choice of these variables is always subjective and requires detailed understanding of the process, experience, intuition and good luck for successfully selecting them.

- BPs characteristics (dynamic operating point, nonlinear behavior and constrained operation) are not taken into account during the scale-up task. This fact highlights the gaps in the scale-up of this type of process.

- A phenomenological-based model is a powerful tool that can be exploited in the scale-up field, but there is no general rule on how to use it.
CHAPTER 3
Dynamic analysis of chemical processes

The purpose of this chapter is to summarize the theoretical background on the mathematical tools used in this thesis for the development of the scale-up methodology. In Section 3.1, a brief introduction on chemical processes models is presented, indicating the specific model type used in this thesis. Then, in Section 3.2, the Hankel matrix is defined through observability and controllability definitions, based on a phenomenological-based model of the process. Afterwards, Section 3.3 presents the Singular Value Decomposition (SVD) as a tool to analyze chemical processes dynamics, emphasizing in the SVD of the Hankel matrix and its interpretation. Then, Section 3.4 shows the route to quantify the dynamic impact of each process input and output, by means of their corresponding singular values and vectors of the Hankel matrix. Finally, Section 3.5 presents some concluding remarks.

3.1. Chemical processes modeling

Mathematical models of chemical processes have great potential in engineering applications [69]. They can be used as a tool for prediction [70], control [62], design [71], optimization and fault diagnosis [72]. Applications such as advanced control, and simultaneous design of process and its control system (integrated design) are supported on the availability of good enough models that enable the analysis of the process dynamics [73].

From a design perspective, a fundamental premise underlying the scale-up task is that physical principles of nature apply to systems of different sizes [1; 11]. Following this foundation, an introduction to chemical processes modeling is presented within this chapter, highlighting the particular model type used in this thesis for developing the scale-up methodology.

Bearing this in mind, a general definition of a model in an engineering environment is provided as follows:

Definition 3.1. A model is a representation of the essential aspects of an existing system (or a system to be constructed) which presents knowledge of that system in a usable form [74].

This means that a model is always a simplified representation of the real system [1; 75]. In addition, such representation can provide insight (not necessarily a physical one) of the studied system [76].

The information that a model can supply depends on its structure, and therefore, its application and final use are also determined by it [70]. According to this, a model is a system itself composed by (i) a structure and (ii) parts [73]. The former refers to the model layout and is obtained from the modeling objective (explain, describe, predict) and mathematical operators [75; 77]. The latter refers to model terms composed by all involved parameters within the
model. In this sense, Fig. 3.1 presents a characterization of the mathematical models according to their structure.

Considering that each sort of model shown in Fig. 3.1 can provide diverse and complementary process information [70], the following subsections briefly describe each one of them as well as the knowledge that can be gained from all of them.

3.1.1. White-box, gray-box and black-box models

From a physical insight, models can be classified as one of the following: (i) white-box, (ii) black-box and (iii) gray-box.

**White-box models:** are also called explanatory [70], phenomenological or first-principle models because they seek to increase the understanding on the underlying phenomena of a given process [77]. This kind of model is used when the process is perfectly known and is entirely obtained from a *priori* process knowledge and physical insight [78; 79]. This means that they are based on physical and chemical laws (thermodynamics and continuity equations) [80] that allow the model to explain precisely the system behavior [73; 81]. White-box models can even be built when the process is not yet constructed [76; 82]. They are considered complex and difficult to solve [83].

**Black-box models:** are also known as empirical or purely predictive models [23; 77] because their structure does not reflect the physical foundation of the studied system [83], so this sort of model is usually simple and easy to solve. Empirical models provide an input/output relation of the process variables [79]. According to this, they are useful if a physical understanding of the process is absent or is not relevant for the model purpose [76]. Black-box models are constructed from experimentation and observation [38; 78]. The experimental data is used for adjusting parameters in a specific mathematical structure [80] that narrows the operating range of the model [81]. Here, the chosen model structure belongs to mathematical function families that are known to have good flexibility and have been successful in the past [79; 84].

**Gray-box models:** are also called descriptive models because they seek a suitable representation for design purposes. This kind of model is usually less complex than white-box models and more difficult to solve than black-box models [77; 78]. Descriptive models are combinations of the two previously mentioned model families (white-box and black-box) [80], they are classified in two types: (i) semiphysical (if they have a phenomenological structure) [73; 81] and (ii) semiempirical (if they have an empirical structure) [84].
The semiphysical family is also known as Phenomenological-Based Semiphysical Models (PBSM) [73]. This type of model can be developed from certain process knowledge and process operating data taking advantage of the physical insight provided by the mass, momentum and energy balances [73; 79; 81]. In this case, several parameters are determined from observed data or using black-box models [83; 84].

From the previous classification, the physical insight increases as the model gets closer to a white one. Considering this, Fig. 3.2 presents the relation of each type of model with the scale-up methods described in Chapter 2.

![Figure 3.2. Models physical interpretability and its relation with the scale-up approaches.](image)

If physical interpretability is important, then the models should be as white as possible, meaning that the structure of the model should be based on first principles as much as possible [76]. Bearing this in mind, fundamental scale-up methods are based on white or gray box models, experimental scale-up methods are based mostly on black-box models, and physical scale-up methods on gray-box models (see Fig. 3.2). This thesis is framed in the fundamental scale-up approach using a PBSM to represent the process to be scaled-up because it adds sufficient physical insight being of easy solution.

### 3.1.2. Linear and nonlinear models

In linear models, the net response of a system to a weighted sum of signals is equal to the corresponding weighted sum of responses (outputs) of each individual input signal (principle of superposition) [85; 86]. This type of behavior is rarely exhibited in chemical processes that are known for being nonlinear. To model chemical processes, linear models can be used but only in a narrow operating range [76]. According to this, the process is expected to remain in its operating point or trajectory vicinity.

The Jacobian linearization is the most common approximation for linearizing nonlinear models [87]. This approximation is based on the Taylor series expansion and on knowledge of nominal trajectories and inputs of the system [88]. Here, the first derivative of the series describes the system behavior around a working point or trajectory [76].

In practice, the ability of using linear models for processes representation is of great significance, since linear models solution is easier than nonlinear ones [1]. As a consequence of linear models being of easy implementation and solution, many of the optimization methods [76] and control applications [87] use them. Taking into account this fact, a linear model (obtained by Jacobian linearization of a nonlinear PBSM of the process) is used within work for scaling up BPs.
3.1.3. Static and dynamic models

Static models are also called stationary models [1] because their state variables do not change in time [76]. This type of model calculates the system equilibrium or steady-state process conditions with the aim of designing process units [23; 70]. An important characteristic of stationary models is that the process state is studied without concerning the state variables route that enables reaching the steady-state [23].

In contrast, a dynamic model considers that process variables change with time [38]. They are also known as non-steady state or transient models [1] and are used to represent the transient behavior of dynamic processes in many engineering applications. For instance, modeling a batch process always results in a dynamic model [76] mainly because they have inherent time-varying characteristics [70]. According to this, a dynamic phenomenological-based model is used for representing the behavior of discontinuous processes in this thesis.

3.1.4. Continuous-time and discrete-time models

In continuous models, dependent variables on space and/or time are defined as continuous variables; instead discrete models are only defined for discrete values of time and/or space [86]. Although models can be discrete to any variable, the distinction between continuous and discrete models is typically done with respect to time. These models are known as discrete-time models and they calculate the system state at given time intervals [76].

The discrete concept of time is based upon the distinction between time points and time intervals. Oppositely, the continuous concept of time is related to infinitesimal mathematics [76]. In this sense, continuous variables can have any value at a given interval, whereas discrete variables can only take a specific value out of a given set [1]. Continuous-time models (left) can be differentiated from discrete-time ones (right) [89] from the following equations:

$$\begin{align*}
\text{Continuous-time} \\
\dot{x} &= A_c x + B_c u \quad (3.1) \\
y &= C_c x \quad (3.2)
\end{align*}$$

$$\begin{align*}
\text{Discrete-time} \\
x(j + 1) &= A_d x(j) + B_d u(j) \quad (3.3) \\
y(j) &= C_d x(j) \quad (3.4)
\end{align*}$$

Discrete-time models as shown in (3.3) and (3.4) are commonly used for sampling continuous signals [85]. They are particularly important in control theory of linear systems when designing and analyzing control loops. In this field, the most popular discretization method is the Zero-Order Hold (ZOH) mainly because of its simplicity [90]. This method considers that the control inputs are piecewise constant over the sampling period. Bearing this in mind, a discrete-time model is obtained within this work in order to use the Hankel matrix during the scale-up procedure application. Here, the model is discretized using ZOH method.

3.1.5. Distributed-parameter and lumped-parameter models

In a lumped-parameter models, dependent variables are not a function of position [86], this means that the system state can be considered homogeneous throughout the entire volume [1]. According to this, the obtained model is composed by ordinary differential equations [91].

On the other hand, dependent variables are function of position in distributed-parameter models [86], this means that they consider detailed variations in the state behavior from point to point
throughout the system [1]. In this sense, the obtained model is composed by partial differential equations [91].

All real systems are spatially distributed but if the variation is relatively small, it can be neglected, and the system is then simplified into a lumped-parameter one [1]. For instance, criteria such as the Peclet number \((Pe)\) that is defined as the ratio between the transport rate by advection and the transport rate by diffusion, can help the designer to decide if spatial variation might be dismissed [76].

In this thesis, a phenomenological-based model of lumped parameters is used for representing the dynamic behavior of a batch process.

### 3.1.6. Frequency domain and time domain models

The distinction between time domain and frequency domain models is only made for dynamic models, because time dependence is, by definition, not incorporated in static models [76]. Direct transformation between the time and frequency domain is possible only for linear models in time domain [86]. In essence, frequency domain models are employed instead of time domain models for one of the following reasons [1]: (i) the analytic solution may be simpler in the frequency domain or (ii) analytic particular solutions can only be obtained in the frequency domain.

Frequency response analysis is an important tool in controller design mainly when analyzing control systems stability [76]. Within this field, empirical models can be formulated directly in the frequency domain [1], given the possibility to describe diverse processes with transfer functions that are linear time-invariant models (black-box models). This type of function relates inputs and outputs with zero initial conditions and zero equilibrium point [86].

In this work, time domain models must be considered for the proposed scale-up methodology implementation.

Finally, as a way to completely characterize the type of model employed in this thesis, the proposed scale-up procedure uses linear, dynamic, discrete, lumped-parameter and time domain Phenomenological-Based Semiphysical Models for describing the dynamic behavior of BPs. Bearing this in mind, once a process PBSM is obtained, this work takes advantage of the Hankel matrix as a tool for determining the OR along the batch and scaling up the process. The next section introduces the use of the latter tool to chemical processes analysis.

### 3.2. Hankel matrix and its interpretation

Hankel matrix usage arises in diverse areas of mathematics such as problems involving power moments, interpolation theory and control theory [92]. Within these areas, the potential of this tool has been exploited in model reduction [93], systems identification, digital filter design [94], model order determination [95], and controllers design when determining input-output pairings [96; 97].

For Hankel matrix definition and interpretation, consider the linear discrete-time system described by the following state space model [98; 99; 100]:

\[
x(j + 1) = A_d x(j) + B_d u(j), \quad x(0) = x_0
\]

\[
y(j) = C_d x(j)
\]
Here, \( x(j) \in \mathbb{R}^n \) is the state vector and \( x_o \) is the corresponding initial state vector. Also, the inputs and outputs vectors being \( u(j) \in \mathbb{R}^p \), \( y(j) \in \mathbb{R}^m \) respectively. \( A_d \in \mathbb{R}^{n \times n} \), \( B_d \in \mathbb{R}^{n \times p} \), \( C_d \in \mathbb{R}^{m \times n} \) are system, control, and outputs matrices respectively; they are constant and in corresponding units. The integer \( j \) represents time steps.

If \( x(0) = 0 \), the Hankel matrix is defined from the Markov parameters of the system, as shown in (3.7) [100; 101].

\[
H_j = C_d A_d^{j-1} B_d, \quad j = 1, 2, 3, \ldots, s
\]  

These parameters are also impulse-response values for the discrete-time system described by (3.5) and (3.6) [102]. Therefore, the layout of the system Hankel matrix is given by [103]:

\[
\mathcal{H} =
\begin{bmatrix}
H_j & H_{j+1} & H_{j+2} & \cdots & H_{j+s} \\
H_{j+1} & H_{j+2} & H_{j+3} & \cdots & H_{j+s+1} \\
H_{j+2} & H_{j+3} & H_{j+4} & \cdots & H_{j+s+2} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
H_{j+s} & H_{j+s+1} & H_{j+s+2} & \cdots & H_{j+2s}
\end{bmatrix}
\]  

Here, \( \mathcal{H} \) elements are constant along the anti-diagonals [103]. If \( m > 1 \) or \( p > 1 \), \( H_j, H_{j+1}, \ldots, H_{j+s} \) represent blocks of matrices or vectors (depending on the number of inputs or outputs), meaning that \( \mathcal{H} \) is not necessarily a square matrix. The rank of \( \mathcal{H} \) is the number of linearly independent rows of the matrix [104] and, hence, the order of the system [102; 105]. Also, for square Hankel matrices, if \( \text{rank}(\mathcal{H}) = r \), the matrix is non-singular for \( r \leq n \) and singular for \( r > n \) [94].

Afterwards, considering the special case when \( j = 1 \) and \( s = n - 1 \) in (3.8), the Hankel matrix takes the following layout [10; 96; 103]:

\[
\mathcal{H} =
\begin{bmatrix}
C_d B_d & C_d A_d B_d & C_d A_d^2 B_d & \cdots & C_d A_d^{n-1} B_d \\
C_d A_d B_d & C_d A_d^2 B_d & C_d A_d^3 B_d & \cdots & C_d A_d^n B_d \\
C_d A_d^2 B_d & C_d A_d^3 B_d & C_d A_d^4 B_d & \cdots & C_d A_d^{n+1} B_d \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
C_d A_d^{n-1} B_d & C_d A_d^n B_d & C_d A_d^{n+1} B_d & \cdots & C_d A_d^{2n-2} B_d
\end{bmatrix}
\]  

Here, \( \mathcal{H} \) such is presented in (3.9) can be deduced as the product of the observability and controllability matrices of the system [102; 106; 107]. To make this deduction, in Subsections 3.2.1 and 3.2.2, the observability and controllability matrices for discrete systems are defined, and then in Subsection 3.2.3 equation (3.9) is verified.

### 3.2.1. Observability of discrete systems

For the system composed by (3.5) and (3.6), consider that \( u(j) = 0 \), \( x(0) = x_o \) is unknown, and outputs are measured [10; 108]:

\[
x(j+1) = A_d x(j), \quad x(0) = x_o = \text{unknown}
\]  

\[
y(j) = C_d x(j)
\]  

For determining the observability matrix, it is necessary to establish if it is possible to know the complete dynamic behavior of the system defined in (3.10) by using only the information provided by the outputs measurement obtained from (3.11) [108; 109], i.e. if knowing the outputs sequence \( y(0), y(1), \ldots, y(n-1) \) is enough to determine the system initial state \( x(0) = x_o \) [97].
Then, considering \( j = 0, 1, 2, \ldots, n-1 \) in (3.10) and (3.11), the following sequence is obtained [90; 108]:

\[
\begin{align*}
y(0) &= C_d x(0) \\
y(1) &= C_d x(1) = C_d A_d x(0) \\
y(2) &= C_d x(2) = C_d A_d x(1) = C_d A_d^2 x(0) \\
& \vdots \\
y(n-1) &= C_d x(n-1) = C_d A_d^{n-1} x(0)
\end{align*}
\]  

(3.12)

Rewriting (3.12) in matrix form [106; 108]:

\[
\begin{bmatrix}
y(0) \\
y(1) \\
y(2) \\
\vdots \\
y(n-1)
\end{bmatrix}_{nm \times 1} =
\begin{bmatrix}
C_d \\
C_d A_d \\
C_d A_d^2 \\
\vdots \\
C_d A_d^{n-1}
\end{bmatrix}_{nm \times n}
\begin{bmatrix}
x(0)
\end{bmatrix}_{n \times 1}
\]  

(3.13)

The right side matrix in (3.13) is the observability matrix \( O(A_d, C_d) \in \mathbb{R}^{nm \times n} \) [108]. It represents the relation between the initial state sequence \( x(0) = x_o \) and the outputs measurements sequence \( y(0), y(1), \ldots, y(n-1) \) [38; 96].

### 3.2.2. Controllability of discrete systems

For the system composed by (3.5) and (3.6), consider that \( x(0) = x_o \) is known [10; 108]:

\[
x(j + 1) = A_d x(j) + B_d u(j), \quad x(0) = x_o \quad \text{known}
\]  

(3.14)

For determining the controllability matrix, it is necessary to know if it is possible to transfer the system from any initial state to any desired final state in a finite time [108; 109], i.e. if it is possible to find a control sequence \( u(0), u(1), \ldots, u(n-1) \) such as \( x(j) = x_f \) [97].

Then, considering \( j = 0, 1, 2, \ldots, n \) the following sequence is obtained [90; 108]:

\[
x(1) = A_d x(0) + B_d u(0)
\]

\[
x(2) = A_d x(1) + B_d u(1) = A_d^2 x(0) + A_d B_d u(0) + B_d u(1)
\]

\[
x(3) = A_d x(2) + B_d u(2) = A_d^3 x(0) + A_d^2 B_d u(0) + A_d B_d u(1) + B_d u(2)
\]

(3.15)

\[
x(n) = A_d^n x(0) + A_d^{n-1} B_d u(0) + A_d^{n-2} B_d u(1) + \cdots + A_d B_d u(n-2) + B_d u(n-1)
\]

Rewriting (3.15) in matrix form [106; 108]:

\[
x(n) - A_d^n x(0) = \begin{bmatrix} B_d & A_d B_d & \cdots & A_d^{n-2} B_d & A_d^{n-1} B_d \end{bmatrix}_{n \times np}
\begin{bmatrix}
u(n-1) \\
u(n-2) \\
\vdots \\
u(1) \\
u(0)
\end{bmatrix}_{np \times 1}
\]  

(3.16)

The right side matrix in (3.16) is the controllability matrix \( C(A_d, B_d) \in \mathbb{R}^{n \times np} \). It provides the relation between the past inputs sequence \( u(0), u(1), \ldots, u(n-1) \) and the current state \( x(n) \) [38; 96].
3.2.3. Hankel matrix definition

For computing Hankel matrix, it is necessary to evaluate (3.13) at time \( n \) as shown [10; 97]:

\[
\begin{bmatrix}
y(n) \\
y(n+1) \\
y(n+2) \\
\vdots \\
y(2n-1)
\end{bmatrix}
= \begin{bmatrix}
C_d \\
C_d A_d \\
C_d A_d^2 \\
\vdots \\
C_d A_d^{n-1}
\end{bmatrix}
\begin{bmatrix}
x(n)
\end{bmatrix}
\] (3.17)

Then, replacing (3.16) in (3.17):

\[
\begin{bmatrix}
y(n) \\
y(n+1) \\
y(n+2) \\
\vdots \\
y(2n-1)
\end{bmatrix}
= A_d^o x(0) O(A_d, C_d) + O(A_d, C_d) C(A_d, B_d) \begin{bmatrix}
\mathbf{u}(n-1) \\
\mathbf{u}(n-2) \\
\vdots \\
\mathbf{u}(1) \\
\mathbf{u}(0)
\end{bmatrix}
\] (3.18)

where \( \mathcal{H}(A_d, B_d, C_d) = O(A_d, C_d) C(A_d, B_d) \) verifying (3.9) [102; 106; 107]. In this sense, the Hankel matrix rank defines the dimension of both controllable and observable subsystems, which, as mentioned at the beginning of this section, is the system order [95].

According to (3.18), \( \mathcal{H} \) can be interpreted as the mapping from the past inputs to the future outputs via \( x(0) \) of the system described by (3.5) and (3.6) [106; 110]. The same effect can be seen from Fig. 3.3, where past inputs are considered to obtain future outputs (solid line) via \( x(0) \), not the past ones (dotted line).

![Figure 3.3. Hankel graphical matrix interpretation.](image)

Finally, considering that \( x(0) = 0 \) in (3.18), the following expression is obtained [100; 101]

\[
\begin{bmatrix}
y(n) \\
y(n+1) \\
y(n+2) \\
\vdots \\
y(2n-1)
\end{bmatrix}
= \mathcal{H}_{nm \times np}(A_d, B_d, C_d) \begin{bmatrix}
\mathbf{u}(n-1) \\
\mathbf{u}(n-2) \\
\vdots \\
\mathbf{u}(1) \\
\mathbf{u}(0)
\end{bmatrix}
\] (3.19)

From (3.19), it can also be noticed that \( \mathcal{H} \) is a dynamic representation of the system that relates a sequence of previous inputs \( \mathbf{u}(0), \mathbf{u}(1), ..., \mathbf{u}(n-2), \mathbf{u}(n-1) \) to the subsequent outputs \( y(n), y(n+1), y(n+2), ..., y(2n-1) \) at instant \( n \) [96].

3.3. Singular Value Decomposition (SVD) and its interpretation

The Singular Value Decomposition (SVD) is an important tool for solving linear problems in various engineering and theoretical fields [111]. It plays a fundamental role in different
applications such as digital image processing [112; 113], solution of linear least squares problems [114; 115], analysis of experimental data [116], dynamics analysis of constrained systems [117; 118] and model order identification [95; 119].

In this thesis, this tool will contribute to the determination of the dynamics hierarchy, and hence, the scale-up methodology development. Bearing this in mind, Subsections 3.3.1 and 3.3.2 present the SVD general concept and its application to the Hankel matrix.

3.3.1. Definition of the Singular Value Decomposition (SVD)

Let $R \in \mathbb{R}^{l \times q}$ a matrix with rank $r$. There exist orthogonal unitary matrices $U \in \mathbb{R}^{l \times l}$ and $V \in \mathbb{R}^{q \times q}$, and a diagonal matrix $\Sigma \in \mathbb{R}^{l \times q}$ such that the following equality holds [95; 115; 120]:

$$R = U\Sigma V^T$$  \hfill (3.20)

The matrix $U$ consists of the orthonormalized eigenvectors associated with the largest eigenvalues of $RR^T$ [111] and are called left singular vectors of $R$ [104]. The matrix $V$ consists of the orthonormalized eigenvectors of $R^T R$ [120] and are called right singular vectors of $R$ [117]. The diagonal elements of $\Sigma$ are the non-negative square roots of the eigenvalues of $R^T R$ and are called singular values of $R$ [121]. Additionally, it is considered that [113; 117]:

$$\Sigma = \begin{bmatrix} S & 0 \\ 0 & 0 \end{bmatrix}$$  \hfill (3.21)

Here, $S = \text{diag} \{ \sigma_{11}, \sigma_{22}, ..., \sigma_{rr} \}$ with $\sigma_{11} \geq \sigma_{22} \geq ... \geq \sigma_{rr} > 0$. In this sense, a graphical illustration of the resulting decomposition of $R$ is shown in Fig. 3.4.

![Figure 3.4. Graphical illustration of the SVD of R.](image)

where $\text{rank}(R) = \text{rank}(\Sigma) = r$ [122]. Also, from Fig. 3.4, it can be seen that the column space of $R$ is spanned by the first $r$ columns of $U$, highlighted in blue at Fig. 3.4. The extra columns of $U$ (highlighted in gray) represent the null space of $R^T$ spanned by the last $l - r$ columns. The row space of $R$ is spanned by the first $r$ rows of $V^T$, highlighted in red at Fig. 3.4. The extra rows of $V^T$ (highlighted in gray) represent the null space of $R$ spanned by the last $q - r$ rows [119]. According to this, given that the last $l - r$ columns of $U$ and $q - r$ rows of $V^T$ are additional; they are not needed to reconstruct $R$, so the actual matrices order are: $U^* \in \mathbb{R}^{l \times r}$, $\Sigma^* \in \mathbb{R}^{r \times r}$ and $V^* \in \mathbb{R}^{q \times q}$ [116].

Finally, from a physical perspective, the matrix of singular values ($\Sigma$) provides the information intensity of the system represented by $R$, where the highest singular value contains most of the system information [112]. Therefore, by means of singular values analysis, the information
3.3.2. The SVD of the Hankel matrix

From Section 3.2, the Hankel matrix \( \mathcal{H} \), associated with discrete-time systems characterized by Markov parameter sequences (impulse response), is defined as shown in (3.9) for the system described by (3.5) and (3.6). Considering a specific case where the number of state variables \( n = 2 \), number of inputs \( p = 2 \) and number of outputs \( m = 2 \) in (3.19), the resulting system of equations written in matrix form is provided as follows.

\[
\begin{bmatrix}
y_1(2) \\
y_2(2) \\
y_1(3) \\
y_2(3)
\end{bmatrix} =
\begin{bmatrix}
C_d B_d & C_d A_d B_d \\
C_d A_d B_d & C_d A_d^2 B_d
\end{bmatrix}
\begin{bmatrix}
u_1(1) \\
u_2(1) \\
u_1(0) \\
u_2(0)
\end{bmatrix}
\quad (3.22)
\]

Then, by decomposing \( \mathcal{H} \) in singular values, and considering that \( \text{rank}(\mathcal{H}) = n = 2 \) the following factorization is obtained.

\[
\mathcal{H} =
\begin{bmatrix}
U_1 & U_2 & U_3 & U_4 \\
U_2 & U_2 & U_3 & U_4 \\
U_3 & U_3 & U_3 & U_4 \\
U_4 & U_4 & U_4 & U_4
\end{bmatrix}
\begin{bmatrix}
\sigma_{11} & 0 & 0 & 0 \\
0 & \sigma_{22} & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{bmatrix}
\begin{bmatrix}
V_{11}^T & V_{12}^T & V_{13}^T & V_{14}^T \\
V_{21}^T & V_{22}^T & V_{23}^T & V_{24}^T \\
V_{31}^T & V_{32}^T & V_{33}^T & V_{34}^T \\
V_{41}^T & V_{42}^T & V_{43}^T & V_{44}^T
\end{bmatrix}
\quad (3.23)
\]

where the output (column) space of \( \mathcal{H} \) is composed by the first two columns of \( \mathbf{U} \), and the input (row) space of \( \mathcal{H} \) is given by the first two rows of \( \mathbf{V}^T \), so \( \mathcal{H} \) can be reconstructed from [116]:

\[
\mathcal{H} =
\begin{bmatrix}
U_1 & U_2 \\
U_2 & U_2 \\
U_3 & U_3 \\
U_4 & U_4
\end{bmatrix}
\begin{bmatrix}
\sigma_{11} & 0 \\
0 & \sigma_{22}
\end{bmatrix}
\begin{bmatrix}
V_{11}^T & V_{12}^T & V_{13}^T & V_{14}^T \\
V_{21}^T & V_{22}^T & V_{23}^T & V_{24}^T \\
V_{31}^T & V_{32}^T & V_{33}^T & V_{34}^T \\
V_{41}^T & V_{42}^T & V_{43}^T & V_{44}^T
\end{bmatrix}
\quad (3.24)
\]

From a control viewpoint, the Hankel singular values \( \sigma_{ii} \) are closely related with the controllability and observability of the system [123]. For instance, a relatively small value of \( \sigma_{ii} \) (compared with the highest singular value) means that the process is difficult to control [96; 107]. Bearing this in mind, the Hankel singular values can also be used to quantify the significance of each state in the corresponding input-output system [124]. If the Hankel singular values decrease rapidly, it can be concluded that most of the input-output behavior is determined by the first few states [125].

3.4. Weighting of inputs–outputs dynamic effects

For computing each input and output impactability over the process, (3.24) is replaced in (3.22) as follows:

\[
\begin{bmatrix}
y_1(2) \\
y_2(2) \\
y_1(3) \\
y_2(3)
\end{bmatrix} =
\begin{bmatrix}
U_1 & U_2 \\
U_2 & U_2 \\
U_3 & U_3 \\
U_4 & U_4
\end{bmatrix}
\begin{bmatrix}
\sigma_{11} & 0 \\
0 & \sigma_{22}
\end{bmatrix}
\begin{bmatrix}
V_{11}^T & V_{12}^T & V_{13}^T & V_{14}^T \\
V_{21}^T & V_{22}^T & V_{23}^T & V_{24}^T \\
V_{31}^T & V_{32}^T & V_{33}^T & V_{34}^T \\
V_{41}^T & V_{42}^T & V_{43}^T & V_{44}^T
\end{bmatrix}
\begin{bmatrix}
u_1(1) \\
u_2(1) \\
u_1(0) \\
u_2(0)
\end{bmatrix}
\quad (3.25)
\]

Solving the product of matrices in (3.25), the following equation is obtained.
\[
\begin{bmatrix}
  y_1(2) \\
  y_2(2) \\
  y_1(3) \\
  y_2(3)
\end{bmatrix}
= \begin{bmatrix}
  \sigma_{11} \left( V_{11}^T u_1(1) + V_{21}^T u_2(1) + V_{31}^T u_1(0) + V_{41}^T u_2(0) \right) \\
  \sigma_{11} \left( V_{11}^T u_1(1) + V_{21}^T u_2(1) + V_{31}^T u_1(0) + V_{41}^T u_2(0) \right) \\
  \sigma_{11} \left( V_{11}^T u_1(1) + V_{21}^T u_2(1) + V_{31}^T u_1(0) + V_{41}^T u_2(0) \right) \\
  \sigma_{11} \left( V_{11}^T u_1(1) + V_{21}^T u_2(1) + V_{31}^T u_1(0) + V_{41}^T u_2(0) \right)
\end{bmatrix}
+ \begin{bmatrix}
  \sigma_{22} \left( V_{12}^T u_1(1) + V_{22}^T u_2(1) + V_{32}^T u_1(0) + V_{42}^T u_2(0) \right) \\
  \sigma_{22} \left( V_{12}^T u_1(1) + V_{22}^T u_2(1) + V_{32}^T u_1(0) + V_{42}^T u_2(0) \right) \\
  \sigma_{22} \left( V_{12}^T u_1(1) + V_{22}^T u_2(1) + V_{32}^T u_1(0) + V_{42}^T u_2(0) \right) \\
  \sigma_{22} \left( V_{12}^T u_1(1) + V_{22}^T u_2(1) + V_{32}^T u_1(0) + V_{42}^T u_2(0) \right)
\end{bmatrix}
\]

where each output is discriminated by \( U_{j1} \sigma_{11} \) and \( U_{j2} \sigma_{22} \) and, each input is distinguished by \( V_{j1}^T \sigma_{11} \) and \( V_{j2}^T \sigma_{22} \). Here, \( j = 1, 2, 3, 4 \) for both cases.

For quantifying the dynamic impact of each input and output, the concept of Euclidean norm is considered. In this case, the Euclidean norm is calculated by means of the singular vectors entries related to each output, \( y_1(2), y_1(3), y_2(2), y_2(3) \), and input, \( u_1(0), u_1(1), u_2(0), u_2(1) \), weighted by the corresponding singular value, as shown in (3.27)–(3.30) [96]:

\[
\begin{align*}
OII_{y_1} &= \sqrt{U_{11}^2 \sigma_{11}^2 + U_{21}^2 \sigma_{11}^2 + U_{31}^2 \sigma_{12}^2 + U_{41}^2 \sigma_{22}^2} \\
OII_{y_2} &= \sqrt{U_{12}^2 \sigma_{11}^2 + U_{22}^2 \sigma_{11}^2 + U_{32}^2 \sigma_{12}^2 + U_{42}^2 \sigma_{22}^2} \\
III_{u_1} &= \sqrt{V_{11}^T \sigma_{11}^2 + V_{12}^T \sigma_{12}^2 + V_{13}^T \sigma_{13}^2 + V_{14}^T \sigma_{14}^2} \\
III_{u_2} &= \sqrt{V_{21}^T \sigma_{11}^2 + V_{22}^T \sigma_{12}^2 + V_{23}^T \sigma_{13}^2 + V_{24}^T \sigma_{14}^2}
\end{align*}
\]

where \( OII_{y_k} \) is the Output Impactability Index of the \( k \)-th output and \( III_{u_l} \) is the Input Impactability Index of the \( l \)-th input. Here, the Euclidean norm of each input or output is a scalar that provides a measure of the effect of each one of them in the process [97].

In addition, reorganizing (3.27)–(3.30) and knowing that \( V_{ji}^T = V_{ij} \) the following expressions are obtained.

\[
\begin{align*}
OII_{y_1} &= \sqrt{\sigma_{11}^2 (U_{11}^2 + U_{31}^2) + \sigma_{22}^2 (U_{12}^2 + U_{32}^2)} \\
OII_{y_2} &= \sqrt{\sigma_{21}^2 (U_{11}^2 + U_{41}^2) + \sigma_{22}^2 (U_{22}^2 + U_{42}^2)} \\
III_{u_1} &= \sqrt{\sigma_{11}^2 (V_{11}^2 + V_{13}^2) + \sigma_{11}^2 (V_{21}^2 + V_{23}^2)} \\
III_{u_2} &= \sqrt{\sigma_{11}^2 (V_{12}^2 + V_{14}^2) + \sigma_{11}^2 (V_{22}^2 + V_{24}^2)}
\end{align*}
\]

Then, generalizing to a system with \( r \) singular values, i.e. with order \( r \), equations (3.35)–(3.38) are obtained.

\[
\begin{align*}
OII_{y_1} &= \sqrt{\sum_{i=1}^{r} \sigma_{11}^2 (U_{1i}^2 + U_{3i}^2)} \\
OII_{y_2} &= \sqrt{\sum_{i=1}^{r} \sigma_{21}^2 (U_{2i}^2 + U_{4i}^2)} \\
III_{u_1} &= \sqrt{\sum_{i=1}^{r} \sigma_{11}^2 (V_{1i}^2 + V_{13}^2)} \\
III_{u_2} &= \sqrt{\sum_{i=1}^{r} \sigma_{11}^2 (V_{2i}^2 + V_{24}^2)}
\end{align*}
\]

Also, generalizing to a system with \( p \) inputs and \( m \) outputs, the following indexes are obtained [96; 97].
CHAPTER 3. Dynamic analysis of chemical processes

\[ OII_{y_k} = \sqrt{\sum_{i=1}^{n} \sum_{g=0}^{n-1} \sigma_{ii}^2 \sum_{h=0}^{m} U_{k+mg+i}^2}, \quad k = 1, 2, \ldots, m \] (3.39)

\[ III_{u_l} = \sqrt{\sum_{i=1}^{n} \sum_{h=0}^{m} V_{i,l+ph}^2}, \quad l = 1, 2, \ldots, p \] (3.40)

Here, \( OII_{y_k} \) and \( III_{u_l} \) represent the impactability of process manipulated inputs \( u \) as a whole over a \( k \)-th given output \( y_k \), and the impactability of a \( l \)-th given process manipulated input \( u_l \) over process outputs \( y \) as a whole, respectively.

This thesis exploits the potential of the Output Impactability Index \( OII_{y_k} \) shown in (3.39) for scaling up batch processes, since it offers the possibility of quantifying the effect of each dynamics over the process. Although the Input Impactability Index \( III_{u_l} \) shown in (3.40) provides information of the effect of each input over the process, this thesis is focused on the determination of a dynamics hierarchy, i.e. the establishment of the most impacted dynamics of the process. According to this, the \( III_{u_l} \) is not implemented within work.

3.5. Concluding remarks

This chapter is focused on the theoretical aspects of the mathematical tools used in this thesis for developing the scale-up methodology. Here, it is worth highlighting:

- Given that the model resolution for scaling up chemical processes is the macroscopic scale, the most proper model type for scaling up BPs is a Phenomenological-Based Semiphysical Model (PBSM). This type of model adds sufficient physical insight for understanding process phenomena and its formulation is easy enough to not incorporate higher level of complexity to the scale-up.

- If it is considered the Hankel matrix as the mapping from the past inputs to the future outputs via the process state, it arises as a powerful tool that can be used for analyzing chemical processes dynamics, mainly because the singular values of the Hankel matrix are closely related with the process controllability and observability.

- Knowing that the \( OII_{y_k} \) and \( III_{u_l} \) quantify the relevance of the each output and input over the process, the potential of these indexes can be exploited to improve BPs scale-up. Bearing this in mind, the \( OII_{y_k} \) can be used for establishing the effect of the scale-dependent variables over the process dynamics.
This chapter presents the proposed methodology for scaling up batch processes and its application to a simple batch reactor. The chapter is organized as follows: the methodology is presented in Section 4.1, explaining and justifying each step of it. Then, in Section 4.2, the procedure introduced in Section 4.1 is applied to a non-isothermal batch reactor. Finally, Section 4.3 presents some concluding remarks.

4.1. Scale-up proposed methodology

As a way to overcome the limitations mentioned in Chapter 2 during the scale-up of BPs and considering that a PBSM is the most useful tool for scaling up chemical processes [10; 15; 32], Fig. 4.1 presents the proposed methodology for scaling up BPs.

The procedure herein proposed is an extension of a previous one developed in [58] for scaling up CPs and it was a keystone for the development of this thesis. Also, it is worth clarifying that the mathematical tools previously described in Chapter 3 for control systems are used for developing the methodology taking into consideration that input variables, used as manipulated variables \((u)\), are design variables \((z)\) within this chapter and they are influenced by scale increments. The thirteen steps of the procedure are described as follows.

**Step 1:** the Capacity Variables at the current scale \((CV_{cs})\) and new scale \((CV_{ns})\), and Capacity Variable step \((\Delta CV)\) are defined. The definition of \(CV\) is provided as follows.

**Definition 4.1.** Capacity Variable \((CV)\) is any process variable indicating a processing capacity of a process unit. It is associated with process hold-up or an extensive variable.

This means that \(CV\) is set by the designer in order to carry out the process at the desired scale. Bearing this in mind, \(CV\) alters all scale-dependent parameters while the scale is incremented.

**Step 2:** a PBSM of the process is obtained, using the methodology developed by Alvarez et al. [73]. The obtained model has the following layout.

\[
\dot{x} = \mathcal{F}(x(t), z(t)), \quad x(0) = x_0 \tag{4.1}
\]

\[
y(t) = \mathcal{G}(x(t)) \tag{4.2}
\]

where \(x(t) \in \mathbb{R}^n\) is the system state space vector, \(z(t) \in \mathbb{R}^p\) is the design variables space vector, \(y(t) \in \mathbb{R}^m\) is the system output space vector, \(x_0\) is the initial state vector and the continuous variable \(t\) represents the time. Considering that a model is a simplified representation of the real process, the model needs to be validated at the current scale \((cs)\) in order to represent the process at the new scale \((ns)\). Therefore, by using a validated PBSM at the \(cs\), the dynamic
CHAPTER 4. Scale-up methodology based on the SVD of Hankel matrix

Figure 4.1. Scale-up proposed procedure.
behavior of the process at the cs is transferred to the ns by means of the proposed procedure. Here, the PBSM structure (material and energy balances) enables the model to be valid at both scales.

Step 3: state variables (x), design variables (z), synthesis parameters (p) and design-variable-dependent parameters (w) are defined from the obtained model. Definitions of x, z, p, w are provided as follows.

**Definition 4.2.** State variables (x) are the smallest set of variables that must be specified at time \( t = t_0 \) in order to predict the behavior of the process for any time \( t \geq t_0 \) [126].

**Definition 4.3.** Design variables (z) are the variables whose values can be freely varied by the designer to define a designed process.

**Definition 4.4.** Synthesis parameters (p) are characteristic (inherent) parameters of the process, set from the process conception. Once established, they remain fixed during the scale-up.

**Definition 4.5.** Design-variable-dependent parameters (w) are the parameters that depend on the design variables (z), i.e. w can be written as an explicit function of z.

According to this, CV may also be design variable because it can be freely varied by the designer when scaling up the process.

Step 4: the Operating Trajectory (OT) is fixed. The definition of OT is provided as follows.

**Definition 4.6.** The Operating Trajectory (OT) is the value of the state vector at each time instant. The OT is obtained by solving the mathematical model including the adequate values of the manipulated input variables.

It is assumed that the nominal OT is known from process synthesis at the cs and the proposed methodology does not optimize it. Thus, this trajectory must be properly chosen to carry out the scale-up. The works of Bonvin et al. [3; 34] describe the main issues for determining the optimal OT of a batch process.

Intermediate steps (a)–(f): these steps are followed in order to compute the State Impactability Index of each state variable at the current scale \( (SII_{x_i, a}) \).

(a) An equation for each \( w_i |_{cs} = f (z_{cs}) \) is found. These expressions only need to be valid at the cs in order to represent the process dynamic behavior at this scale.

(b) It is assumed that the process dynamics, in the immediate proximity of the nominal OT, can be approximated by the first terms of the Taylor series. Thus, the model is linearized along the OT, discretizing it on a number of finite points so a continuous linear models ensemble can represent the OT as shown in (4.3) and (4.4).

\[
\delta \dot{x}(t) = A_c(t)\delta x(t) + B_c(t)\delta z(t), \quad \delta x(0) = x(0) - x_N(0) \tag{4.3}
\]

\[
\delta y(t) = C_c(t)\delta x(t) \tag{4.4}
\]

where \( A_c = \frac{\partial F}{\partial x} \bigg|_{x_N, z_N} \), \( B_c = \frac{\partial F}{\partial z} \bigg|_{x_N, z_N} \) and \( C_c = \frac{\partial G}{\partial x} \bigg|_{x_N, z_N} \) are the Jacobian matrices of the continuous linear systems. The subscript \( N \) represents the nominal OT.

(c) \( B_c \) and \( C_c \) are modified to make both design and output variables dimensionless and normalized, see (4.5) and (4.6). According to this, \( A_c \) is not altered because the Hankel matrix is a tool that only considers the inputs and outputs of the system [106; 110],
so any mathematical operation done over $x$ will be annulled during the Hankel matrix calculation [96].

$$\overline{b}_{ij} = b_{ij} (z_{j,\text{max}} - z_{j,\text{min}}) \quad (4.5)$$

$$\tau_{ij} = \frac{c_{ij}}{(y_{i,\text{max}} - y_{i,\text{min}})} \quad (4.6)$$

The subscripts max and min are the maximum and minimum values of $z_j$ and $y_i$ in each case. They are established from the process synthesis based on the knowledge of the process design and desired performance targets. If these limits are not adequately chosen, the dynamics hierarchy may be altered and, hence, the selection of the main dynamics might be wrong. Here, $z_{j,\text{min}}$ and $z_{j,\text{max}}$ may depend on the scale while $y_{i,\text{min}}$ and $y_{i,\text{max}}$ do not. Also, it is considered that the system is completely observable or its state is fully measured, which leads to $C_C$ being the Identity matrix and, $y_i$ and $x_i$ limits being the same.

This type of normalization, called “scaling” in [127], is commonly used when studying control systems with the aim of all process variables to be in comparable ranges. Here, the word “scaling” is avoided in order to prevent any confusion when mentioning the words “scale-up” associated with scale increments. Also, it is worth clarifying that there are several ways to carry out the normalization of the variables. In this case, $B_c$ and $C_c$ are transformed for normalizing both design and state variables because it is a simpler procedure than constructing a dimensionless model of the process.

(d) Linear models at each point of the OT are discretized. Here, the sampling time ($t_s$) must be carefully chosen in order to each discrete model be able to represent each continuous one. The layout of the ensemble of models is shown as follows.

$$\delta x(j + 1) = A_d(j) \delta x(j) + B_d(j) \delta z(j), \quad \delta x(0) = x(0) - x_N(0) \quad (4.7)$$

$$\delta y(j) = C_d(j) \delta x(j) \quad (4.8)$$

where $A_d = I + A_c t_s$, $B_d = t_s B_c$ and $C_d = C_c$ are process discrete matrices.

(e) Observability ($O \in \mathbb{R}^{nm \times n}$), controllability ($C \in \mathbb{R}^{n \times np}$) and Hankel ($H \in \mathbb{R}^{nm \times np}$) matrices are computed for each discrete model as shown in (4.9)–(4.11) respectively.

$$O(j) = \begin{bmatrix} C_d(j) & C_d(j) A_d(j) & C_d(j) A_d^2(j) & \cdots & C_d(j) A_d^{n-1}(j) \end{bmatrix}^T \quad (4.9)$$

$$C(j) = \begin{bmatrix} B_d(j) & A_d(j) B_d(j) & A_d^2(j) B_d(j) & \cdots & A_d^{n-1}(j) B_d(j) \end{bmatrix} \quad (4.10)$$

$$H(j) = O(j) C(j) \quad (4.11)$$

Here, observability and controllability are not considered as independent concepts because, as mentioned before, for extending the use of the Hankel matrix from control to design, an analogy between manipulated ($u$) and design ($z$) variables was done. Therefore, $O$ and $C$ have yet to be defined and discussed in the context of process design.

(f) $H$ is decomposed in singular values as shown in (4.12). Here, the matrices $U \in \mathbb{R}^{nm \times nm}$ and $V \in \mathbb{R}^{np \times np}$ are the column and row spaces of $H$. Also, the diagonal elements of $\Sigma \in \mathbb{R}^{nm \times np}$ are the singular values ($\sigma_{ii}$) of $H$ [115; 120].

$$H(j) = U(j) \Sigma(j) V^T(j) \quad (4.12)$$

**Step 5:** the State Impactability Index of each state variable (SII$_{x_k}$) is computed from (4.13). This expression considers that the number of outputs $m$ is equal to the number of states $n$ (the system is observable), so equation (3.39) is simplified into (4.13).

$$SII_{x_k}(j) = \sqrt{\sum_{i=1}^{r} \sum_{g=0}^{n-1} \sum_{j} U_{k+ng,i}(j)^2}, \quad k = 1, 2, \ldots, n \quad (4.13)$$

where $r$ is the rank of $H$, i.e. the number of non-zero $\sigma_{ii}$. This index represents the impactability of the design variables ($z$) as a whole over a $k$-th given state variable ($x_k$). In this
way, the main dynamics (the most impacted dynamics) is the \( x_k \) with the highest \( SII \) along the batch. The \( SII_{cs} \) also determine the Operating Regime (OR) along the batch, since it corresponds to the dynamics hierarchy obtained at each point where the process is linearized, according to Definition 2.3.

**Step 6:** the critical point of the batch is identified. It corresponds to the highest point of the \( SII \) profile for the main dynamics at the cs.

**Step 7:** the batch critical point is selected as the Reference Point (RP) to scale-up the process. So, for any point with a \( SII \) less than the \( SII_{RP} \), process requirements are fulfilled, considering that the requirements were fulfilled at the RP.

**Intermediate steps (i)–(vi):** these steps are followed, using (4.3)–(4.12), for determining the State Impactability Index of each state variable at the Reference Point (\( SII_{cs,RP} \)) as the scale is increased. Here, on intermediate step (i), each \( w_i|_{RP} = f(z_{RP}) \) must be valid at all scales from cs to ns for the model be able to represent the process at both scales in the RP.

**Step 8:** the \( SII_{cs,RP} \) is computed from (4.13).

**Step 9:** steps (i)–(vi), eight and nine are repeated until \( CV = CV_{ns} \). Here, \( w_i|_{RP} \) are computed with scale increments, allowing for the process to be scaled-up at the RP.

**Step 10:** each \( SII_{cs,RP} \) is compared at the cs and ns. If their values are equal at both scales, continue with the eleventh step. On the opposite case, i.e. if at least one of \( SII_{cs,RP} \) is outside the interval \([0.9SII_{cs,RP}, 1.1SII_{cs,RP}] \) at the ns (x and hence \( SII \) are expected to have small changes), each \( w_i|_{RP} = f(z_{RP}) \) must be reviewed (see Fig. 4.1). If these equations are valid at both scales, a successful scale-up is not possible from the established process synthesis. Therefore, the process synthesis must be reviewed. Otherwise, change the corresponding non-valid equations and recompute steps (i)–(vi), eight and nine.

Considering that the \( SII \) is a quantitative measure of the batch behavior, it allows the designer to establish the effect over the quality targets of designing a specific unit (obtained, for instance, by traditional methods) instead of the required one by the process dynamics. Here, if the \( SII \) is altered by scale increments, the process behavior degrades. So, the wider \( SII_{cs,RP} \) interval is, the greater is the risk of not reproducing the dynamic behavior of the process at the ns.

**Step 11:** given that values for each \( w_i|_{RP} \) are determined at the ns, in order to obtain the exact scaled unit design that matches each \( w_i|_{RP} \) requirement, an equation for each \( w_i|_{ns} = f(z_{ns}) \) is established. According to this, these expressions only need to be valid at the ns.

**Step 12:** the process is simulated with \( p, z_{ns} \) and \( w_i|_{ns} \) for verifying that the process at the ns achieved the same performance targets set at the cs.

**Intermediate steps (a)–(f):** these steps are followed, using (4.3)–(4.12), in order to compute the State Impactability Index of each state variable at the new scale (\( SII_{cs,ns} \)).

**Step 13:** the \( SII_{cs,ns} \) is computed from (4.13). Here, it can be establish if the designed unit is over or under sized by comparing both \( SII_{cs,ns} \) and \( SII_{cs,cs} \) profiles. The last two steps are performed for verifying that the process at the ns reproduces the dynamic behavior set at cs.

4.2. Scale-up of a general simple batch reactor

Consider the non-isothermal batch reactor shown in Fig. 4.2, where a second-order reaction, \( A \rightarrow B \), takes place and the jacket removes heat generated by the reaction.
In Fig. 4.2, \( C_A \) is the concentration of \( A \), \( T_r \) is the reactor temperature and \( T_j \) is the cooling fluid temperature at the jacket output. In addition, \( T_{j,in} \) and \( F_j \) are the cooling fluid temperature and flow rate at the jacket input. Each one of the thirteen steps of the procedure is performed as follows, considering that the computational implementation of the proposed methodology was carried out using MATLAB m-code programming language.

**Step 1:** \( CV_{cs} = 0.1\text{m}^3 \), \( CV_{ns} = 1\text{m}^3 \) and \( \Delta CV = 0.1\text{m}^3 \) are defined.

**Step 2:** a PBSM of the process is obtained. The PBSM composed by differential equations (4.14)–(4.16) describes the dynamic behavior of the reactor.

\[
\frac{dC_A}{dt} = -k_0 e^{\frac{E}{RT_r}} C_A^2 \tag{4.14}
\]

\[
\frac{dT_r}{dt} = -\frac{U_r A_i (T_r - T_j)}{\rho_r C_{p,r}} + \frac{(-\Delta H_p)}{\rho_r C_{p,r}} k_0 e^{\frac{E}{RT_r}} C_A^2 \tag{4.15}
\]

\[
\frac{dT_j}{dt} = \frac{F_j}{V_j} (T_{j,in} - T_j) + \frac{U_r A_i (T_r - T_j)}{C_{p,j} \rho_j V_j} \tag{4.16}
\]

where \( k_0, E \) and \( R \) are the frequency factor, activation energy and universal gas constant respectively. \( \rho_r \) and \( \rho_j \) are the reactor and jacket fluids densities. \( C_{p,r} \) and \( C_{p,j} \) are the reactor and jacket fluids specific heat capacities. \( \Delta H_p \) is the heat of reaction, \( U_r \) is the overall heat-transfer coefficient, \( A_i \) is the heat-transfer surface area and \( V_r \) is the reactor volume. Here, \( F_j \) is given by (4.17), since it is a manipulated input variable.

\[
F_j = \frac{V_j}{\tau_{j,bias}} + K_P e(t) + K_I \int_{t_0}^{t} e(t) dt + K_D \frac{de(t)}{dt} \tag{4.17}
\]

where \( K_P, K_I \) and \( K_D \) are the proportional, integral and derivative controller gains, and \( e(t) = T_{r,sp} - T_r \), considering that the subscript \( sp \) represents the set point. Also, \( \tau_{j,bias} \) is the residence time for the nominal cooling fluid flow rate.

**Step 3:** \( x, z, p \) and \( w \) are defined from the model, as shown in (4.18)–(4.20).

\[
x = \begin{bmatrix} C_A & T_r & T_j \end{bmatrix} \quad (4.18) \quad z = \begin{bmatrix} V_r & T_{j,in} \end{bmatrix} \quad (4.19) \quad w = \begin{bmatrix} V_j & F_j & U_r & A_i \end{bmatrix} \quad (4.20)
\]

\[
p = \begin{bmatrix} k_0 & E & R & \rho_r & \rho_j & C_{p,r} & C_{p,j} & \Delta H_p & \tau_{j,bias} & K_P & K_I & K_D \end{bmatrix} \quad (4.21)
\]

**Step 4:** the \( OT \) is fixed at the \( cs \). Here, the \( OT \) is obtained by solving the process model considering that \( T_r = 298.38\text{K} \pm 1\text{K} \) and including the effect of manipulating \( F_j \) in order to the reactor fluid be able to reach this temperature range. The \( OT \) is shown in Fig. 4.3, where the parameters and physical properties used during its calculation are reported in Table A.1.
Intermediate steps (a)–(f): these steps are followed for computing the $SII_{x,cs}$.

(a) an expression for each $w_i|_{cs} = f(z_{cs})$ must be found.

$V_j = \frac{1}{5} V_r$ \hspace{1cm} (4.22) \hspace{1cm} $U_{r,a} = \frac{1}{\frac{1}{h_i} + \frac{\delta}{k_w A_o} + \frac{1}{h_j} A_o}$ \hspace{1cm} (4.23)

Here, $F_j$ is given by (4.17) and (4.22) is a heuristic rule for chemical reactors design, typically selected as $V_j = \frac{1}{10} V_r$ in order to neglect jacket dynamics. In this case, a higher ratio is chosen for considering such dynamics. $U_{r,a}$ is the overall heat-transfer coefficient available. $A_i$, $A_w$ and $A_o$ are the inside, wall and outside heat-transfer surface areas. For $U_{r,a}$ calculation, a standard cylindrical geometry is considered, so the ratio of the impeller to the tank diameter is $D_T = \frac{1}{3}$ and the ratio of the liquid level to the tank diameter is $Z_T = 1$. $h_i$ and $h_j$ are the inner (process side) and outer (cooling fluid side) heat-transfer coefficients, computed with (4.24) and (4.25). $\delta$ and $k_w$ are the vessel wall thickness and thermal conductivity [128; 129].

\[
\frac{h_i T}{k_r} = 0.74 \left[ \frac{D^2 N \rho_r}{\mu_r} \right]^{2/3} \left[ \frac{C_{p,r} H_r}{k_r} \right]^{1/3} \left[ \frac{\mu_r}{\mu_{w,r}} \right]^{0.14} \hspace{1cm} (4.24)
\]

\[
\frac{h_j D_e}{k_j} = 1.86 \left[ \frac{D \rho_j F_j}{A_x \mu_j} \right] \left[ \frac{C_{p,j} H_j}{k_j} \right]^{1/3} \left[ \frac{\mu_j}{\mu_{w,j}} \right]^{0.14} \hspace{1cm} (4.25)
\]

\[
A_x = \frac{\pi}{2} \left[ D_{j0}^2 - D_{ji}^2 \right] \hspace{1cm} (4.26)
\]

\[
D_e = \frac{D_{j0}^2 - D_{ji}^2}{D_{ji}} \hspace{1cm} (4.27)
\]

where $A_x$, $D_e$ and $L$ are the cross-sectional flow area, heat-transfer equivalent diameter and jacket passage length. $N$ is the agitator speed and, $\mu$ and $k$ are the fluids viscosity and thermal conductivity. $D_{ji}$ and $D_{j0}$ are inner and outer diameter of the annular jacket.

(b) the model is linearized along the $OT$ according to (4.3) and (4.4).

c $B_c$ and $C_c$ matrices are modified using (4.5) and (4.6). For this case, it is considered that $y_{i,\min}$ and $y_{i,\max}$ are minimum and maximum values of each $y_i$ during the batch at the cs and, $z_{j,\min}$ and $z_{j,\max}$ are ±10% of their nominal values at the cs, since minor changes are expected for these variables at the same scale.
(d) the model is discretized using $t_s = 10\text{s}$. Here, $t_s$ must be small in order to represent each continuous linear model. For this case, it was chosen equal to time step for constructing the continuous linear models ensemble. Given the slow nature of BPs [3; 34], if $t_s$ is changed (in a consistent value) the dynamics hierarchy is not altered.

(e) the $O$, $C$ and $H$ are computed from (4.9)–(4.11), where $n = 3$, $m = n = 3$ and $p = 2$.

(f) $H$ is decomposed in singular values using (4.12).

Step 5: the $SII_{x_{k,cs}}$ is computed from (4.13) with $\text{rank}(H) = r = 2$. In this sense, Fig. 4.4 shows the $SII_{x_{k,cs}}$ profiles, where it can be seen that $SII_{T_j} > SII_{T_r} > SII_{C_A}$.

According to this, $T_j$ is the most impacted dynamics by the design variables of the process. Here, it is worth clarifying that the $SII$ curves may be affected by the controller tuning, so the designer must be careful to properly tune the controller because using the proposed methodology, the $OT$ at the $cs$ is transferred to the $ns$ and, if the controller is poorly tuned an oversized unit may be designed at the $ns$, instead of the actually required one.

Step 6: the critical point of the batch is identified. It corresponds to $SII_{T_j,cs} = 16.23$ at $t = 80\text{s}$ as can be seen from Fig. 4.4.

Step 7: this point is selected as the $RP$ for scaling up the process. Bearing this in mind, values for the state variables at the $RP$ are reported in Table 4.1.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>SI Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_A$</td>
<td>0.567</td>
<td>kmol/m$^3$</td>
</tr>
<tr>
<td>$T_r$</td>
<td>298.51</td>
<td>K</td>
</tr>
<tr>
<td>$T_j$</td>
<td>293.48</td>
<td>K</td>
</tr>
</tbody>
</table>

Intermediate steps (i)–(vi): these steps are followed in order to determine the $SII_{x_{k,RP}}$ as the scale is increased.

(i) an expression for each $w_i|_{RP} = f(z_{RP})$ is found. Here, it is considered that $V_j$ is given by (4.22) and $F_j$ can be computed from (4.17) evaluated at the $RP$. On the other hand, taking into account that (4.23) fix a geometry of the reactor, two cases for the overall heat-transfer coefficient are considered: available ($U_{r,a}$) and required ($U_{r,r}$). For the
former, (4.23) is used for computing $U_{r,a}$, considering that $h_j$ at $Re < 2100$ is described by (4.25) and at $Re \geq 2100$ by (4.28). For the latter, $U_{r,r}$ is computed using (4.29).

$$\frac{h_jD_e}{k_j} = 0.027 \left[ \frac{D_e j_f}{A_k H_j} \right]^{4/3} \left[ \frac{C_{D,j} h_j}{k_j} \right]^{1/3} \left[ \frac{\mu_j}{\mu_{w,j}} \right]^{0.14}$$

(4.28)

where $U_{r,r}$ is also evaluated at the $RP$. Considering that most of the scale-up methods involve the fulfillment of the geometrical similarity, this comparison allows the designer to determine the effect of set up a unit geometrically similar instead of a required one. Notice that in the first case, the process is scaled-up keeping $U_r$ fixed by the current scale design. Opposite to the second case, where $U_r$ is computed from the process energy requirements without fixing the geometry of the reactor, making (4.29) valid when increasing the scale.

(ii) the model is linearized around the $RP$.

(iii) $B_c$ and $C_c$ matrices are modified according to (4.5) and (4.6), considering $y_j$ limits are the same as those set at the $cs$, since minor changes are expected for these limits while the scale is increased because the process dynamic behavior is transferred from the $cs$ to the $ns$ within the use of this methodology. Here, $T_{j,\text{in}}$ limits are equal to those set at the $cs$ and, $V_j$ limits are computed as the ±10% of its nominal value at each scale.

(iv) The linear model at $RP$ is discretized as shown (4.7) and (4.8) as the scale is increased, with $t_s = 10$. Here, each discrete model represents each continuous one at the $RP$.

(v) $O$, $C$ and $H$ are computed in the $RP$ at each scale, using (4.9)–(4.11).

(vi) $H$ is decomposed in singular values as shown in (4.12).

**Step 8:** the $SII_{s_{4,RP}}$ is computed from (4.13), where the Hankel matrix rank is $r = 2$.

**Step 9:** as can be seen from Fig. 4.1, steps five to twelve are repeated until $CV = CV_{ns}$.

**Step 10:** the $SII_{s_{4,RP}}$ values are compared at the $cs$ and $ns$ as can be seen from Table 4.2. Here, the $SII$ values remain constant when the process is scaled-up restraining the energy requirements ($U_{r,r}$) and change when the geometrical similarity is held ($U_{r,a}$). This fact indicates that the process behavior deteriorates when using $U_{r,a}$ during the scale-up.

| Variable | $SII_{cs}$ | $SII_{ns|U_{r}}$ | $SII_{ns|U_{r,a}}$ |
|----------|------------|-----------------|-----------------|
| $C_A$    | 0.00       | 0.00            | 0.00            |
| $T_R$    | 0.57       | 0.57            | 0.51            |
| $T_j$    | 16.23      | 16.23           | 19.43           |

In addition, $w_{|RP}$ for all cases are reported in Table 4.3. It can be seen that a smaller value for the overall heat-transfer coefficient is computed when using $U_{r,a}$ than $U_{r,r}$, this means that a smaller process unit than the required one was designed.

| Sym.     | $w_{cs}$ | $w_{ns|U_{r}}$ | $w_{ns|U_{r,a}}$ | SI Unit |
|----------|----------|----------------|-----------------|---------|
| $V_j$    | 0.02     | 0.2            | 0.2             | m$^3$   |
| $F_{j,\text{max}}$ | 2.7     | 27             | 27              | m$^3$/h |
| $U_{r|RP}$ | 198      | 426            | 261             | W/m$^2$K |
| $A_j$    | 0.99     | 4.61           | 4.61            | m$^2$   |
**Step 11:** Given that values for each $w_i|_{RP}$ are determined at the $ns$ (see Table 4.3), in order to obtain the exact scaled unit design that matches each $w_i|_{RP}$ requirement, an equation for each $w_i|_{ns} = f(z_{ns})$ is established. Here, only (4.29) satisfied the scale-up requirements (see Table 4.2), so a new jacket geometry is set. According to this, two internal baffles are added to the annular jacket, using (4.30)–(4.32) [128] to satisfy the heat transfer demand ($U_r$) in the $RP$ at the $ns$. From here, $U_r$ is computed using (4.23), with $h_j$ given by (4.30).

\[
\frac{h_j D_e}{k_j} = 0.027 \left[ \frac{D_e \mu_j F_j}{A_x \mu_j} \right]^{4/5} \left[ \frac{C_p \mu_j}{k_j} \right]^{1/3} \left[ \frac{\mu_j}{\mu_{w,j}} \right]^{0.14} \left[ 1 + 3.5 \frac{D_e}{D_c} \right]^{0.4} \tag{4.30}
\]

\[
D_e = 2 \left[ D_{ja} - D_{ji} \right] \tag{4.31}
\]

\[
A_x = p_b \left[ \frac{D_{ja} - D_{ji}}{2} \right] \tag{4.32}
\]

where $D_c$ is the center line diameter of the annular jacket and $p_b$ is the position of each baffle.

**Step 12:** The process is simulated with $p$, $z_{ns}$ and $w_{ns}$ values. As it was mentioned before, changes in the $SII$ through scale increments show a degradation of process behavior. According to this, the evolution of $T_r$ and $F_j$ are compared in Fig. 4.5 for both cases, i.e. (i) energy requirements and (ii) geometrical similarity, holding the controller parameter for the $cs$ design.

![Figure 4.5. Comparison of $T_r$ and $F_j$ at $cs$ and $ns$.](image)

It can be seen from Fig. 4.5 that is not possible to scale-up the process maintaining the geometrical similarity. Despite $T_r$ changes are small, less than $1^\circ C$, $F_j$ reaches its maximum value during the first five minutes of the batch. During this time, any disturbance introduced to the process cannot be countered by the controller. Bearing this in mind, $x$ values and conversion of $A$ ($X$) at the end of the batch for both scales are reported in Table 4.4.

| Sym. | $x_{cs}$ | $x_{ns}|_{U_{r}}$ | $x_{ns}|_{U_{a}}$ | SI Unit |
|------|----------|------------------|------------------|---------|
| $C_A$ | 0.0763   | 0.0763           | 0.0768           | $\text{kmol/m}^3$ |
| $T_r$ | 298.38   | 298.38           | 298.40           | K       |
| $T_j$ | 294.40   | 294.50           | 293.39           | K       |
| $X$   | 0.9152   | 0.9152           | 0.9147           | –       |
As can be seen from Table 4.4, the concentration of \( A \) \(( C_A)\) and conversion \(( X)\) are virtually unaffected by the scale-up procedure. This result was expected, since \( C_A \) is the less impacted dynamics by the process design variables (see Fig. 4.4).

**Intermediate steps (a)–(f):** these steps are followed for computing the \( SII_{ns} \).

**Step 13:** the \( SII_{ns} \) is computed using (4.13). In this way, values of this index for the main dynamics \(( T_j)\) at each scale are compared in Fig. 4.6 for all cases.

It can be seen that the \( SII_{Tj} \) profile for the geometrical similarity case is highly different from the \( cs \) profile. According to this, it is not possible to reproduce the same dynamic behavior of the reactor at the \( ns \) by keeping the geometrical similarity. Fig. 4.6 also shows that there is small difference between the \( SII_{Tj} \) curves at \( cs \) and \( ns \) for the energy requirements case, this difference is because the jacket must be designed with a integer number of baffles. Here, two baffles were added to the annular jacket but the real requirement were 1, 6 units. The difference in the \( F_j \) profiles between \( cs \) and energy requirements case in Fig. 4.5 is also attributed to this reason.

### 4.3. Concluding remarks

This chapter has focused on the development of the scale-up methodology. Here, it is worth noting:

- The incorporation of the State Impactability Index to the scale-up of \( BPs \) enables the establishment of real scale factors of the process, keeping the same Operating Regime (dynamics hierarchy) as the scale is changed. This index allows the designer to determine the effect of the design variables as a whole over each state variable.

- The use a process \( PBSM \) and its Hankel matrix, for analyzing the process dynamic behavior and scaling it up, is the key for carrying out a successful scale-up. In this sense, the classification of the process variables in: state variables, design variables, synthesis
parameters, and design-variable-dependent parameters is also a keystone of this work. This classification allows extending the use of the Hankel matrix from control to processes design.

- A non-isothermal batch reactor was scaled-up from $0.1\,\text{m}^3$ to $1\,\text{m}^3$. As a result of this, the scale factors for maintaining the same operating trajectory at both scales were found. From this example, it is illustrated that traditional scale-up methods do not always lead into the best commercial unit design; and if the geometrical similarity is held, other parameters of the process need to be changed in order to achieve the same performance targets set at the current scale at an industrial unit.
CHAPTER 5
Scale-up of a batch suspension polymerization reactor

This chapter presents the implementation of the proposed methodology for scaling up batch processes to a batch suspension polymerization reactor. The chapter is organized as follows: in Section 5.1, a phenomenological-based model of a batch suspension polymerization is obtained, with the purpose of using it when scaling up the process. Then, in Section 5.2, the scale-up procedure introduced in Chapter 4 is applied to the polymerization process, comparing the scaled unit design when using this approximation and a traditional method. Finally, Section 5.3 presents some concluding remarks.

5.1. Modeling of a batch suspension polymerization reactor

Poly(methyl methacrylate) (PMMA) is a transparent thermoplastic widely used as a replacement of glass in the manufacturing industry [130], mainly because of its high resistance to ultraviolet degradation and corrosion [131]. This polymeric material is generally produced by free radical suspension polymerization of methyl methacrylate (MMA) [132; 133], where the monomer, relatively insoluble in water, is dispersed as liquid droplets with suspending agents (steric stabilizers) and strong agitation (which is maintained during the polymerization) to produce polymer particles as a dispersed solid phase [134]. Here, the initiator is soluble in the organic phase, i.e. it is soluble in the liquid monomer phase [132].

Within the polymer industry, batch operation remains as the predominant processing technique [133; 135; 136], despite the challenges of obtaining polymeric products with desired molecular and mechanical properties (e.g. density, melt index, impact strength, rigidity, tensile strength, chemical resistance, thermal stability, etc.) [137] in such type of unit. For this sort of processing, the literature has shown that there is no simple rule or procedure to scale-up suspension polymerization reactors [134; 138], so combinations of the methods described in in Chapter 2 have been used when scaling up these processes [139; 140; 141]. Therefore, in this chapter, a batch suspension polymerization reactor is scaled-up, comparing the proposed methodology with a traditional method. Despite a PBSM must be validated at the cs in order to use the methodology, within this chapter, a complete PBSM is used as real process and a simplified one for scaling up the process. So, the scale-up is verified by means of the complete model.

5.1.1. Process description and process flow diagram

The model herein proposed is obtained using the methodology of Alvarez et al. [73], Fig. 5.1 shows the process flow diagram. At the beginning of the polymerization process the reactor is charged with: (i) monomer (methyl methacrylate), (ii) initiator (benzoyl peroxide) (iii) continuous phase precursor (water) and (iv) suspending agents. These compounds are heated until the reaction temperature (358.15K) is reached, when the polymerization process starts.
Since the polymerization reactions are highly exothermic, the reactor is cooled using a double-pipe heat exchanger in series with the reactor jacket that keeps its temperature at 358.15K.

During the polymerization, it is assumed that the kinetic mechanism shown in (5.1)–(5.6) governs the PMMA synthesis [138; 141; 142; 143].

Decomposition of initiator: \[ I \xrightarrow{k_d} 2R \]  
Formation of active species: \[ M + R \xrightarrow{k_I} P_1 \]  
Propagation: \[ P_\alpha + M \xrightarrow{k_{pg}} P_{\alpha+1} \]  
Chain transfer to polymer: \[ P_\alpha + M \xrightarrow{k_{fm}} P_1 + D_\alpha \]  
Termination by recombination: \[ P_\alpha + P_\beta \xrightarrow{k_{tc}} D_\alpha + D_\beta \]  
Termination by disproportionation: \[ P_\alpha + P_\beta \xrightarrow{k_{td}} D_\alpha + D_\beta \]

Here, \( I, R \) and \( M \) represent initiator, primary radicals and monomer concentrations respectively. \( P_\alpha, P_\beta \) and \( D_\alpha, D_\beta \) are the concentrations of live and dead polymer chains, where \( \alpha \) and \( \beta \) represent chains with different lengths. \( k_d, k_I, k_{pg}, k_{fm}, k_{tc} \) and \( k_{td} \) are decomposition, initiation, propagation, chain transfer to polymer, termination by recombination, and termination by disproportionation kinetic constants respectively. Finally, the PMMA polymerization process ends after five hours of reaction, when the polymer is discharged from the reactor.

### 5.1.2. Model resolution and process systems

Given that the model resolution is the macroscopic scale, two process systems are considered at the reactor: \( S_I \) as the process side, and \( S_{II} \) as the jacket side. The interaction between these two process systems is only energetic as can be seen from Fig. 5.2. On the other hand, two process systems are associated with the heat exchanger: \( S_{III} \) as the annulus side and \( S_{IV} \) as the...
inner tube side. The interaction between these two process systems is also merely energetic (see Fig. 5.2).

![Figure 5.2. Batch polymerization reactor blocks diagram.](image)

The conservation principle (mass and energy balances) is applied to all process systems shown in Fig. 5.2 for obtaining the model structure. In the next subsection, the obtained PBSM is presented, including the constitutive equations that represent all parameters.

### 5.1.3. Conservation principle application and constitutive equations

Based on the free radical mechanism shown (5.1)–(5.6) a model composed by an infinite number of radical population equations is obtained. Therefore, for simplifying the infinite number of radical population equations \(P_1, P_2, \ldots, P_\alpha, P_\beta\) and \(D_1, D_2, \ldots, D_\alpha, D_\beta\) into a smaller set of modeling equations, (5.7) is used for computing zero \((\lambda_0)\), first \((\lambda_1)\) and second \((\lambda_2)\) moments of the live polymer chains and (5.8) for computing zero \((\eta_0)\), first \((\eta_1)\) and second \((\eta_2)\) moments of the dead polymer chains [137; 138; 144; 145; 146].

\[
\lambda_\gamma = \sum_{\alpha=1}^{\infty} \alpha^\gamma P_\alpha \quad (5.7) \quad \eta_\gamma = \sum_{\alpha=1}^{\infty} \alpha^\gamma D_\alpha \quad (5.8)
\]

where \(\gamma = 0, 1, 2\). According to this, when applying the conservation principle to the four process systems shown in Fig. 5.2, a reduced model composed by differential equations (5.9)–(5.21) and algebraic equations (5.22)–(5.108) is obtained. In this case, mass balances by components were applied over \(S_I\) for concentrations of initiator \((I)\), primary radicals \((R)\), monomer \((M)\), zero \((\lambda_0)\), first \((\lambda_1)\) and second \((\lambda_2)\) moments of the live polymer chains, and zero \((\eta_0)\), first \((\eta_1)\) and second \((\eta_2)\) moments of the dead polymer chains. For the reactor temperature \((T_r)\) dynamics, an energy balance was made over \(S_I\). Also, for the cooling fluid temperatures at jacket input \((T_1)\) and output \((T_2)\), energy balances were performed over \(S_{III}\) and \(S_{II}\) respectively. Finally, for the cooling fluid temperature at inner tube output of the heat exchanger \((T_4)\), an energy balance was done over \(S_{IV}\).

\[
\frac{dI}{dt} = -k_{dl}I \quad (5.9)
\]

\[
\frac{dR}{dt} = 2fk_{dl}I - k_1MR \quad (5.10)
\]

\[
\frac{dM}{dt} = -k_1MR - (k_{pg} + k_{fm})M\lambda_0 \quad (5.11)
\]
In (5.19)–(5.21), cooling fluid densities at the jacket input (\(\rho\)) and output (\(\rho\)). Also, kinetic constants, from (5.33) and (5.34) \[153\]. In addition, cooling fluid densities at the inner tube input (\(\rho\)) and output (\(\rho\)) in (5.9)–(5.18), \(\rho\). The densities of the monomer (\(\rho\)) input and output, and \(T\). Here, \(k\) is the termination constant rate and \(r\) represents the monomer conversion, given by (5.29) \[135; 148\]. Equations (5.28)–(5.108) are in SI units.

\[
\frac{d\lambda_0}{dt} = k_1 MR - (k_{tc} + k_{td})\lambda_0^2
\]  
\[
\frac{d\lambda_1}{dt} = k_1 MR + k_{pg} M\lambda_0 + k_{fm} M(\lambda_0 - \lambda_1) - (k_{tc} + k_{td})\lambda_0\lambda_1
\]  
\[
\frac{d\lambda_2}{dt} = k_1 MR + k_{pg} M(\lambda_0 + 2\lambda_1) + k_{fm} M(\lambda_0 - \lambda_2) - (k_{tc} + k_{td})\lambda_0\lambda_2
\]

\[
\frac{d\rho_1}{dt} = k_{fm} M\lambda_0 + \left[k_{td} + \frac{1}{2}k_{tc}\right] \lambda_0^2
\]  
\[
\frac{d\rho_1}{dt} = k_{fm} M\lambda_1 + (k_{td} + k_{tc})\lambda_0\lambda_1
\]  
\[
\frac{d\rho_2}{dt} = k_{fm} M\lambda_2 + k_{td}\lambda_0\lambda_2 + k_{tc}(\lambda_0\lambda_2 + \lambda_1^2)
\]

\[
\frac{dT_2}{dt} = -\frac{1}{C_{p,2}\rho_2 V_f} \left[F_1 \rho_1 C_{p,1}(T_1 - T_{ref}) - F_2 \rho_2 C_{p,2}(T_2 - T_{ref}) + \dot{Q}_1\right]
\]  
\[
\frac{dT_1}{dt} = -\frac{1}{C_{p,1} \rho_1 V_a} \left[F_2 \rho_2 C_{p,2}(T_2 - T_{ref}) - F_1 \rho_1 C_{p,1}(T_1 - T_{ref}) - \dot{Q}_2\right]
\]  
\[
\frac{dT_4}{dt} = -\frac{1}{C_{p,4} \rho_4 V_t} \left[F_3 \rho_3 C_{p,3}(T_3 - T_{ref}) - F_4 \rho_4 C_{p,4}(T_4 - T_{ref}) + \dot{Q}_2\right]
\]

where \(T_r\) is the reactor temperature, \(T_1\) and \(T_2\) are the cooling fluid temperatures at jacket input and output, and \(T_4\) is the cooling fluid temperature at inner tube output of the heat exchanger.

In (5.9)–(5.18), \(f\) represents the initiator efficiency and \(\Delta H_p\) is the heat of polymerization. Also, kinetic constants, \(k_d\) [1/min], \(k_l\) [m³/min kmol], \(k_{pg}\) [m³/min kmol], \(k_{fm}\) [m³/min kmol], \(k_{td}\) [m³/min kmol] and \(k_{tc}\) [m³/min kmol], are given by [130; 144; 147]:

\[
k_d = 1.014 \times 10^{16} e^{\frac{-3200}{T_r}}
\]  
\[
k_l = k_{pg} = 2.95 \times 10^7 e^{\frac{4385}{T_r}}
\]  
\[
k_{fm} = 9.48 \times 10^3 k_{pg} e^{\frac{-13880}{T_r}}
\]  
\[
k_{td} = k_{tc} = 3.956 \times 10^{-4} k_{td} e^{\frac{4090}{T_r}}
\]

Here, \(k_1\) is the termination constant rate and \(R_g [cal/mol \cdot K]\) the ideal gas constant. The reactor fluid (\(\rho_r\)) density is given by (5.28) \[148; 149\]. Equations (5.28)–(5.108) are in SI units.

\[
\rho_r = \frac{\rho_{r,0}}{1 + \epsilon X_m}
\]

where \(X_m\) represents the monomer conversion, given by (5.29) \[135; 148\], and \(\rho_{r,0}\) the reactor fluid initial density. Also, the contraction factor (\(\epsilon\)) can be computed from (5.30) \[135; 150\]:

\[
X_m = \frac{M_0 - M}{M_0 + \epsilon M}
\]  
\[
\epsilon = \frac{\rho_m}{\rho_p} - 1 \phi_{m,0}
\]

Here, \(M_0\) is the initial monomer concentration and \(\phi_{m,0}\) the initial volume fraction of monomer. The densities of the monomer (\(\rho_m\)) and polymer (\(\rho_p\)) can be calculated from [151; 152]:

\[
\rho_m = 968 - 1.225(T_r - 273.15)
\]  
\[
\rho_p = 1212 - 0.845(T_r - 273.15)
\]

In (5.19)–(5.21), cooling fluid densities at the jacket input (\(\rho_1\)) and output (\(\rho_2\)) are obtained from (5.33) and (5.34) \[153\]. In addition, cooling fluid densities at the inner tube input (\(\rho_3\)) and output (\(\rho_4\)) are computed using (5.35) and (5.36) \[151\].
In addition, the cooling fluid flow rate at jacket output \((F_2)\) is given by (5.37), and the cooling fluid flow rates at inner tube input \((F_3)\) and output \((F_4)\) are given by (5.39) and (5.38).

\[
F_2 = F_1 \frac{\rho_1}{\rho_2} \quad (5.37)
\]

\[
F_3 = F_3,\text{bias} + K_p e(t) + K_I \int_{t_0}^{t} e(t) dt + K_D \frac{de(t)}{dt} \quad (5.39)
\]

\[
F_4 = F_3 \frac{\rho_2}{\rho_4} \quad (5.38)
\]

where \(F_1\) is the cooling fluid flow rate at jacket input and \(F_3,\text{bias}\) is the nominal cooling fluid flow rate at the inner tube. \(K_p, K_I\) and \(K_D\) are the proportional, integral and derivative controller gains, and \(e(t) = T_r,sp - T_r\), considering that the subscript \(sp\) represents the set point. On the other hand, in (5.18), the reactor fluid specific heat capacity \((C_{p,r})\) is given by (5.40), considering that the use of volume fractions for computing mixture properties is a common practice when modeling polymerization processes [144, 147, 149].

\[
C_{p,r} = \phi_mC_{p,m} + \phi_p C_{p,p} + \phi_s C_{p,s} \quad (5.40)
\]

Here, volume fractions of monomer \((\phi_m)\), polymer \((\phi_p)\), and water \((\phi_s)\) are given by (5.41)–(5.43) [137]. Also, \(C_{p,m}, C_{p,p}\) and \(C_{p,s}\) are the monomer, polymer and water specific heat capacities.

\[
\phi_m = \left[\frac{1 - X_m}{1 + \epsilon X_m}\right] \phi_{m,0} \quad (5.41) \quad \phi_p = \phi_{m,0} - \phi_m \quad (5.42) \quad \phi_s = 1 - \phi_p - \phi_m \quad (5.43)
\]

Also, cooling fluid specific heat capacities at the jacket input \((C_{p,1})\) and output \((C_{p,2})\) are obtained from (5.44) and (5.45) [153]. Additionally, cooling fluid specific heat capacities at the inner tube input \((C_{p,3})\) and output \((C_{p,4})\) are given by (5.46) and (5.47) [154].

\[
C_{p,1} = 1.64 \times 10^3 + 7.06 T_1 - 5.71 \times 10^{-3} T_1^2 \quad (5.44)
\]

\[
C_{p,2} = 1.64 \times 10^3 + 7.06 T_2 - 5.71 \times 10^{-3} T_2^2 \quad (5.45)
\]

\[
C_{p,3} = 1.02 \times 10^3 + 2.63 \times 10^1 T_3 - 7.45 \times 10^{-2} T_3^2 + 7.28 \times 10^{-5} T_3^3 \quad (5.46)
\]

\[
C_{p,4} = 1.02 \times 10^3 + 2.63 \times 10^1 T_4 - 7.45 \times 10^{-2} T_4^2 + 7.28 \times 10^{-5} T_4^3 \quad (5.47)
\]

The heat-transfer rates at the reactor \((\dot{Q}_1)\) and at the double-pipe heat exchanger \((\dot{Q}_2)\) can be calculated using (5.48) and (5.49) [128; 155].

\[
\dot{Q}_1 = U_t A_t (T_r - T_2) \quad (5.48) \quad \dot{Q}_2 = U_{he} A_t N_{hp} (T_1 - T_4) \quad (5.49)
\]

where \(N_{hp}\) is the number of hairpins. Also, the overall heat transfer coefficients at the reactor \((U_r)\) and heat exchanger \((U_{he})\) are given by (5.50) and (5.51) [128; 129; 155; 156].

\[
U_r = \frac{1}{\frac{1}{h_r} + \frac{T_r}{2 \pi d_i \ln \left[ \frac{D_i}{d_i} \right]} + \frac{T_r}{h_l L_t}} \quad (5.50)
\]

\[
U_{he} = \frac{1}{\frac{1}{h_{he}} + \frac{A_e R_h}{2 \pi d_i L_t} + \frac{A_{he}}{2 \pi d_o L_t} \ln \left[ \frac{D_o}{d_o} \right] + \frac{h_o}{c_{he}} + \frac{1}{c_{eh}}} \quad (5.51)
\]

Notice that (5.50) and (5.51) are only valid for the current scale design. So, in the following subsection, (5.50) will be replaced by a valid expression at all scales and (5.51) will be changed according to the new scale requirements. \(k_{w,r}\) and \(k_{w,he}\) are the reactor wall and heat exchanger pipe thermal conductivities. \(T\) is the tank diameter and \(D_{ji}\) the inner diameter of the annular jacket. \(d_i\) and \(d_o\) are inside and outside diameters of the heat exchanger inner tube, and \(L_t\)
CHAPTER 5. Scale-up of a batch suspension polymerization reactor

is the nominal length of the exchange section. \( R_{i} \) and \( R_{o} \) are inner tube and annulus fouling resistances. Also, in (5.48), \( A_{r} \) is the reactor transfer area, given by (5.52).

\[
A_{r} = \pi TZ + \frac{\pi}{4} T^{2}
\]  

(5.52)

Here, the reactor fluid height \( (Z) \) can be computed from (5.53), where the reactor volume (\( V_{r} \)) is given by (5.54) [137]. Also, \( V_{r,0} \) is the initial reactor volume and \( V_{bottom} \) the volume of the reactor bottom. In addition, in (5.19), \( V_{j} \) is the jacket volume, calculated from (5.55).

\[
Z = \frac{4(V_{r} - V_{bottom})}{\pi T^{2}}  
\]  

(5.53)

\[
V_{r} = V_{r,0}(1 + cX_{m})  
\]  

(5.54)

\[
V_{j} = \frac{2}{5}V_{r}
\]  

(5.55)

In (5.51), \( A_{t} \) is the overall outside area of the inner tube, given by (5.56), where the outside area of the inner tube \( (A_{u}) \) and the area of a fin \( (A_{f}) \) are calculated from (5.57) and (5.58). Also, \( A_{i} \) is the inside area of the inner tube, computed from (5.59) [155].

\[
A_{t} = A_{u} + A_{f}
\]  

(5.56)

\[
A_{u} = 2[\pi d_{o}L_{i} - N_{f}L_{f}\delta_{f}]  
\]  

(5.57)

\[
A_{i} = 2\pi d_{i}L_{i}
\]  

(5.59)

where \( N_{f} \) is the number of fins and \( \delta_{f} \) is the fin thickness. The fin height \( (H_{f}) \) is given by:

\[
H_{f} = 0.75\left[ \frac{D_{i} - d_{o}}{2} \right]
\]  

(5.60)

where \( D_{i} \) is the inner diameter of the heat-exchanger annulus. Additionally, in (5.51), the overall surface efficiency \( (\xi_{o}) \) is given by (5.61), where the fin efficiency \( (\xi_{f}) \) is calculated using (5.62). Here, \( m_{r} \) is given by (5.63) [155].

\[
\xi_{o} = 1 - (1 - \xi_{f})\frac{A_{f}}{A_{t}}
\]  

(5.61)

\[
\xi_{f} = \tanh\left( \frac{m_{r}H_{f}}{m_{r}H_{f}} \right)
\]  

(5.62)

\[
m_{r} = \sqrt{\frac{2h_{a}}{k_{w,he}\delta_{f}}}
\]  

(5.63)

where \( h_{a} \) is the heat transfer coefficient at the annulus side computed from (5.70), considering that \( Nu_{a} \) is given by (5.83). Then, in order to compute the inner \( (h_{r}) \) and outer \( (h_{j}) \) heat transfer coefficients at the reactor, equations (5.64) and (5.65) are used [128].

\[
Nu_{r} = 0.85Re_{r}^{2/3}Pr_{r}^{1/3}\left[ \frac{Z}{T} \right]^{-0.56}\left[ \frac{D}{T} \right]^{0.13}
\]  

(5.64)

\[
Nu_{j} = \begin{cases} 
1.86 \left[ Re_{j}Pr_{j}D_{a,j}^{4/3}\left( \frac{\mu_{j}}{\mu_{w,j}} \right) \right]^{0.14} & \text{Re}_{j} \leq 2300 \\
0.027Re_{j}^{4/3}Pr_{j}^{1/3}\left[ \frac{\mu_{j}}{\mu_{w,j}} \right]^{0.14} & \text{Re}_{j} > 2300
\end{cases}
\]  

(5.65)

Here, \( D \) represents the impeller diameter. The equivalent diameter for heat transfer at the jacket \( (D_{e,i}) \) is given by (5.66). Also, the length of jacket passage \( (L_{j}) \) can be computed from (5.67), where the center-line jacket radius \( (r_{c}) \) is given by (5.68) [128].

\[
D_{e,i} = 2[D_{ja} - D_{ji}]
\]  

(5.66)

\[
L_{j} = 2\pi r_{c}N_{t}
\]  

(5.67)

\[
r_{c} = \frac{D_{ja} + D_{ji}}{4}
\]  

(5.68)

On the other hand, in order to compute the inner \( (h_{r}) \) and outer \( (h_{a}) \) heat transfer coefficients at the heat exchanger, equations (5.69) and (5.70) are used [155; 157].

\[
Nu_{r} = \begin{cases} 
1.86 \left[ Re_{r}Pr_{r}D_{a,r}^{4/3} \right]^{1/3} & \text{Re}_{r} < 2300 \\
\left( \frac{(r_{r}/2)(Re_{r} - 1000)Pr_{r}}{1 + 12.7(r_{r}/2)^{2/3}(Pr_{r}^{0.1} - 1)} \right)^{0.8} & 2300 \leq \text{Re}_{r} \leq 10^{4}
\end{cases}
\]  

(5.69)

\[
Nu_{a} = \begin{cases} 
1.86 \left[ Re_{a}Pr_{a}D_{a,a}^{4/3} \right]^{1/3} & \text{Re}_{a} < 10^{4} \\
\left( \frac{(r_{a}/2)(Re_{a}Pr_{a}^{0.1} - 1)}{1 + 8.7(r_{a}/2)^{2/3}(Pr_{a}^{0.1} - 1)} \right)^{0.8} & \text{Re}_{a} > 10^{4}
\end{cases}
\]  

(5.70)
where the Fanning friction factors for the inner tube \( f_i \) and annulus \( f_a \) are given by [157]:

\[
f_i = \begin{cases} 
0.079 \text{Re}_t^{-1/4} & 2300 \leq \text{Re}_t \leq 10^4 \\
\frac{1}{4} \left[ 1.82 \log(\text{Re}_t) - 1.64 \right]^{-2} & \text{Re}_t < 10^4
\end{cases}
\]

\[
f_a = \begin{cases} 
0.079 \text{Re}_e^{-1/4} & 2300 \leq \text{Re}_e \leq 10^4 \\
\frac{1}{4} \left[ 1.82 \log(\text{Re}_e) - 1.64 \right]^{-2} & \text{Re}_e < 10^4
\end{cases}
\]

In (5.64)–(5.72), the Reynolds numbers at the reactor \( \text{Re}_r \), jacket \( \text{Re}_j \), annulus \( \text{Re}_a \), and inner tube \( \text{Re}_t \) can be computed using (5.73)–(5.76). Prandtl numbers at the reactor \( Pr_r \), jacket \( Pr_j \), annulus \( Pr_a \), and inner tube \( Pr_t \) are calculated with (5.77)–(5.80). Also, in (5.64)–(5.70), Nusselt numbers at the reactor \( Nu_r \), jacket \( Nu_j \), annulus \( Nu_a \), and inner tube \( Nu_t \) are given (5.81)–(5.84) [128; 155].

\[
\text{Re}_r = \frac{D_i^2 Nu_r}{\mu r} \quad (5.73) \quad Pr_r = \frac{C_{p,r} \mu r}{k_r} \quad (5.77) \quad Nu_r = \frac{h_r T}{k_r} \quad (5.81)
\]

\[
\text{Re}_j = \frac{D_{ij} \rho_1 F_1}{A_{x,j} \mu_1} \quad (5.74) \quad Pr_j = \frac{C_{p,1} \mu_1}{k_1} \quad (5.78) \quad Nu_j = \frac{h_j D_{e,j}}{k_1} \quad (5.82)
\]

\[
\text{Re}_a = \frac{D_{o2} F_2}{A_{x,a} \mu_2} \quad (5.75) \quad Pr_a = \frac{C_{p,2} \mu_2}{k_2} \quad (5.79) \quad Nu_a = \frac{h_a D_{e,a}}{k_2} \quad (5.83)
\]

\[
\text{Re}_t = \frac{d_i^2 F_3}{A_{x,t} \mu_3} \quad (5.76) \quad Pr_t = \frac{C_{p,3} \mu_3}{k_3} \quad (5.80) \quad Nu_t = \frac{h_t d_i}{k_3} \quad (5.84)
\]

In addition, in (5.74)–(5.76), the cross-sectional flow areas at the jacket \( A_{x,j} \), annulus \( A_{x,a} \), and inner tube \( A_{x,t} \) are computed from (5.85)–(5.87) [128; 155].

\[
A_{x,j} = L \left[ \frac{D_{io} - D_{ii}}{2} \right] \quad (5.85) \quad A_{x,a} = \frac{\pi}{4} \left[ D_i^2 - d_o^2 \right] - H_f \delta_f N_f \quad (5.86) \quad A_{x,t} = \frac{\pi d_i^2}{4} \quad (5.87)
\]

Here, \( L \) and \( N_{\text{turns}} \) represent the jacket fluid length and the number of fluid turns at the jacket. Also, in (5.75), \( D_h \) is the hydraulic diameter, given by (5.88). In (5.83), \( D_{e,a} \) is the equivalent diameter for heat transfer at the annulus, computed from (5.89) [155].

\[
D_h = 4 \frac{A_{x,a}}{P_w} \quad (5.88) \quad D_{e,a} = 4 \frac{A_{x,a}}{P_h} \quad (5.89)
\]

where the total wetted perimeter of the annulus \( P_w \) can be obtained from (5.90), and the heat transfer perimeter of the annulus \( P_h \) can be calculated from (5.91) [155].

\[
P_w = \pi d_o [D_i + d_o] + 2H_f N_f \quad (5.90) \quad P_h = \pi d_o + 2H_f N_f \quad (5.91)
\]

In (5.20) and (5.21), volumes of the inner tube \( V_t \) and annulus \( V_a \) are given by [155]:

\[
V_t = A_{x,t} 2L_t N_{hp} \quad (5.92) \quad V_a = A_{x,a} 2L_t N_{hp} \quad (5.93)
\]
In (5.77) and (5.81), the reactor fluid thermal conductivity \( k_r \) is calculated from [144].

\[
k_r = \phi_m k_m + \phi_p k_p + \phi_s k_s
\]  
(5.94)

where \( k_m, k_p, k_s \) are thermal conductivities of the monomer, polymer and water. Cooling fluid thermal conductivities at the jacket input \( (k_1) \) and output \( (k_2) \) are given by [153]:

\[
k_1 = -2.429 \times 10^{-2} + 1.615 \times 10^{-3} T_1 - 1.912 \times 10^{-6} T_1^2
\]

\[
k_2 = -2.429 \times 10^{-2} + 1.615 \times 10^{-3} T_2 - 1.912 \times 10^{-6} T_2^2
\]

(5.95) (5.96)

In addition, in (5.73) and (5.77), the reactor fluid dynamic viscosity \( (\mu_r) \) is given by (5.97).

\[
\mu_r = x_m k_m + x_p k_p + x_s k_s
\]

(5.97)

where \( \mu_m, \mu_p, \mu_s \) are dynamic viscosities of the monomer, polymer and water. Here, the monomer \( (x_m) \) and polymer \( (x_p) \) and water \( (x_w) \) mole fractions are obtained from (5.98)–(5.100) [130]. Here, \( \mu_r \) is computed by means of the mole fraction of pure species because this property is highly dependent on the polymer molecular weight [130; 138; 141].

\[
x_m = \frac{\phi_m x_m}{M_{w,m}} + \frac{\phi_p x_p}{M_{w,p}} + \frac{\phi_s x_s}{M_{w,s}}
\]

(5.98)

\[
x_p = \frac{\phi_m x_m}{M_{w,m}} + \frac{\phi_p x_p}{M_{w,p}} + \frac{\phi_s x_s}{M_{w,s}}
\]

(5.99)

Cooling fluid dynamic viscosities at the jacket input \( (\mu_{j1}) \) and output \( (\mu_{j2}) \) are computed using (5.101) and (5.102) [153]. Also, cooling fluid dynamic viscosities at the jacket wall \( (\mu_{w,j}) \) and at the annulus wall \( (\mu_{w,a}) \) are given by (5.103) and (5.104) [153].

\[
\mu_{j1} = 0.73439 e^{-0.01663 T_1}
\]

(5.101)

\[
\mu_{j2} = 0.73439 e^{-0.01663 T_2}
\]

(5.102)

\[
\mu_{w,j} = 0.73439 e^{-0.01663 T_{w,j}}
\]

(5.103)

\[
\mu_{w,a} = 0.73439 e^{-0.01663 T_{w,a}}
\]

(5.104)

Here, wall temperatures at the jacket \( (T_{w,j}) \) and annulus \( (T_{w,a}) \) are given by [155].

\[
T_{w,j} = \frac{T_r + T_1}{2}
\]

(5.105)

\[
T_{w,a} = \frac{T_2 + T_3}{2}
\]

(5.106)

Number average \( (M_n) \) and weight average \( (M_w) \) molecular weights are given by [133; 137]:

\[
M_n = \frac{\lambda_1 + \eta_1}{\lambda_0 + \eta_0} M_{w,m}
\]

(5.107)

\[
M_w = \frac{\lambda_2 + \eta_2}{\lambda_1 + \eta_1} M_{w,m}
\]

(5.108)

Since \( M_n \) and \( M_w \) are strongly related with functional properties of the polymer such as particle size, impact strength, rigidity, tensile strength, chemical resistance, thermal stability, among others [137; 138; 145], this work seeks to maintain their values when scaling up the process.

It is worth clarifying that values of constant parameters and initial conditions are not reported because of a confidentiality clause with New Stetic.

### 5.1.4. Batch suspension polymerization reactor simulation

The solution of the previously presented coupled differential and algebraic equations was done in EMSO (Environment for Modeling, Simulation and Optimization). Fig. 5.3 shows the dynamic evolution of the the reactor temperature \( (T_r) \) and cooling fluid flow rate at the inner tube input \( (F_j) \). For the polymerization process, it is considered that the optimal process trajectory occurs when the reactor temperature is kept at 358.15K.
In addition, Fig. 5.4 shows the number average \((M_n)\) and weight average \((M_w)\) molecular weights profiles for the batch. As it was mentioned at the beginning of this chapter, the aim of this work is to reproduce the trajectories of both molecular weights set at the cs in the ns.

In the following subsection, the scale-up methodology presented in Chapter 4 is implemented to the previously presented polymerization process.

### 5.2. Scale-up procedure implementation

As mentioned before, the PBSM shown in Section 5.1 is reduced within the procedure application. In this sense, the next subsection presents the simplified version of the model.
5.2.1. Model simplification for scaling up the process

For the model simplification the following assumptions are considered:

- The reactor fluid density dependency on temperature is neglected, only the concentration dependency is considered, since the reactor temperature is controlled [133; 149].
- Kinetic constants, \( k_d \), \( k_l \), \( k_{pg} \), \( k_{fm} \), \( k_t \), \( k_{tc} \) and \( k_{td} \) are evaluated at \( T_{r,sp} \), given the reactor isothermal operation [158].
- Given that \( C_{p,r} \), \( \mu_t \) and \( k_r \) variations with concentration and temperature are small, they are considered constant (average values) along the batch [133; 158].
- Quasi-steady-state approximation (QSSA) for primary radicals (\( R \)), and zero (\( \lambda_0 \)), first (\( \lambda_1 \)) and second (\( \lambda_2 \)) moments of the live polymer chains [133].
- \( T_1 \) is considered as a known input variable to the process, i.e. its value at each stage of the batch is known.

The simplified model is composed by differential equations: (5.9), (5.11) and (5.15)–(5.19). Also, in equations (5.10) and (5.12)–(5.14) the time-dependence of each species is neglected, according to the QSSA for \( R \), \( \lambda_0 \), \( \lambda_1 \) and \( \lambda_2 \), giving place to (5.109)–(5.112). These algebraic equations describe the behavior of these species during the batch.

\[
R = \frac{2f_{kd}d}{k_lM} \quad (5.109) \quad \lambda_0 = \lambda_0 \quad [1 + \frac{k_{pg}M}{k_{fm}M + k_t\lambda_0}] \quad (5.111)
\]

\[
\lambda_0 = \left[ \frac{2f_{kd}d}{k_t} \right]^{1/2} \quad (5.110) \quad \lambda_2 = \lambda_1 \quad [1 + \frac{2k_{pg}M}{k_{fm}M + k_t\lambda_0}] \quad (5.112)
\]

Here, \( k_d \), \( k_l \), \( k_{pg} \), \( k_{fm} \), \( k_t \), \( k_{tc} \) and \( k_{td} \), given by (5.22)–(5.27), are evaluated at \( T_{r,sp} \). Also, \( \rho_m \) and \( \rho_p \), computed from (5.31) and (5.32), are evaluated at \( T_{r,sp} \). The rest of the parameters involved in the simplified model (\( V_r \), \( V_f \), \( \rho_1 \), \( \rho_2 \), \( C_{P,1} \), \( C_{P,2} \), \( F_1 \), \( F_2 \) and \( \dot{Q}_1 \)) are computed using the corresponding algebraic equations presented in the previous subsection. In addition, as \( \lambda_0 \ll \eta_0 \), \( \lambda_1 \ll \eta_1 \) and \( \lambda_2 \ll \eta_2 \) (since they are highly reactive species), number average (\( M_n \)) and weight average (\( M_w \)) molecular weights are simplified into (5.113) and (5.114).

\[
M_n = \frac{\eta_1}{\eta_0} M_{w,m} \quad (5.113) \quad M_w = \frac{\tau_0}{\eta_1} M_{w,m} \quad (5.114)
\]

5.2.2. Process scale-up using the simplified polymerization model

Each one of the thirteen steps of the procedure is performed as follows.

**Step 1**: \( CV_{es} = 0.1 \text{m}^3 \), \( CV_{ns} = 1.5 \text{m}^3 \) and \( \Delta CV = 0.1 \text{m}^3 \) are defined.

**Step 2**: a PBSM of the process is obtained. The PBSM composed by differential equations (5.9), (5.11) and (5.15)–(5.19) describes the dynamic behavior of the reactor.

**Step 3**: \( x, z, p \) and \( w \) are defined from the model as shown in (5.115)–(5.118).

\[
x = \begin{bmatrix} I & M & \eta_0 & \eta_1 & \eta_2 & T_r & T_2 \end{bmatrix} \quad (5.115)
\]

\[
z = \begin{bmatrix} V_{r,0} & T_1 \end{bmatrix} \quad (5.116)
\]

\[
p = \begin{bmatrix} f & k_d & k_l & k_{pg} & k_{fm} & k_t & k_{tc} & k_{td} & \Delta H_p & C_{p,r} & T_{ref} & M_{w,m} & \tau_j & \phi_{m,0} & M_0 & \rho_{r,0} \end{bmatrix} \quad (5.117)
\]

\[
w = \begin{bmatrix} V_r & V_f & F_1 & F_2 & U_r & A_r \end{bmatrix} \quad (5.118)
\]
Step 4: the OT is fixed at the cs. Here, the OT is obtained by solving the process model considering that \( T_r = 358.15K \pm 1K \) and including the effect of manipulating \( F_3 \) in order to the reactor fluid be able to reach this temperature range. Here, it is considered that the optimal OT occurs when \( T_r \) is set on 358.15K \([138]\), where the polymerization can take place achieving the desired polymer molecular weight with minor risk of a thermal runaway \([68]\).

Intermediate steps (a)–(f): these steps are followed for computing the \( SII_{x_k,cs} \).

(a) an expression for each \( w_i|_{cs} = f(z_{cs}) \) must be found. Thus, \( V_r \) is calculated from (5.54), \( V_j \) from (5.55), \( F_1 \) from (5.119), \( F_2 \) from (5.37), \( U_r \) from (5.50), and \( A_r \) from (5.52).

\[
F_1 = \frac{V_j}{\tau_j}
\]  

(5.119)

where \( \tau_j \) is the residence time for the cooling fluid at the jacket input.

(b) the model is linearized along the OT according to (4.3) and (4.4).

(c) \( B_c \) and \( C_c \) matrices are modified using (4.5) and (4.6), considering that \( y_i,\text{min} \) and \( y_i,\text{max} \) are minimum and maximum values of each \( y_i \) during the batch at the cs, since minor changes are expected for these limits at the cs. Here, \( T_1,\text{min} \) and \( T_1,\text{max} \) are also minimum and maximum values of \( T_1 \) and, \( V_r,0 \) limits are computed as the \( \pm 10\% \) of its nominal value at the cs.

(d) the model is discretized using \( t_s = 120s \). Here, \( t_s \) must be small in order to represent each continuous linear model. For this case, it was chosen equal to time step for constructing the continuous linear models ensemble. Given the slow nature of BPs \([3; 34]\) if \( t_s \) is changed (in a consistent value) the dynamics hierarchy is not altered.

(e) the \( \mathcal{O}, \mathcal{C} \) and \( \mathcal{H} \) are computed from (4.9)–(4.11), where \( n = 7, m = n = 7 \) and \( p = 2 \).

(f) \( \mathcal{H} \) is decomposed in singular values using (4.12).

Step 5: the \( SII_{x_k,cs} \) is computed from (4.13) with \( \text{rank}(\mathcal{H}) = r = 2 \). Fig. 5.5 shows the \( SII_{x_k,cs} \) profiles, where it can be seen that \( SII_T > SII_T^{M} > \{SII_I, SII_M, SII_{\eta_0}, SII_{\eta_1}, SII_{\eta_2} \} \).

Figure 5.5. State Impactability Index at cs for the polymerization process.

According to this, \( T_r \) is the most impacted dynamics by the design variables of the process. Here, it is worth clarifying that the \( SII \) curves may be affected by the controller tuning, so the designer must be careful to properly tune the controller because by using the proposed
methodology, the OT at the cs is transferred to the ns and, if the controller is poorly tuned an oversized unit may be designed at the cs, instead of the actually required one.

**Step 6:** the critical point of the batch is identified. It corresponds to \( \text{SII}_{T,cs} = 4.97 \) at \( t = 5h \) as can be seen from Fig. 5.5.

**Step 7:** this point is selected as the RP for scaling up the process. In this sense, values for the state variables at the RP are reported in Table 5.1.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>SI Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I )</td>
<td>( 9.56 \times 10^{-4} )</td>
<td>( \text{kmol/m}^3 )</td>
</tr>
<tr>
<td>( M )</td>
<td>( 3.75 \times 10^{-1} )</td>
<td>( \text{kmol/m}^3 )</td>
</tr>
<tr>
<td>( \eta_0 )</td>
<td>( 6.33 \times 10^{-3} )</td>
<td>( \text{kmol/m}^3 )</td>
</tr>
<tr>
<td>( \eta_1 )</td>
<td>( 2.19 \times 10^{0} )</td>
<td>( \text{kmol/m}^3 )</td>
</tr>
<tr>
<td>( \eta_2 )</td>
<td>( 1.67 \times 10^{3} )</td>
<td>( \text{kmol/m}^3 )</td>
</tr>
<tr>
<td>( T_r )</td>
<td>358.14</td>
<td>K</td>
</tr>
<tr>
<td>( T_2 )</td>
<td>357.41</td>
<td>K</td>
</tr>
</tbody>
</table>

**Intermediate steps (i)–(vi):** these steps are followed in order to determine the \( \text{SII}_{x_k,RP} \) as the scale is increased.

(i) an expression for each \( w_i|_{RP} = f(z_{RP}) \) is found. Considering that (5.50) fix a given geometry of the reactor, two cases for the overall heat-transfer coefficient are considered: available \( (U_{r,a}) \) and required \( (U_{r,r}) \). For the former, (5.50) is used for computing \( U_{r,a} \) and, for the latter, \( U_{r,r} \) is computed from (5.120).

\[
U_{r,r} = -\frac{F_1 C_{p,1}|_{RP} \rho_1|_{RP} (T_1|_{RP} - T_{ref}) - F_2 C_{p,2}|_{RP} \rho_2|_{RP} (T_2|_{RP} - T_{ref})}{A_r (T_r|_{RP} - T_2|_{RP})} \quad (5.120)
\]

where \( U_{r,r} \) is evaluated at the RP. In addition, considering that most of the traditional scale-up methods involve the fulfillment of the geometrical similarity, this comparison allows the designer to establish the effect of building a unit geometrically similar instead of the required one. Notice that, in the first case, the process is scaled-up keeping the overall heat-transfer coefficient fixed by the current scale design. Opposite to the second case, where the overall heat-transfer coefficient is computed from the process energy requirements without fixing the geometry of the reactor, making (5.120) valid when increasing the scale.

(ii) the model is linearized around the RP.

(iii) \( B_c \) and \( C_c \) matrices are modified according to (4.5) and (4.6), considering \( y_i \) limits are the same as those set at the cs, since minor changes are expected for these limits while the scale is increased because the process dynamic behavior is transferred from the cs to the ns using this methodology. Here, \( T_1 \) limits are also equal to those set at the cs and, \( V_{r,0} \) limits are computed as the \( \pm 10\% \) of its nominal value at each scale.

(iv) The linear model at \( RP \) is discretized as shown (4.7) and (4.8) as the scale is increased, with \( t_s = 120 \). Here, it is also expected that each discrete model represents each continuous one at the \( RP \).

(v) \( O, C \) and \( H \) are computed in the \( RP \) at each scale, using (4.9)–(4.11).

(vi) \( H \) is decomposed in singular values as shown in (4.12).

**Step 8:** the \( \text{SII}_{x_k,RP} \) is computed from (4.13), where the Hankel matrix rank is \( r = 2 \).

**Step 9:** as can be seen from Fig. 4.1, steps five to twelve are repeated until \( CV = CV_{ns} \).
Step 10: the $SII_{cs,RP}$ values are compared at the $cs$ and $ns$ as can be seen from Table 5.2. Here, the $SII$ values remain constant when the process is scaled-up restraining the energy requirements ($U_r$) and change when the geometrical similarity is held ($U_{r,a}$). This fact indicates that the process behavior deteriorates when using $U_{r,a}$ during the scale-up.

| Variable | $SII_{cs}$ | $SII_{ns}|_{U_r}$ | $SII_{ns}|_{U_{r,a}}$ |
|----------|-------------|-------------------|---------------------|
| $I$      | 0.00        | 0.00              | 0.00                |
| $M$      | 0.00        | 0.00              | 0.00                |
| $\eta_0$ | 0.00        | 0.00              | 0.00                |
| $\eta_1$ | 0.00        | 0.00              | 0.00                |
| $\eta_2$ | 0.00        | 0.00              | 0.00                |
| $T_r$    | 4.97        | 4.97              | 3.35                |
| $T_2$    | 0.96        | 0.96              | 0.98                |

In addition, $w_{RP}$ for all cases are reported in Table 5.3. It can be seen that a smaller value for the overall heat-transfer coefficient is computed when using $U_{r,a}$ than $U_{r,r}$, this means that a smaller process unit than the required one was designed.

| Sym. | $w_{cs}$ | $w_{ns}|_{U_r}$ | $w_{ns}|_{U_{r,a}}$ | SI Unit |
|------|----------|-----------------|---------------------|---------|
| $V_r$| $8.96 \times 10^{-2}$ | $1.34 \times 10^{0}$| $1.34 \times 10^{0}$| m$^3$ |
| $V_j$| $3.61 \times 10^{-2}$ | $5.41 \times 10^{-1}$| $5.41 \times 10^{-1}$| m$^3$ |
| $F_1$| $3.56 \times 10^{0}$  | $5.34 \times 10^{1}$  | $5.34 \times 10^{1}$  | m$^3$/h |
| $F_2$| $3.56 \times 10^{0}$  | $5.34 \times 10^{1}$  | $5.34 \times 10^{1}$  | m$^3$/h |
| $U_r|_{RP}$ | $2.45 \times 10^{2}$ | $6.05 \times 10^{2}$ | $3.40 \times 10^{2}$ | W/m$^3$K |
| $A_r$ | $7.68 \times 10^{-1}$ | $4.67 \times 10^{0}$ | $4.67 \times 10^{0}$ | m$^2$ |

Step 11: Given that values for each $w_{RP}$ are determined at the $ns$, in order to obtain the exact scaled unit design that matches each $w_{RP}$ requirement, an equation for each $w_{ns}$ is established. Therefore, taking into account that only (5.120) satisfied the scale-up requirements (see Table 5.2), two cases are considered to fulfill $U_{r,a}$: (i) increasing the cooling fluid flow rate at jacket input, and (ii) setting a new jacket geometry. For the first case, $F_1$ is changed from $53.4$ m$^3$/h to $159$ m$^3$/h in order to increase $U_{r,a}$ to the desired value. For the second case, three internal baffles are added to the jacket, using (5.121) [128] instead of (5.65), to satisfy the heat transfer demand ($U_{r,r}$) in the RP at the $ns$. From here, $U_{r,r}$ is computed using (5.50) for the baffles case, with $Nu_j$ is given by (5.121) where $h_j$ is computed from (5.82).

$$Nu_j = \begin{cases} 1.86 \left[ Re_j Pr_j \frac{D_{in}}{L_j} \right]^{\frac{1}{4}} \left[ \frac{\mu}{\nu_{w,j}} \right]^{0.14} & Re_j \leq 2300 \\ 0.027 Re_j^{\frac{1}{3}} Pr_j^{\frac{1}{4}} \left[ \frac{\mu}{\nu_{w,j}} \right]^{0.14} \left[ 1 + 3.5 \frac{D_{in}}{2r_j} \right] & Re_j > 2300 \end{cases} \quad (5.121)$$

Step 12: the process is simulated with $p$, $z_{ns}$ and $w_{ns}$ values. As it was mentioned before, changes in $SII$ values with scale increments show the degradation of process behavior. Bearing this in mind, the dynamic evolution of $T_r$ and $F_3$ are compared in Fig. 5.6 and Fig. 5.7 for both cases, i.e. (i) energy requirements and (ii) geometrical similarity, holding the controller parameter of the $cs$ design. Here, although $T_r$ has a small range of variation (less than 2K,
$F_3$) reaches its maximum value during the first hour of reaction. In this sense, any disturbance introduced to the process cannot be countered by the controller during this time.

![Graph of temperature vs. time for different scales](image1)

Figure 5.6. Comparison of $T_r$ at $cs$ and $ns$ using the simplified model.

![Graph of flow rate vs. time for different scales](image2)

Figure 5.7. Comparison of $F_3$ at $cs$ and $ns$ using the simplified model.

**Intermediate steps (a)–(f):** these steps are followed for computing the $SII_{T_r}$. 

**Step 13:** the $SII_{T_r}$ is computed using (4.13). In this way, values of this index for the main dynamics ($T_r$) at each scale are compared in Fig. 5.8. It can be seen that the $SII_{T_r}$ profile for the geometrical similarity case is highly different from the $cs$ profile. According to this, it is not possible to reproduce the same dynamic behavior of the reactor at the $ns$ by keeping the geometrical similarity.

Fig. 5.8 also shows that there is small difference between the $SII_{T_r}$ curves at $cs$ and $ns$ for the baffles case, this difference is because the jacket must be designed with a integer number of baffles. Here, three baffles were added to the annular jacket but the real requirement were
2.8 units. So, the overall heat transfer coefficient in the reactor increases from $605\,\text{W/m}^2\text{K}$ to $611\,\text{W/m}^2\text{K}$, decreasing the $F_3$ demand (see Fig. 5.7).

Also, from Fig. 5.8, it can be seen that there is a small difference between the $SI_{T_r}$ profiles at $cs$ and $ns$ for the flow rate case. This effect is because although the cooling fluid flow rate at the jacket input satisfies the energy requirements at the end of the batch ($U_{r,r} = 605\,\text{W/m}^2\text{K}$), it also has greater cooling capacity from the process start, causing less energetic requirements at the heat exchanger throughout the batch, and hence decreasing the flow rate needed at the heat exchanger for holding $T_r = 358.15\,\text{K}$ (see Fig. 5.7).

![Figure 5.8. State Impactability Index at $ns$ for $T_r$.](image)

### 5.2.3. Results using the non-simplified model

For verifying the process dynamic behavior at the $ns$, in this subsection the complete model, composed by (5.7)–(5.108), is used for simulating both units designs. In Fig. 5.9, a comparison of $M_n$ and $M_w$ dynamic evolution for all cases is done.

![Figure 5.9. $M_w$ and $M_n$ at $cs$ and $ns$ using the complete model.](image)
It can be seen that there is a difference between $M_n$ and $M_w$ at $cs$ and $ns$ for the geometrical similarity case. This difference is because when scaling up the process using $U_{r,a}$ a smaller process unit was designed than the required, causing that the reactor temperature ($T_r$) increases at the beginning of the batch (see Fig. 5.6), which elevates the values of the kinetic constants ($k_d$, $k_l$, $k_{fg}$, $k_{fm}$, $k_t$, $k_{tc}$ and $k_{td}$), and hence rises termination rates in order to produce shorter polymer chains. From Fig. 5.9, it can also be seen that $M_n$ and $M_w$ curves at $cs$ and $ns$ overlap when the energy requirements are held, demonstrating that the process reaches the same quality targets at $ns$ from the $cs$ when the proposed procedure is implemented.

On the other hand, a comparison of $T_r$ and $F_3$ for all cases are shown in Fig. 5.10 and Fig. 5.11 using the complete model.

From these figures, it can be seen that $T_r$ and $F_3$ profiles are highly similar to the simplified model profiles (see Fig. 5.6 and Fig. 5.7). Therefore, scale factors (see Table 5.3) determined
by means of the simplified model are validated by simulating the process using the complete model. In addition, Fig. 5.11 shows that a greater cooling fluid flow rate is required. This result was expected because the reactor was scaled-up considering an isothermal operation. Here, it is even more clear that when the geometrical similarity is held the designed unit has a smaller size than the actually required.

Finally, the difference between the profiles of the baffles case and the $c_s$, as mentioned before, is due to the addition of three baffles instead of 2.8 unit. Bearing this in mind, the difference between profiles of the flow rate case and the $c_s$ is due to the increment of the cooling capacity from the process start, also mentioned before.

### 5.3. Concluding remarks

This chapter has focused on the application of the proposed scale-up methodology to a batch suspension polymerization reactor. Here, it is worth highlighting:

- The effort in the process modeling allows the understanding of the process dynamics. By means of the obtained model, it was possible to establish the most important dynamics from a design perspective.

- The proposed scale-up methodology for BPs was proved in a complex system (see Definition 1.1), illustrating its suitability for real processes.

- A non-isothermal batch polymerization reactor was scaled-up from $0.1m^3$ to $1.5m^3$. As a result of this, the scale factors for keeping the same molecular weight at both scales were found. From this example, it was also shown that traditional scale-up methods do not always winds up into a good industrial unit design.
Conclusions

Within this thesis, a methodology for scaling up batch processes was developed, involving the use of: (i) a phenomenological-based model for representing the process to be scaled-up, and (ii) the State Impactability Index (SII) for determining the operating regime at each stage of the batch. The proposed methodology: (a) considers the dynamic behavior of the process throughout the scale-up, (b) determines the effect of the design variables as a whole over each state variable from SII calculation, and (c) increases the process scale maintaining its dynamics hierarchy.

The main contributions of this work are:

- The integration of the SII to the scale-up of batch processes. This index allows the designer to determine the dynamics hierarchy of the process under study and, hence, establish if two or more designed units can carry out the same process with the same performance targets.

- Considering that phenomenological-based models are increasingly used as a tool for scaling-up chemical processes, and no formal procedure about how to use them has been introduced until today, this thesis presents a clear and simple way to use phenomenological models as a tool for finding the scale factors when scaling up batch processes.

- The classification of process variables in: state variables, design variables, synthesis parameters, and design-variable-dependent parameters is also a keystone of this work. This classification allows extending the use of the Hankel matrix from control applications to processes design and scale-up, by establishing a connection between manipulated variables for control purposes and design variables for scale-up purposes.

While the proposed methodology allows the determination of the scale factors of batch processes, its main limitations are related to:

- For the methodology implementation, a dynamic lumped-parameter model is required. Given that some chemical processes must be represented by distributed-parameter models, it is always necessary to discretize the model in the space in order to use the proposed methodology. So, the designer must be careful to not lose information when discretizing the model in the space.

- As the Hankel matrix is a discrete tool, a discrete-time process model is required for implementing the proposed methodology. This fact always represents a disadvantage, since the use of discrete models always involve information loss from going to continuous to discrete models. Therefore, in order to succeed by applying the methodology, the discrete-time model must be able to represent precisely the continuous-time one.
Regarding the objectives completion, it can be concluded:

**General objective:**

Propose a methodology for scaling-up batch processes using a Phenomenological-Based Semi-physical Model (PBSM), and considering the Operating Regime (OR) along each stage of the batch, using Hankel matrix singular value decomposition as a tool for finding the Operating Regimes of the process.

- A methodology for scaling-up batch processes using a PBSM was proposed, including the OR at each stage of the batch. Here, it is worth highlighting that the definition of Operating Regime was extended to batch processes applications (see Definition 2.3).
- By means of the Hankel matrix calculation and its singular value decomposition, the determination of the SII was possible, which also allowed the establishment of the dynamics hierarchy throughout each stage of the batch.

**Specific objectives:**

For the first two objectives:

1. **Identify the most popular methods for scaling chemical processes.**
2. **Differentiate the principles underlying traditional scale-up methods and their limitations.**
   - As was shown in Chapter 2, the main approximations to the scale-up procedure were identified. Here, three basic approaches were distinguished: (i) experimental, (ii) physical, and (iii) fundamental. From this review, it was found that there is no general rule for successfully scale-up chemical processes, so combinations of the scale-up approaches are used to obtain an acceptable outcome of the process at an industrial scale.
   - Within the review made in Chapter 2, it was found that there is no general criterion for the selection of the list of the relevant variables when scaling up chemical processes, so the choice of these variables is always subjective and requires detailed understanding of the process. It was also found that BPs characteristics (dynamic operating point, nonlinear behavior and constrained operation) are not taken into consideration during the scale-up task, highlighting the gaps in the scale-up of this sort of process.

For the rest of the objectives:

3. **Extend the usage of the Hankel matrix singular value decomposition to the scale-up of batch processes.**
   - Given that this objective involved the use three mathematical tools: (i) a process model, (iii) the Hankel matrix, and (iii) Singular Value Decomposition (SVD), a review of these tools was done within Chapter 3. Here, it was found that if the Hankel matrix is interpreted as the mapping from the past inputs to the future outputs via the process state, it can be used as a tool for scaling up processes, mainly because its singular values are closely related with the process controllability and observability.
• In Chapter 4, the proposed methodology for scaling up batch processes was presented, highlighting that the key for carrying out a successful scale-up task was using the discrete form of the Hankel matrix that allowed the designer to determine the $SII$ of the process at each stage of the batch.

4. Validate the proposed methodology by scaling up a specific batch process.

• The methodology was implemented into two examples: (i) a simple batch reactor (see Chapter 4) and (ii) a batch suspension polymerization reactor (see Chapter 5). For both cases, it was shown that by means of the $SII$ calculation, it was possible to identify if a process unit was over or under sized.

• The proposed methodology was compared with a traditional scale-up method in each example, showing that traditional scale-up methods do not always conclude with a good commercial unit design; and if the geometrical similarity is kept, other parameters of the process need to be changed in order to achieve the same performance targets set at the current scale at an industrial unit.
Future work

Some ideas for the future work toward complementing the outcomes achieved in this thesis are:

- Extending the use of Hankel representation from discrete-time to continuous-time systems. Even though results with discrete-time models in this study were satisfactory, using continuous-time models would decrease computational load and avoid information loss when applying the proposed scale-up methodology.

- It is well known that singular values of the Hankel matrix are related to the process controllability and observability when the system layout is $\mathbf{x}(j + 1) = \mathbf{A}_d \mathbf{x}(j) + \mathbf{B}_d \mathbf{u}(j)$. Given that within this thesis an analogy between manipulated variables ($\mathbf{u}$) and design variables ($\mathbf{z}$) was done for representing the system as $\mathbf{x}(j + 1) = \mathbf{A}_d \mathbf{x}(j) + \mathbf{B}_d \mathbf{z}(j)$, it is worth exploring the meaning of the controllability concept from a design perspective.

- The proposed scale-up methodology must be implemented to various batch and fed-batch processes in order to verify its generality.


BIBLIOGRAPHY


### Parameters and physical properties

#### Table A.1. Illustrative example parameters and physical properties.

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