Mathematical Modelling and Simulation of a Trickle-Bed Reactor for Petroleum Feedstocks Hydrotreating

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MATHEMATICAL MODELLING AND SIMULATION OF A TRICKLE-BED REACTOR FOR PETROLEUM FEEDSTOCKS HYDROTREATING

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2019-05-14
The submission of this thesis fulfils the last of the requirements for obtaining a Doctor of Philosophy (PhD) degree at the Technical University of Denmark. The thesis presents the main research results obtained during the period between November 2014 to February 2018. The PhD project was accomplished at the Department of Chemical and Biochemical Engineering (PROSYS) under the supervision of Associate Professor Jakob Kjøbsted Huusom and co-supervised by Professor Anker Degn Jensen. An important part of the work was conducted in collaboration with Jacob Brix and Angélica Hidalgo Vivas at Haldor Topsøe A.S., Denmark. The project was financed by Consejo Nacional de Ciencia y Tecnología (CONACyT) and Haldor Topsøe A.S., Denmark.

The journey toward a PhD is a treasurable experience. It is demanding as it is enriching. Therefore, as the author of this thesis, I sincerely hope that this work will be considered as a contribution to the development of the field of the simulation of trickle-bed reactors for hydrotreating. It is a fascinating field full of challenges and opportunities with great potential for alluring developments. I hope that the obtained results will be found useful and inspire future researchers to contribute to the field.

Carlos Eduardo Ramírez Castelán
Kgs. Lyngby, 2019
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I feel exceptionally thankful for the people that I met here in Denmark. Friends who became my family, Francesco, Cigdem, Carolina, Tiago and Dasha who always took care of me in both, good and hard times. Thanks to Morten for being an awesome office mate and even greater friend. To Katrin, Simoneta and Roxana for being such an important part of my life. To my very best friends Amata and Ludovica. Also, to Valeria, Clementine, Seyed and Tannaz that made sure that my stay in Denmark was extraordinary. And, of course, a huge thank to Johanna, for always being an inspiration to me, for believing in me and being one of the very best human beings that I was fortunate to meet in this life. Thank you to the rest of my friends whose names are simply too numerous to write here, but if any of you are reading this, be sure that I had you in mind.

Carlos Eduardo Ramírez Castelán
Kgs. Lyngby, 2019
Summary

Petroleum refining is one of the most important industries worldwide with a continuous and increasing demand of higher quality products that requires novel frameworks to develop better technology. One of the most compelling processes is hydrotreatment, where light and heavy vacuum gas oils (VGO) that go out of the atmospheric distillation process of crude oil are converted into more valuable products under high hydrogen pressures taking place at trickle-bed reactors.

Trickle-bed reactor models to portray hydrotreating processes are frequently limited to study the performance at micro- and pilot-scale. Most of these studies take into account the conditions typical of industrial processes to report tendencies and behaviour of the model solutions. However, the reproducibility of industrial data is still a shortcoming of existing models, especially predicting the phase change of species. In addition, the vaporization of light ends due to the heat released by the reactions is generally not addressed in literature due to the complexity of modelling and solving vapor-liquid equilibrium (VLE) in a trickle-bed reactor model.

The focus of this thesis is the simulation of a large-scale hydrotreating unit using a thorough reactor model based on first principles. The model is developed as a plug-flow reactor (PFTR) model, and alternatively, as a series of continuous stirred-tank reactors (CSTR). The mass and energy balance equations describe the transport of heat and species between the gas, liquid and the solid phase where the reaction takes place.

The performance of both models is tested against each other. The simulation of a hydrotreating reactor using the CSTR in series approach is quick but imprecise nonetheless. An additional optimization study is required to make this approach reliable. On the other hand, the plug-flow reactor model is an appropriate choice since it presents a good trade-off between the solution time and the consistency of the results.
The model parameters were taken from different sources in literature for similar systems, which presents an undeniable source of uncertainty. Therefore, the implementation of the plug-flow model is tested using a sensitivity analysis to determine the most influential parameters to the model solution. The results show that the selection of the kinetic model parameters is critical to obtain realistic results. This is especially relevant for the kinetics of aromatics saturation.

The plug-flow model is further developed to account for phase change, which is scarcely addressed in literature. A simulation framework is proposed and the methodology goes through the steps necessary to couple the reactor model, solved in Matlab, with a vapor-liquid equilibrium calculation from a process simulator such as ProII. Said simulation framework is able to handle the phase change in the reactor without increasing the complexity of the mathematical model. Moreover, the database available from ProII for petroleum streams allows us to take advantage of the use of pseudocomponents. The pseudocomponents provide supplementary attributes to simulated petroleum streams that resemble real feedstocks.

Using the simulation framework, the solution of the plug-flow reactor model obtained in MatLab is partitioned and coupled with a flash calculation carried out in ProII. The results are compared to the data available from a real large-scale hydrotreating trickle-bed reactor, demonstrating the capabilities of the simulation approach.
Petroleum-raffinering er en af de vigtigste industrier verden over med en kontinuerlig og stigende efterspørgsel efter produkter af højere kvalitet, der kræver nye rammeværktøjer for at udvikle bedre teknologi. En af de mest overbevisende processer er hydro-treatment, hvor lette og tunge vakuumgasolier (VGO), der kommer ud af atmosfærisk destillationsproces af råolie, omdannes til mere værdifulde produkter.


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**Resumé**

Petroleum-raffinering er en af de vigtigste industrier verden over med en kontinuerlig og stigende efterspørgsel efter produkter af højere kvalitet, der kræver nye rammeværktøjer for at udvikle bedre teknologi. En af de mest overbevisende processer er hydro-treatment, hvor lette og tunge vakuumgasolier (VGO), der kommer ud af atmosfærisk destillationsproces af råolie, omdannes til mere værdifulde produkter.


Plug-flow reaktor modellen er videreudviklet til at tage højde for faseændring, som sjældent behandles i litteraturen. Der foreslås en simuleringsmetode, der går gennem de trin, der er nødvendige for at forbinde reaktormodellen, som er løst i Matlab, med en damp-væske-ligevægtsberegning fra en processimulator, såsom Pro/II. Den nævnte simuleringsmetode er i stand til at håndtere faseændringen i reaktoren uden at øge kompleksiteten af den matematiske model. Desuden giver databasen tilgængelig fra Pro/II for petroleumsstrømme os mulighed for at udnytte brugen af pseudokomponenter. Pseudokomponenterne giver supplerende egenskaber til simulerede petroleumsstrømme, som ligner ægte råmateriale.

Ved hjælp af simuleringsmetoden opdeles løsningen af plug-flow-reaktormodellen opnået i MatLab og kobles med en flashberegning udført i Pro/II. Resultaterne sammenlignes med de data, der er tilgængelige fra en reel storskala hydrotreat- ing trickle-bed reaktor, hvilket demonstrerer simuleringsmetoden egenskaber.
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PART I:

HYDROTREATING IN PETROLEUM INDUSTRY

A complex system that works is invariably found to have evolved from a simple system that works

JOHN GALL
Chapter 1

Introduction and Thesis Overview

This chapter presents an introduction and overview of the thesis. First, the context of the environmental impact of petroleum and fuel industry is established. Afterwards, the overall refinery flow is exhibited in order to set the focus in the hydrotreating process. Furthermore, some of the current challenges in the field are acknowledged, hence, displaying the motivation of why the work is needed. Finally, the objectives of the thesis are presented.
1.1 Introduction

The society of today is characterized by a growing number of individuals that will not cease in the near future. This causes a never-ending energy demand by population to remain functional, driving scientists and engineers to look after alternative energy sources such as biomass, wind and solar energy. These technologies have proven to be effective under certain circumstances. However one cannot deny that fossil fuels are still the predominant source of energy to date for logistic purposes mainly [86].

As a matter of fact, fossil fuels are deeply embedded in our frame for centuries, and its demand has been thriving as we, as civilization evolve and proliferate. The consumption of fossil fuels is no different, however, the environmental impact caused by the contaminants released in the course of combustion can carry irreversible consequences alongside [9]. One of the most noteworthy concerns is the release of harmful contaminants, such as sulphur-, that can lead to health issues in the population. Nevertheless, it is possible to reduce the impact of contaminants by changing the conditions in which we utilize fossil fuels and strengthening the regulations accordingly [11] [79].

A big challenge emerges for refineries and companies that produce fuels, who face the investment of millions of dollars in equipment that allows them to craft their products in agreement with the specifications, laws and regulations stipulated by authorities and consumers.

The environmental, health and safety regulations have a huge sway in the investment costs of big refineries. Starting with the design of the building that entails several years of lead time, and all the way to the design and construction of the processing units and equipment, that may not meet the most recent specifications in the long run. Therefore, most of the efforts are devoted to the short-term solutions by developing reformulated fuels. These reformulated fuels are expected to have minimal emissions of harmful compounds, as well as minor impact on the deterioration on the environment.

At the present time, a number of alternative less-polluting and less harmful energy sources are gaining attention: Electric energy, hydrogen, solar energy and renewable fuels obtained from biomass such as ethanol. However, it is difficult to replace fossil fuels in the area of transportation. It is worth to point out that the non-renewable fossil resources are the basis of numerous other chemical products besides the energy generation. With this conjunction, the petroleum industry is left with a short time to recover the large investment required to meet the present legal requirements.
It becomes evident that the companies that survive this period will be those that draw upon the experience and skill of their engineers and scientists to the highest possible level of efficiency.

### 1.2 The refinery process

The typical refinery has as a goal the conversion of as much of the barrel of crude oil into transportation fuels as is economically practical. Although refineries produce many profitable products, the high-volume profitable products are the transportation fuels gasoline, diesel and turbine (jet) fuels, and the light heating oils. These transportation fuels have boiling points between 0 and 345°C [54]. Light heating oils are not properly transportation fuels but the hydrocarbon components are interchangeable with those of diesel and jet fuels, only the additives are different.

The quality of crude oils processed by refineries is expected to worsen slowly in the future with increase in the sulfur contents and densities [86]. Greater densities will mean more of the crude oil will boil above 566°C. Historically this high-boiling material or residua has been used as heavy fuel oil but the demand for these heavy fuel oils has been decreasing because of stricter environmental requirements. This will require refineries to process the entire barrel of crude rather than just the material boiling below 566°C. Sulfur restrictions on fuels will affect bottom-of-the-barrel processing as well [54]. These factors will require extensive refinery additions, modernization and the shift in market requirements for gasolines and reformulated fuels. Reformulated fuels for transportation will challenge catalyst suppliers and refinery engineers to develop innovative solutions to these problems [9].

The environmental impacts of fuel preparation and consumption will require that a significant shift takes place in product distribution i.e., less conventional gasoline and more reformulated and alternative fuels. This will have a major effect on refinery processing operations and will place a burden on refinery construction in addition to the need to provide increased capacity for high sulfur and heavier crude oils [28].

In modern days, the refinery operations consist of a wide and complex variety of processes, nevertheless, the crude refining process is of great interest [36]. The refining process begins with distillation processes that separate the crude oils into fractions in relation to the boiling point (Figure 1.1), meaning that each of the processing units have feedstocks that meet their particular specifications.

One achieves higher efficiencies and lower operation costs when the crude oil separation is performed in two steps: the first step is the separation of the total crude oil into fractions at atmospheric pressure; the second step is the feeding of
Figure 1.1. Refinery flow diagram. The diagram shows a schematic representation of the petroleum processing from crude oil to different products [64].
the bottoms with high boiling points from the first step into a second fractionator
operating at high vacuum [54] [64].

After these fractions are obtained, chemical reactions are carried out. Certain
chemical reactions are the basis for further refining stages, i.e. hydrotreating, cat-
alytic cracking, hydrocracking, hydroprocessing and hydrodesulfuration, hydroden-
itrification. Even though these terms are used rather loosely, in the industry, these
reactions occur simultaneously and the term often refers to which of the reactions
predominates [64] [8].

Figure 1.1 shows the processing sequence in a modern refinery of high complex-
ity, indicating major process flows between operations. It starts with the heating of
crude oil in a furnace and fed to an atmospheric distillation tower. In the tower,
the crude is separated into butanes and lighter wet gas, unstabilized light naphtha,
heavy naphtha, kerosene, atmospheric gas oil, and topped crude, that is known as
reduced oil. The topped crude is sent to the vacuum distillation tower and sepa-
rated into vacuum gas oil stream and vacuum reduced crude bottoms. Then, the
reduced crude bottoms from the vacuum tower is thermally cracked in a coker to
produce wet gas, coker gasoline, coker gas oil, and coke. In some cases, bottoms
treated without a coker, are gathered as heavy residue remainders that would be
sold for heavy fuel oil or even asphalt. Historically, these heavy bottoms have sold
for about 70% of the price of crude oil [54].

The atmospheric gas oils, the vacuum gas oils and coker gas oil are used as
feedstocks for the catalytic cracking or hydrocracking units. These units break the
heavy molecules into lower molecular weight compounds with a boiling range char-
acteristic of gasoline and distillate fuel. Then, these products are saturated by hy-
drotreating or reforming that improves the quality of the fuels [54] [3] [103].

In contrast, the light naphtha streams from the crude tower, coker and crack-
ing units are sent to an isomerization unit to convert straight-chain paraffins into
isomers, in this way higher octane numbers are obtained. On the other hand, the
heavy naphtha streams from the crude tower, coker, and cracking units are fed to
the catalytic reformer to improve their octane numbers [28]. Finally, the products
from the catalytic reformer are blended into i.e. regular and premium gasolines for
sale.

It is important, though, to consider other operations that happen alongside the
gasolines production process. For example, the wet gas streams from the crude
unit, coker, and cracking units are sent to a vapor recovery section where they are
separated into fuel gas, liquefied petroleum gas (LPG) and unsaturated hydrocar-
bons such as propylene, butane, isobutane, butylenes, pentenes, etc. The fuel gas
is burned as a fuel in refinery furnaces and the butane is blended into gasoline
or LPG. Alternatively, the unsaturated hydrocarbons and isobutane are sent to the alkylation unit for processing where either sulfuric or hydrofluoric acid is used as catalyst. In the alkylation process, olefins react with isobutane and form isoparaffins with a boiling range of gasoline. The product is called alkylate, and is a high-octane product that is blended into premium motor gasoline and aviation gasoline [64]. Moreover, the middle distillates from the crude unit, coker, and cracking units are blended into diesel and jet fuels and furnace oils [64][36].

In some refineries, the heavy vacuum gas oil and reduced crude obtained from paraffinic or naphthenic base crude oils are processed into lubricating oils. Furthermore, the asphaltenes are removed in a propane deasphalting unit and the reduced crude bottoms are processed along with the vacuum gas oils to produce lubeoil base stocks [54]. In order to improve their stability and color, some aromatic compounds are removed from the vacuum gas oils and deasphalted stocks by solvent-extraction. However, before blend them into lubricating oils, in many cases, the the vacuum gas oils and deasphalted stocks are subject to high-severity hydrotreating [103] [93].

At the end, it is clear that each refinery has its own unique processing scheme and is determined by countless factors, for instance, the process equipment available, crude oil characteristics, operating costs, and product demand among many others. Ultimately, the economic considerations govern the optimum flow pattern for any refinery, hence no two refineries are identical in their operations.

1.2.1 Hydrotreating process

Catalytic hydrotreating has gained significant attention worldwide due to environmental restrictions on sulphur- and nitrogen- emissions [85]. The reason is that the hydrotreating process is crucial to obtain fuels with improved quality and low polluting compounds content and aids further refining stages. In general, hydrotreating is the process in which petroleum products are catalytically stabilized. The stabilization is obtained by saturating unsaturated hydrocarbons and, at the same time, objectionable elements are removed from products or feedstocks by reacting them with a hydrogen stream and without necessarily changing the boiling range. Some elements that are removed by hydrotreating include sulfur-, nitrogen-, oxygen-, halides, and trace metals, which all can be bound to aromatics. Conversely, the process whose primary purpose is to reduce the boiling range and in which most of the feed is converted to products with boiling ranges lower than the feed, is known as hydrocracking. Hydrocracking takes place at higher temperatures and is usually an undesired reaction when only the hydrotreating reaction is desired [16].

The hydrotreating process is applied to many different refinery streams, such as straight-run distillates, vacuum gas oils, atmospheric and vacuum residua, naphtha,
lube oils, etc. However, not all the refinery streams are treated equally. Depending on the different feedstocks, the operation requirements change accordingly, i.e. temperature, partial pressure of \( H_2 \), \( H_2/Oil \) ratio and space velocity. The type of catalyst used is also important. Among the most used are nickel-molybdenum (\( \text{NiMo} \)) or cobalt-molybdenum (\( \text{CoMo} \)) supported on alumina or silica alumina. The reactor configuration has an impact on the characteristics of the hydrotreating process, whether it is a single reactor, reactors in series, or one catalytic bed with various catalysts [101]. Hence, it becomes evident that hydrotreating is a key operation during the entire refinery process.

Hydrotreating and hydrocracking set the two ends of the spectrum and therefore, those processes with a substantial amount of sulphur- and/or nitrogen- removal and a significant change in boiling range of the products versus the feed altogether are known as hydroprocessing. However, when the process is used specifically for sulphur- or nitrogen- removal it is usually called hydridesulfurization or HDS (Eq.1.1), and hydrodenitrification or HDN (Eq.1.2). Furthermore, consider that, to meet environmental objectives it also may be necessary to hydrogenate aromatic rings by converting aromatics to paraffins, also known as hydrodearomatization reaction or HDA (Eq.1.3), hence reducing the aromatic content of the feedstocks.

\[
S - \text{compound} \xrightarrow{+H_2} H_2S + \text{Hydrocarbon} \quad (1.1)
\]

\[
N - \text{compound} \xrightarrow{+H_2} NH_3 + \text{Hydrocarbon} \quad (1.2)
\]

\[
\text{Aromatic ring} \xrightarrow{+2H_2} \text{Paraffin} \xrightarrow{+3H_2} \text{Paraffin} \quad (1.3)
\]

These reactions are characterized by having both a gas and a liquid feed stream for the reactants. However, the reaction takes place on the surface of a solid catalyst which is completely wetted by the liquid and where some of the gaseous species has been dissolved. The reaction and transport phenomena taking place involves the interaction between all three phases, hence, these reactor systems are known as three-phase reactors. The essential function of the three-phase reactor is to provide efficient mass transfer between the three phases as well as saturating the solid catalyst with liquid.
1.2.2 Reactors for hydrotreating

Several potential reactor arrangements can be applied for heterogeneously catalysed gas-liquid reaction whether the catalyst is suspended in the mixture or fixed in a bed or monolith [1]. However, fixed bed reactors are commonplace in hydrotreating of petroleum feedstocks. Among the fixed bed reactor configurations, the trickle-bed reactor is the most widely used three-phase reactor employed in petroleum industries. Most commercial trickle-bed reactors operate adiabatically at high temperatures and high pressures and generally involve hydrogen and organic liquids [44] [35] [79] [84]. The kinetics and thermodynamics characteristic of petrochemical reactions require trickle-bed reactors to operate at high temperatures and appreciable high pressures, in some cases up to 30 MPa. Elevated pressures are required to improve the gas solubility and the mass transfer rates [64] [54].

The trickle flow regime is reached with relatively low gas and liquid flow rates. The liquid flows as a laminar film over the packing particles, while the gas passes through the remaining void space. Despite the steady state appearance of the trickle flow, when we discern the physical and chemical processes that are taking place at significantly smaller spatial scale, these are inherently unsteady [19]. In reality, the observed macro-scale flow regimes are the result of a number of combinations of micro-scale flow patterns, which are the consequence of local competition between liquid and gas in the packing interstices.

Furthermore, trickle-bed reactors are often applied to perform strong exothermic reactions such as the hydrogenation of unsaturated hydrocarbons. However, one of the major disadvantages of trickle-bed reactors is their poor capability to transport the heat involved with reaction. Considering the low heat capacity of the gas, the liquid retains this heat. Thus, if the generated heat is not adequately removed, hot spots may be created. These hot spots cause the catalyst particles to sinter, which decreases its activity and surface area [42] [69]. This results in a reduced catalyst life span as well as an increase in operating costs. In addition, hot spots are a serious risk to safety as they can damage the reactor vessel and can lead to a reactor runaway. Undesirable side reactions can be promoted as well, due to non-uniform temperature distributions and affecting the residence time of the reactants. For these reasons, it is essential to determine when and how these hot spots are formed so that they can be avoided [69].

If we take into account all the considerations mentioned above, from the point of view of reactor design and operation, the exothermic reactions and the multi step reaction scheme with complex kinetics are crucial interests for industries. The control and safety of reactors are important features in the design as well as in operations of industrial processes that carry out complex reactions with constraints.
of thermal stability and/or selectivity. However, it is interesting to note that rigorous comparisons of the performances of several three-phase reactor models for such reactions have been published scarcely [16] [93][25][5].

The development of efficient and reliable models for trickle-bed reactors is a difficult task because it involves many phenomena such as gas-liquid mass transfer, heat transfer, pore diffusion, and reaction and deactivation kinetics [45]. Additionally, dynamic models of trickle-bed reactors can be used not only for start-up, shut-down or operability studies of the reactors, but also for obtaining a meaningful continuity path to the steady state of the reactor. Dynamic models should be preferred to steady-state models, since the former provides a realistic description of the transient states of three-phase reactors, and the numerical solution strategy of dynamic models is more robust than the solution of steady-state models [84]. Thus, they allow for safe and trustworthy studies of the operation and optimization of reactors. Also, the dynamic models can be used to investigate the existence of exotic phenomena such as oscillations and steady-state multiplicity [10] [68].

1.3 The importance of modelling reactors for petroleum hydrotreating

The continuous technological improvements encourages researchers and developers to enrich the knowledge of hydrotreating reactors and improve the understanding of the physicochemical phenomena involved in the operation of trickle-bed reactors. These pursuits have been subjects of longstanding interest [118] [46].

The complexity of large-scale industrial systems such as hydrotreating, comprise spatial concentration and temperature profiles inside trickle-bed reactors, multiscale systems that have both bulk and regional behaviour. Additionally the environment can become too hostile or fouling for sensors to work where the system measurements must be made. Moreover, whether by sampling and performing laboratory analysis, the results are usually issued with significant delay. On the other hand, experiments to study the hydrotreating process are typically carried out in micro- and pilot-scale reactors. Furthermore, consider that these systems run using the same conditions reported in commercial units but keep the reaction temperature constant. It is worth pointing out that commercial hydrotreating reactors do not operate isothermally and experimental information generated from small reactors does not necessarily mirrors the commercial operation. One of the best and most cost-effective ways to predict industrial-scale behaviour taking into considerations the results from small-scale systems is the use of reactor modelling.

Numerous authors have researched trickle-bed reactors, however, the modelling
compilation made by Korsten and Hoffman in 1996 [70] gained significant attention and the resulting trickle-bed reactor model functioned as a foundation for many other authors to develop different approaches with different levels of sophistication.

Some authors have used pseudo-homogeneous models without distinction between the liquid/gas phase and the solid catalyst, and others have taken into account mass transfer between the phases [70][7][95]. However, in addition to the sophistication of the reactor model, the assortment of the reaction kinetics plays a crucial role in the performance of the simulation [101].

Most of the models found in literature have the HDS reaction as main subject of study since sulfur- compounds are one of the most important environmental pollutants. Commonly, authors prompt kinetic models based on power-law or Langmuir-Hinshelwood. However, it is surprising to know that models to describe the HDA and HDN reactions, are scarce in the literature [101], which are vital for a proper trickle-bed reactor modelling.

In recent years, the environmental constraints have become increasingly more severe, impacting both the quality and the maximum allowable amounts of impurities for commercial fuels such as gasolines and diesels [65].

The limited availability of kinetic models for HDA and HDN and industrial-scale studies become evident if one considers that, besides sulfur specification for diesel, environmental authorities scrutinize maximum limits in aromatics and nitrogen [15]. Then again, by making the model able to respond to the most relevant parameters i.e. feed and product composition analysis, treat gas purity ($H_2$, $H_2S$, $NH_3$) and by estimation of the inlet/outlet bed temperatures, the behaviour of the system can be predicted.

Phase distribution efficiencies are currently evaluated based on temperature spread in the bottom of the reactor. A reconstruction of the phase distribution in the system by a model-based simulation framework would result in a better tool to evaluate the prediction of the behaviour of the real hydrotreating plant.

1.4 Problem statement, thesis objectives and goals

The area of trickle-bed reactor technology is a research topic that gained attention due to the importance of keeping the existing processes up with the tough legislation implemented world wide on a regular basis. Theoretical work related to modelling of trickle-bed reactors for petroleum hydrotreating has been fulfilled in literature, however there are areas that still require additional research to gain understanding of the large-scale hydrotreating process. For example, most of the works available in literature, report behaviour and tendencies of trickle-bed reac-
tors at micro- and pilot-scale; and even though most of these studies are carried out using the conditions reported in large-scale processes, they are still far from reproducing industrial data, especially when it comes to predict the phase change caused by the exothermic reaction.

Therefore, this PhD project contemplates the following topics:

1. **Modelling.** In order to explore the significance of different phenomena, two different approaches for setting up the fundamental balance equations for modelling a trickle-bed reactor are considered: 1) a Plug-flow model for a tubular reactor (PFTR), and 2) a continuous stirred-tank (CSTR) reactor model in series.

2. **Model implementation and analysis.** A comparison between the performance of the two modelling approaches is carried out by simulating a real industrial large-scale trickle-bed reactor for hydrotreating of petroleum feedstocks. Additionally, a sensitivity analysis of different parameters is performed.

3. **Simulation with phase change.** The expanded simulation consists in the use of the dynamic model of a trickle-bed reactor, solved in Matlab, coupled with a flash calculation carried out in ProII. This approach reduces the complexity of the numerical solution compared to the solution of a model that considers vaporization of complex petroleum feedstocks.

The outcome of PhD thesis is the development a proposed simulation framework for a real large-scale hydrotreating reactor, which conveys the use of the databases available from ProII for petroleum streams. One of the main advantages of this approach is that the databases of ProII, and similar process simulators, are utilised by industries nowadays.

The model-based simulation framework proposed in this work encompasses the fundamental modelling approach with the benefits of the characterization of petroleum streams performed in the process simulator. This also allows us to carry out the calculation of phase change in the process simulator, while the trickle-bed reactor model handles mass and energy transport between gas, liquid and solid phases.

One of the main advantages of achieving truthful predictions of the behaviour of trickle-bed reactors with volatile compounds is that, it could reduce significantly the risk of having a product that does not meet specifications, or reaching conditions that reduce the performance of the catalytic bed.

The aim of this project is to establish is a generic framework suited for a wide range of applications of tubular reactor with trickle flow with industrial relevance,
however, the results may also be extended to other process systems with similar characteristics.

1.5 Thesis Outline

This PhD thesis is divided into chapters containing the following written material:

Chapter 2. State of the art on modelling of trickle-bed reactors. A literature review of the hydrotreating reactors. The literature review covers the main features of the hydrotreating process, such as characteristic phenomena of trickle-bed reactors, typical reactions and distinctive kinetics, and a historical overview of hydrotreating reactors modelling, as well as recent publications.

Chapter 3. Trickle-bed reactor model and implementation. The development of a trickle-bed reactor model using fundamental mass and energy balances is presented. The model is build around a set of expressed assumptions using two different approaches: 1) a plug-flow tubular reactor (PFTR) and 2) a continuous stirred-tank reactor (CSTR) and the model parameters are given.

Chapter 4. Model implementation and analysis. The methodology of the implementation of both, PFTR and CSTR models is presented, as well as the description of the petroleum feedstocks characterization using a process simulator (ProII). The analysis of the implementation is also given, along with a comparison between the two models using a model example taken from literature.

Chapter 5. Case study: Part I. A commercial hydrotreating unit is described. The trickle-bed reactor model is implemented for the commercial hydrotreating unit using a kinetic model taken from the literature. The characterization of the feed and product is presented. An evaluation and discussion of the implementation of the PFTR and CSTR models are given. The performance of the simulation is assessed using experimental data.

Chapter 6. Simulation of the trickle-bed reactor with vaporization effects. The methodology of the implementation of the trickle-bed reactor models to account for vaporization effects using a process simulator is presented. The simulation framework comprising the information exchange between the model solver and the process simulator is thoroughly described.
Chapter 7. Case study: Part II.  The simulation framework is implemented for the commercial hydrotreating unit. The performance of the simulation framework is discussed and compared to experimental data using both, PFTR and CSTR models.

Chapter 8. Final Discussion  A final discussion of the work of this thesis is presented as well as recommendations for future work

Chapter 9. Thesis Conclusions  The conclusions derived from this thesis are presented.
Chapter 2

State of the art on modelling of trickle-bed reactors

In this Chapter, a review of the relevant literature on modelling trickle-bed reactors for petroleum hydrotreating is presented. The following topics are considered: features of the trickle-bed reactor and the important phenomena characteristic of trickle flow, as well as efforts and essential contributions on modelling of trickle-bed reactors.
2.1 Trickle-bed reactor: Features and characteristic phenomena

The trickle-bed reactor has been studied by engineers for more than 50 years by now. The characteristic configuration and operation of trickle-bed reactors make them suitable for a wide range of chemical, biochemical and petrochemical applications. Trickle-bed reactors are specifically advantageous when a reaction must be carried out between at least two components, one in gas phase and the other in liquid phase using a solid catalyst (Figure 2.1).

![Figure 2.1. Schematic representation of the Trickle flow](image)

Trickle-bed reactors have been used to a moderate extend in chemical and biochemical applications. The refiners are particularly interested on continuously improving their petroleum processing units because any advance in trickle-bed reactor technology represents substantial savings [119]. Some examples of applications of trickle-bed reactors include [43][44]:

- Synthesis of acetylene and formaldehyde
- Oxidation of organic matter in waste-water with Pd catalyst or biofilters constituted by fixed micro-organisms
- Hydrogenation of various petroleum fractions
- Hydrodesulfuration
- Hydrodemetallization and
2.1. Trickle-bed reactor: Features and characteristic phenomena

- Hydrodenitrification

In principle, trickle-bed reactors consist of a column equipped with a bed of fixed solid catalyst (Figure 2.2).

**Figure 2.2.** Schematic representation of trickle-bed reactors at different operation scales.

The gas and the liquid flow through the fixed bed with either cocurrent or countercurrent flow, depending on the design of the chemical system. In the cocurrent downflow configuration, the liquid flows through the catalyst particles in the form of rivulets, films and droplets. These characteristics has some advantages over other reactor designs i.e. the liquid flow approaches plug flow, which translates to higher reaction conversions and less catalyst loss. In addition, the trickle-bed reactor design has no moving parts which represents lower investments, maintenance and operation costs. Another big advantage of trickle-bed reactors is the possibility of high pressure and temperature operation.

On the other hand, the trickle-bed reactor is disadvantageous for a certain range of application that involve particularly viscous liquids that can obstruct the catalyst pores leading to large pressure drops. Despite of these drawbacks, the trickle-bed reactor is exploited in order to maximize the efficiency of petroleum refinery process, due to economic, safety and environmental factors.

Conversely, if we consider the widespread of the use of trickle-bed reactors at large-scale industry of petroleum refining, it is surprising that not-equally widespread
information has been published concerning the development, design and operation industrial-scale reactors. Limited laboratory-scale studies for specific chemical reactions, in trickle-bed reactors such as hydrogenation of specific aromatic groups has hardly been published [71] [93]. Most of the available trickle-bed reactor studies focus primarily on catalytic behaviour or global chemical kinetics [25][14]. In addition, for fast gas-liquid-solid reactions, the chemical kinetics are often limited by the mass transfer rate of the gaseous species that flow to the surface of the catalyst through the liquid.

Let us take the hydrogenation reactions as an example. Hydrogenation represents a typical gas-liquid-solid type of reaction. Hydrogen is reacted with an organic compound over a supported metal catalyst contained in a packed-bed arrangement. The limited solubility of hydrogen in organic solvents makes mass transfer a primary concern [77] [54][28]. Consequently, the hydrogenation reactions often take place at high pressures, sometimes as high as 100 atm, to increase the reaction rate and counteract the low hydrogen solubility [1][47].

At this point, one could argue that there are other reactor configurations that can deal with this problem such as slurry reactors, in which the catalyst is suspended in the liquid phase; however, the trickle-bed configuration is typically used for hydrotreating processes because the packed beds are easier and less costly to operate. On the other hand, the limitations of trickle-bed reactors become evident when compared to other types of three-phase reactors. In general, the catalyst particle is filled with liquid while the outer surface may not be completely wet or covered by the flowing liquid which leads to a more direct contact between the gas phase and the catalyst [57]. For that reason, if the reaction rate depends on the liquid reactant, the wetting efficiency leads to reduced global reaction rates, on the other hand, if the reaction rate is controlled by the gas phase, the global reaction rate is higher since the resistance to mass transfer in the non-wetted surface is lower than in the covered surface. Figure 2.1 shows the concept of trickle flow.

In practice, the volume of the reactor is predominantly the gas phase, and the liquid forms a thin film around the catalyst pellet. It is clear that one of the biggest concerns is the uniform distribution of the fluids within the reactor. Uneven flows can lead to incomplete utilization or local zones of varying reaction rate and heat transfer. Poor distribution of the fluids can thus lead to local “hot spots”, which can decrease selectivity, reduce catalyst life, or lead to side reactions that can cause reactor runaway [117] [36].

Typically, the amount of catalyst is divided and packed into 1 to 5 beds. The catalyst beds may be equal in depth, or, more commonly, increase in depth as reaction proceeds. In practice, each bed is of about 3 to 6 m deep and up to as much as 3
m in diameter. The maximum height of a single catalyst bed is determined by the importance of achieving redistribution of liquid and gas or by the crushing strength of the catalyst. In present practice, this maximum seems to be about 6 to 8 m [53].

In multiple-bed hydrotreating reactors, the hydrogen is injected between the beds. This has the advantage of providing temperature control of the process, but also, it helps to achieve better liquid distribution and to prolong the life of the catalyst. The quantity of hydrogen injected at each point is adjusted to achieve the desired axial temperature profile, but also, to limit the adiabatic temperature rise along each bed below some maximum, typically about 30°C or less. Hydrogenation is exothermic, and consequently thermal uniformity and adequate temperature control is of primary concern. Efforts on developing technology have emerged as a means for improving process capability and control in chemical synthesis and as means for conducting safer and more efficient chemical kinetics investigations[112][38][32],[108].

The ratio of gas to liquid commonly increases through the successive beds and the amount of gas injected for cooling usually exceeds the amount of gas introduced initially [73]. The amount of H₂ utilized, usually far exceeds that needed for stoichiometric reaction to avoid coking and is commonly determined primarily by the requirements for temperature control[54][64][93].

Trickle-bed reactors in the petroleum industry may be operated over a wide variety of conditions, depending upon the properties of the feedstock and the nature of the reaction. Typically the less reactive fractions, which tend to be in the higher boiling range and more viscous at ambient conditions, are processed at the lower liquid flow rates. Trickle-bed reactors used in petroleum industry consist of a column that may be very high, above 10-30 m, equipped with a fixed bed of solid catalyst, throughout a gas-liquid cocurrent downward flow occurs. According to the chemical system design, sometimes either the liquid move cocurrently upflow or the gas is fed countercurrently upflow.

It is clear that, potential for improvement in trickle-bed reactors working under realistic conditions exist due to the complexities associated with transport-kinetics coupling, general scale-up and scale-down rules for the quantitative and description of transport phenomena.

2.1.1 Hydrodynamics

In trickle-bed reactors as in any continuous operation, hydrodynamics is a crucial aspect of the performance of the reactor and it is fundamental to evaluate its role. Several factors must be considered in order to design a trickle-bed reactor, i.e. optimal energetic requirements, adequate gas and liquid flow rates which relate to
physical and chemical interactions such as hold-ups, pressure drops, heat and mass transfer. Additionally, many other parameters must be associated, i.e. gas and liquid physical characteristics; size and porosity of the catalyst pellets; ratio between column diameter and height [48][91][67][84].

Different hydrodynamic regimes have been examined for different flow arrangements in packed-bed reactors, such as down and upward flows using diverse experimental procedures, i.e. visual and/or optical observations, electro-conductimetric and thermo-conductimetric tests and pressure drop measures [120][51][20].

Many authors believe that understanding the hydrodynamics is not limited to the phenomena at a macro level, but also the micro-kinetics at a pellet level must be taken into account. Micro-kinetics has a big impact on the rate and the selectivity of the reactions, therefore, a good number of parameters affect the apparent reaction rates [67][36][79]. Consider, for example the reaction orders, the activation energy, the catalyst size, the size and distribution of the catalyst pores, the diffusivities and vapor pressures of reactants and products, but also, the possible depletion of the gas or liquid reactants, as well as the external wetting efficiency of the pellets, the intraparticle bed porosity and the pore liquid filling [107][67]. In addition, with highly exothermic reactions, the heat effects must be considered i.e. heat dispersion and vaporization or condensation within the catalyst [44].

All the mentioned parameters along with gross parameters such as fluids dispersion, liquid, solid and gas contacting efficiency, temperature gradients, catalyst effectiveness dictate the apparent reactor rate and its dimensions. Therefore, it is evident that this large number of interconnected parameters define the hydrodynamic regimes and the operating conditions and deserve scientific and technical attention, hence the importance of the selection of the modelling approach.

A significant number of trickle-bed reactors models used to study hydrotreating reactors are based on the modelling approach published by Korsten and Hoffman in 1996 [70][1][3][84]. These modelling approach is validated experimentally for lab-scale [89][95] and pilot plants [25][5], although, a fewer number of studies has been carried out to study industrial large-scale cases in detail.

### 2.1.2 Flow maldistribution

Liquid phase maldistribution is an essential factor in the design, scale-up and operation of trickle-bed reactors [82]. Ineffective liquid distribution causes obstruction that can affect large sections of the catalytic bed and even change the physical properties of the liquid [113].

Additionally, liquid maldistribution may result in other undesirable effects, i.e. if the liquid is not supplied to a section of catalyst bed, dry zones are formed, which
translates to no reaction in these regions and the reactor is not fully utilized. Moreover, without the liquid phase removing the reaction heat hot spots occur. However, it is interesting to note that if a sufficient amount of liquid is vaporized, reaction still proceeds in these dried out regions, therefore it becomes clear that understanding the impact of liquid maldistribution on reactor performance is essential.

As mentioned earlier in this Chapter, characteristics of the trickle flow regime are the liquid present as films, rivulets, and liquid pockets [129] [99] over the solid catalyst that are highly stagnant in nature (Figure 2.3).

Rivulets form due to the inhomogeneous porosity and capillary pressure effect and expand gradually with increasing liquid flow rate, even if the liquid is perfectly distributed initially. That is the reason why pre-wetting the bed is an important factor for improving the liquid distribution during operating conditions [99].

Note that it is appropriate to distinguish between bed-scale and particle-scale partial wetting. During the trickle-flow-regime, regions of catalyst particles that are non-irrigated, partially irrigated as well as completely irrigated coexist at particle-scale [29]. Regimes, in which the complete wetting occurs at bed-scale, are achieved at high liquid flow rates. Therefore, acknowledging the importance of the distribution of bed-scale and particle-scale wetting is fundamental for a correct outlining of the reactor performance, because comprehensive representation of the flow conditions and the resulting interactions of heat and mass transfer is crucial for a fundamental modelling approach.

The industrial hydrotreating reactors operate at conditions in which nearly plugflow is achieved in order to avoid flow maldistribution. This is stated by many authors and works published in literature, hence, the traditional modelling of hydrotreating reactors is the plug-flow reactor approach [1][7][84][58][125][3][8].
2.1.3 Catalyst Wetting

Perhaps one of the most troublesome phenomena regarding operation of trickle-bed reactors, is the catalyst wetting. After taking a look at the hydrodynamics of the trickle-flow regime, it is easy to see that incomplete catalyst utilization may occur during the operation of the reactor. The incomplete catalyst utilization may occur at two different scales. One is at reactor scale in which portions of the catalyst remain poorly irrigated. This can be counteracted by a proper design of the distributor and packing that assures minimal pressure drop and redistribution of the liquid. Large-scale computational fluid dynamic (CFD) computations can be helpful to study the liquid distribution and the effect of the catalyst packing. The other cause of incomplete catalyst utilization is wetting at particle scale [58]. This is the result of low liquid flow velocities causing insufficient coverage of the catalyst particle with a liquid film continuously.

Several attempts were made to predict effectively the catalyst wetting in terms of catalyst area covered by the flowing liquid film using models and correlations [129][1][63]. Catalyst wetting can translate to catalyst effectiveness and overall reactor performance, consequently, many important contributions such as correlations for high pressure conditions have been documented by a number of authors [13][67] [68]. These studies conclude that the contacting efficiency improves noticeably with the increase in pressure at fixed liquid mass flux, and at high gas velocities. Moreover, high pressure drop and high liquid mass velocity increase contacting efficiency also. Hence, both liquid and gas velocity increase the contacting efficiency at high pressures. Additionally, close to complete external wetting can be achieved in upflow reactors, however, this means a much larger liquid holdup than in the commercial scale trickle-bed reactor, which is not always desirable. A larger liquid holdup can cause unwanted side reactions, or impaired gas-liquid mass transfer rate triggered by a larger liquid film resistance.

2.1.4 Mass transfer

Additionally to the catalyst wetting, the prediction of mass transfer coefficients in trickle-bed reactors has been studied using different models and correlations [68], nonetheless, there is a lack of experimental data on the gas-liquid mass transfer coefficient at high-pressure operation. It becomes clear that this gap in knowledge must be filled considering the large number of chemical and biochemical processes that take place in trickle-bed reactors. A significant step forward in this field was achieved when mass transfer could be measured in pressurized vessels [94] and from these experimentally determined data the following qualitative observations
can be made: at a given gas density, gas-liquid interfacial areas, the magnitude of the mass transfer coefficients increase as liquid and gas mass fluxes or superficial velocities increase.

2.1.5 Formation of hot spots

As mentioned earlier in this chapter, trickle-bed reactors are often used to perform highly exothermic reactions such as the hydrogenation of unsaturated hydrocarbons. One of the main disadvantages of trickle-bed reactors is the poor capability to offload the heat released while the reactions take place. Due to the low heat capacity of the gas, in a typical operation of a trickle-bed reactor the liquid phase is the main heat sink. Therefore Hot spots tend to appear if the heat is not dissipated or adequately removed. These hot spots are considerably undesired because they cause a decrease in the activity of the catalyst particles and even decrease its life span. This can be directly translated to an increase in operation costs. In addition, hot spots are a threat to safety because they can lead to a reactor runaway or damage the reactor casing. Now consider the issue of undesirable side reactions that are promoted due to uneven temperature distributions and varying residence time of the reactants. For these reasons, it is essential to determine when and how these hot spots are formed so that they can be avoided. Literature reports that hot spots are observed at industrial scale trickle-bed reactors running highly exothermic reactions [106] [62] [12] and laboratory-scale reactors [33] [98][105] [72].

2.2 Modelling of trickle-bed reactors

With all the given understanding of trickle-bed reactors, the idea of the development of a generalized model for these reactor configuration seems challenging [105] [56]. The modelling of trickle-bed reactors is still a difficult task due to their complex hydrodynamics and mass transfer characteristics, unknown reaction chemistry, nonlinear relations, and all the numerous variables that are involved. Furthermore, industrially relevant reactions have complex kinetics and are multi-step reactions that are usually highly exothermic and therefore are mingled to the reactor design.

In practice, the relationship between the input and the output of a real system is resolved by system identification using industrial data or first principles or a combination of both [17]. It is worth mentioning that there are different levels of modelling sophistication depending on the available information. For example, when the process behaviour can be represented mathematically using algebraic and/or differential equations, then the model is categorized as white-box or mechanistic model,
another view is when there is no physical insight is available, then we encounter what is known as black-box models. Furthermore, when some physical insight is available we can say that we have a gray-box or hybrid model [17].

Most of the trickle-bed reactor models reported in the literature consider isothermal operation and use either a pseudo-homogeneous approach [27] or a heterogeneous model with plug flow for gas and liquid phase [39] [98]. Some models account for liquid flow non-uniformity and maldistribution by using an axial dispersion model [26]. Most investigations dealt with hydrogenation or oxidation in pure or moderately concentrated organic or aqueous solutions with large excess of liquid reactant. Hence, they consider zero-order rate with respect to the liquid reactant concentration and first order with respect to dissolved gaseous reactant concentration.

Liquid reactants and solvents are normally assumed to be non-volatile and the gas phase assumed to be pure at constant partial pressure of the reacting gas. Thus, the primary model variables of interest are the dissolved liquid-phase concentrations of the gaseous reactant and the conversion of the liquid-phase reactants. The key phenomenon that has been incorporated in most recent models is the partial wetting and transport of gaseous reactant to dry external areas of the catalyst resulting in higher rates than observed in most of the experimental data [39][102][33].

At the same time, other authors considered adiabatic effects and used a pseudo-homogeneous energy balance to solve for the temperature at any axial location [98][87]. Others considered evaporation effects by adding vapor-liquid equilibrium calculations and flash units to simplified pseudo-homogeneous or equilibrium model mass balance equations on the reactor scale [74][126]. Particularly, the work from Al-Dahhan et. al. in 1997 [1] and Khadilkar in 1999 [67] served as encouragement for other authors that model trickle-bed reactors with vaporization effects [7][89][24][23].

Pellet-scale reaction and diffusion have been studied by taking reactant limitation in account in simpler versions [13]. The general case considered partial internal wetting of pellets, resulting in gas and liquid-phase reaction zones, and solving for the gas-liquid interface by accounting for pore filling and capillary condensation in one term. This modelling strategy was considered in the works from Khadilkar et. al. and Korsten and Hoffman [68][67][70].

The earliest unsteady-state modelling used a plug-flow equilibrium model for predicting the hot spot formation and movement during start-up of a trickle bed and investigated the effect of a gas/liquid quench stream axial position on the developing hot spot [126]. Pseudotransient behavior was also modeled by considering similar equations. Mass transfer terms are considered in extension of these models.
2.2. Modelling of trickle-bed reactors to predict periodic variation of temperature and concentration [96].

Spatial terms were dropped in some subcases of this model to study time variation of mass transfer coefficients and enhancement in rates and selectivity for the model reaction system. Catalyst wetting effects during periodic operation were also studied with elimination of spatial terms in the model equations [42]. This was done primarily to reduce computational complexity. Activity modulation was incorporated in recent transient models for optimizing the performance on the basis of catalyst activity [48].

The level of complexity and features available in the models in the literature are sufficient for evaluation of steady-state experiments. However, these models are still far from mimicking reality in industrial hydrotreating applications due to three main shortcomings: 1) They do not consider multicomponent transport and multiple reactions properly, 2) do not account for change of phase (evaporation and condensation) and 3) do not consider the effect of phase change effect on holdup and velocities [68].

2.2.1 Trickle-bed reactor models for petroleum hydrotreating.

A number of authors have approached the modelling of trickle-bed reactors focused on petroleum hydrotreating. The outcome of their work branches into two main approaches to hydrotreating trickle-bed reactor modelling: Using a heterogeneous model with plug flow of gas and liquid phases [39][98]; and pseudo-homogeneous approach [27]. An important milestone on hydrotreating trickle-bed reactor modelling was reached with the work from Korsten and Hoffman [70], in which they proposed an isothermal trickle-bed reactor model using the film theory. The modelling of hydrotreating trickle-bed reactors using the film theory served as the foundations for a substantial number of models.

The principle of the model proposed by Korsten and Hoffmann is that liquid reactants/solvents are assumed non-volatile and the gas phase assumed to be pure at constant partial pressure of the reacting gas [70]. Thus, the primary model variables were the dissolved liquid-phase concentrations of the gaseous reactant and the conversion of the liquid-phase reactants. This scheme is widely used in recent works [84][25].

A significant number of the hydrotreating trickle-bed reactor models available assume isothermal operation. Isothermal models have their merits since most lab-scale reactors are operated at constant temperatures to study reactions kinetics. These investigations deal mainly with hydrogenation or oxidation reactions in pure or moderately concentrated organic or aqueous solutions (large excess of liquid re-
actant), and, hence, considered zero-order rate with respect to the liquid reactant concentration and first order with respect to dissolved gaseous reactant concentration [125][89].

Some authors that followed the pseudo-homogeneous approach, took advantage of the energy balance to account for non-isothermal effects, hence, calculating the temperature at any axial location [98]. Approximate solutions of the gas-solid catalyst level equations was also verified by numerical solution for non-linear kinetics. On the other hand, the plug-flow model approach contributed with one of the earliest unsteady-state models [126], in which, vapor and liquid phases are assumed to be in equilibrium at the phase boundary.

Unsteady-state models are useful to predict hot spot formation and development during start-up of a trickle bed reactor and investigate the effect of a gas/liquid quench stream axial position [36][76].

In many cases, spatial terms were dropped into subcases of the model to study time variation of mass transfer coefficients and enhancement in rates and selectivity for the model reaction system and to reduce computational complexity.

These models are far from reflecting the intricacy in industrial hydrotreating applications due to two central limitations. First, they do not consider multicomponent transport and multiple reactions properly as pointed out by [67], and secondly, they do not consider the transient behaviour simultaneously.

Dynamic trickle-bed reactors models have recently been published in literature [84]. Whilst the energy balance was taken into account, the model was solved considering a constant gas velocity throughout the reactor. More recently, a dynamic trickle-bed reactor model for hydrodemetallization of residual oil was proposed, in which the gas velocity is variable over the reactor length, nevertheless, the model considers the catalyst and the liquid as a single phase [3]. Modelling the solid phase independently can be important if the heat released by the reactions taking place is very significant.

In order to broaden the knowledge of large-scale hydrotreating reactors, a dynamic three-phase reactor model must consider multiple reactions: Hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and saturation of aromatics (HDA) with pseudo-components of the feedstock comprising mono-, di-, poly-aromatics and naphthenes. It is sought after that forthcoming hydrotreating-reactor models are useful to study the static and dynamic behavior of large-scale industrial hydrotreating units. Moreover, simulations of large-scale hydrotreating reactors allow us to perform model-based analysis of key model parameters and input variables. To illustrate, the following table summarizes the characteristics of trickle-bed reactor models available in literature.
2.2. Modelling of trickle-bed reactors

### Table 2.1. Assumptions of respective references for Trickle-bed reactor models available in literature.

<table>
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<tbody>
<tr>
<td>Gas and liquid flows are considered in axial dimension</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Radial concentration and temperature gradients are neglected</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Vaporization of light ends is neglected</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Variable density of liquid phase is assumed</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Changes in catalyst activity with time are neglected</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>The process operates at constant pressure</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Chemical reactions only at the solid catalyst surface</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Mass transfer resistance only on the liquid side</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Dynamic balance for the linear gas velocity</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Adiabatic model</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>Dynamic model</td>
<td>✓</td>
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2.2.2 Petroleum feedstocks characterization

The models for hydrotreating trickle-bed reactors are based on mass and energy balances. The fundamental modelling must account for species in the system, whether is the gas, liquid or the solid phase. One of the main issues of working with petroleum feedstocks is the complex composition. Depending on the boiling point range, oil fractions may contain from a few hundred to thousands of different components. For modelling and simulation purposes, this implies dealing with reaction networks in specific boiling point ranges. To alleviate this situation, for practical purposes, most kinetic models are based on lumps of compounds. The feedstock is represented by lumps of compounds with similar characteristics or pseudo-components, which are delimited by the feed and product specifications. The use of pseudo-components is a rather recent addition to the trickle-bed reactor modelling. One of the first authors to employ the concept of pseudo-components to describe the hydrotreating reactions was Mothany et al. in 1991 [87]. Since then, the concept of pseudo-components is extensively used by other authors in their modelling [25][17][84][58][24][3][5].

The delimitation of pseudo-components is traditionally performed by dividing the boiling point curve of the feedstock into boiling point ranges [58]. Then, the assortment of pseudo-components is performed by dividing the boiling point curve of the feedstock into groups of hydrocarbons with similar characteristics and specific boiling point ranges, rather than making a distinction between individual molecules. In industry, the composition of petroleum feedstocks can be reported in terms of hydrocarbon types, e.g. paraffins, olefins, naphthenes and aromatics (PONA). However, the work by Alvarez et al. in 2014 [4] apply the idea of feedstock reconstruction for simulation purposes by developing a molecule-based simulation algorithm. The algorithm is able to capture information about reaction paths and reactivities in order to develop detailed kinetics. However, a practical approach, which is common practice in industry, is to define additional groups of compounds...
Chapter 2. State of the art on modelling of trickle-bed reactors

according to the necessity to reflect the main reactions taking place, e.g. in gas oil hydrotreating some of the main reactions involve mono-, di- and polyaromatic compounds. The properties of the pseudo-components, e.g. molecular weights, molar volumes, etc. are then considered in the reactor model [25][17][84][58][24][5].

2.3 Kinetics of hydrotreating

The current knowledge of aromatic saturation allowed us to recognize HDA reactions are subject to thermodynamic limitations. It becomes clear that, understanding the chemistry and thermodynamic equilibrium of aromatic compounds present in feedstocks, is indispensable to determine relevant process variables and apposite operation strategies.

Notwithstanding the importance of HDA reactions, the research in the subject is not as broad as the research on HDS and HDN processes. Surprisingly, the number of publications on aromatic hydrogenation is noticeably small. Usually, the subject is addressed by researchers that focus on hydrotreating catalysts. However, the HDS and HDN reactions still excel in literature which makes publications dedicated to HDA reactions scarce.

2.3.1 Types of aromatic compounds in petroleum fractions

In order to understand the type of compounds characteristic of petroleum feedstocks, researchers use a wide variety of techniques. A few examples of the techniques that allow us to know what kind of aromatics exist in petroleum and synthetic middle distillates include [66][50][81][123][111][90][59]

• High-pressure liquid chromatography (HPLC)

• $^{13}$C nuclear magnetic resonance ($^{13}$CNMR)

• Gas chromatography-mass spectrometry

• Ultraviolet (UV) and infrared (IR)

Amongst the results of these aromatics studies, two important conclusions stand out, 1) the polycyclic aromatics with four or more condensed benzene rings are mostly present in many high-boiling petroleum fractions (BP>350°C, whereas the other three types are characteristic components of middle distillates; 2) condensed multi-ring aromatics compounds are hydrotreated more easily to corresponding mono-aromatics under mild hydrotreating conditions. Typical analysis data [59] on the type of aromatic compounds present in untreated gas oil fractions of Kuwait petroleum are presented in Table 2.2
Table 2.2. Aromatic Compounds in Kuwait Atmospheric Gas Oil [114]

<table>
<thead>
<tr>
<th>Aromatic type</th>
<th>Aromatic content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mono-aromatics</strong></td>
<td></td>
</tr>
<tr>
<td>(C_3 - C_6) Alkylbenzenes</td>
<td>3.68</td>
</tr>
<tr>
<td>(C_1 - C_5) Benzo thiophenes</td>
<td>14.24</td>
</tr>
<tr>
<td><strong>Di-aromatics</strong></td>
<td></td>
</tr>
<tr>
<td>(C_0 - C_4) Naphthalenes</td>
<td>52.81</td>
</tr>
<tr>
<td>(C_0 - C_4) Dibenzothiophenes</td>
<td>14.38</td>
</tr>
<tr>
<td>(C_0 - C_4) Fluorenes</td>
<td>4.12</td>
</tr>
<tr>
<td>(C_1)-benzyls + dibenzofuran</td>
<td>4.07</td>
</tr>
<tr>
<td><strong>Triaromatics</strong></td>
<td></td>
</tr>
<tr>
<td>(C_0 - C_4) Phenanthrenes</td>
<td>6.2</td>
</tr>
<tr>
<td>(C_0 - C_4) pyrenes/fluoranthrenes</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100</td>
</tr>
</tbody>
</table>

Additionally, aromatics in straight-run gas oil are comprised mainly by alkyl-nap thalenes, which belong in the di-aromatic group. In contrast, mono-aromatics such as alkylbenzenes, benzocycloparaffins, and benzodicycloparaffins prevail over di- and tri-aromatics in hydrotreated oils. Table 2.3 presents an example of the difference in the concentration of the aromatic groups in hydrotreated and unhydrotreated oils.

Table 2.3. Properties of Hydrotreated an Unhydrotreated Gas Oils [114]. Note: LGO = light gas oil; LCO = light cycle oil

<table>
<thead>
<tr>
<th>Aromatic type</th>
<th>Unhydro-</th>
<th>Hydro-</th>
<th>Unhydro-</th>
<th>Hydro-</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>treated</td>
<td>treated</td>
<td>treated</td>
<td>treated</td>
</tr>
<tr>
<td><strong>Total aromatics (wt%)</strong></td>
<td>33.7</td>
<td>31.6</td>
<td>70.2</td>
<td>70.9</td>
</tr>
<tr>
<td>Mono- (wt%)</td>
<td>17.7</td>
<td>22.4</td>
<td>11.2</td>
<td>38.5</td>
</tr>
<tr>
<td>Di- (wt%)</td>
<td>11.5</td>
<td>5.7</td>
<td>49.5</td>
<td>26.9</td>
</tr>
<tr>
<td>Tri- (wt%)</td>
<td>4.5</td>
<td>3.5</td>
<td>9.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Poly- (wt%)</td>
<td>-</td>
<td>-</td>
<td>0.8</td>
<td>0</td>
</tr>
</tbody>
</table>

2.3.2 Kinetic studies on industrial feedstocks

Petroleum streams are comprised by a too many different compounds, that it becomes impossible to identify every single one of them. However, several types of aromatic are used as model compounds. The model compounds are generally regarded as mono-, di- and poly-aromatics and are represented by i.e. benzene, toluene, alkylbenzene, biphenyl and phenanthrene [45]. Using the model compounds, makes it easier to develop kinetic models that account for the key reactions of hydrotreating.

One of the most referenced works regarding hydrotreating kinetics, was the
work by Mears in 1975 [83]. Mears studied the kinetics of desulfuration experimentally for a small hydroprocessing trickle-bed reactor. In his work, he was able to formulate a criteria for the minimum bed length for a trickle-flow operation. However, the kinetic results obtained from his experimental setup was not suitable for scale-up data due to back-mixing and incomplete catalyst wetting. Satterfield et al. concluded that there was interaction between desulfurization and denitrogenation in their experimental studies [105]. Nevertheless, the laboratory observations provide insight on how the industrial processes behave, yet, experimental conditions were very different from the real industrial ones. Moreover, pure model compound rather than a petroleum fraction was used in the laboratory. Experimental results for a single model compound will probably be very different from those of a petroleum fraction. For some years there was a lack of reliable data for hydrogenation of feedstocks, hence, constraining the understanding of crude upgrade.

In 1974, Quader investigated the hydrocracking of poly-nuclear aromatic compounds and found that the predominant products from reactions of two-, three-, and four-ring types to be mainly monoaromatics with only small amounts of condensed ring saturates being formed [97]. Shabtai et al. in 1974 [109] carried out a similar study to evaluate hydrotreating catalysts. Here, the effects of temperature and pressure were reported, but the occurrence of equilibrium limitations was not accounted.

Studies involving the hydrogenation of model aromatic compounds typical of those found in petroleum have been done by using sulfided CoMo catalysts [21]. In 1985, Stephens et al. studied the equilibrium-limited hydrogenation of pyrene in selected solvents and suggested strategies for maximizing the yield of the intermediate dihydropyrene [115].

In 1988, one of the first studies of hydrogenation kinetics using the three predominant hydrocarbon groups in petroleum distillates, was the work by Fisher [40]. Fisher’s work determined hydrogenation rate constants and the associated Arrhenius parameters for hydrogenation of mono-aromatics over CoMo, and Ni–W catalysts. Additionally, values of the equilibrium constant were determined for hydrogenation of alkylbenzenes and benzocycloparafins. Dehydrogenation constants were determined from the values of the equilibrium constant, the heat of hydrogenation reaction and hydrogenation rate constants. The Arrhenius parameters for dehydrogenation reactions were also calculated. Moreover, Fisher’s work accounts for compensations effects for hydrogenation and dehydrogenation. Leading to conclude that complete removal of aromatics from synthetic distillates, requires more active catalysts operating in regimes from conditions where equilibrium reactions limit the kinetics.
2.3. Kinetics of hydrotreating

In 1987, Lepage et al. [75], proposed an overall kinetic order of 1 relative to the whole concentration of aromatics. However, Lepage's approach does not consider the reversible reaction, which represents a disadvantage. The conversion of aromatics is a reversible reaction and is straightaway related to the chemical equilibrium that is temperature dependent. The concentration of aromatics in the product decreases with temperature, but then increases as the temperature is further raised. Therefore, it is important to consider the rate of reversible reaction and thermodynamic equilibrium in the development of kinetic models for aromatic hydrogenation [123][80].

The following equilibrium reaction was proposed by Wilson, Kriz and Fisher, as a basis for developing a model for kinetics of hydrogenation of aromatics in middle distillates [124][122]:

\[ \text{Aromatics} + nH_2 \rightleftharpoons \text{naphthene} \]  

(2.1)

Hydrogenation is commonly performed at large hydrogen excess at close to constant partial pressure, hence assuming that the forward reactions are pseudo-first order. Wilson et. al. also considered that the reverse reaction is first-order in naphthene, hence, the rate expression is given by:

\[ -\frac{dC_A}{dt} = k_f C_A P_{H_2}^n - k_r C_{naph} \]  

(2.2)

where: \( C_A \) = fractional aromatic content; \( C_{naph} \) = fractional naphthene content; \( t \) = time, \( k_f \) = forward rate constant; \( k_r \) = reverse rate constant; \( P_{H_2} \) = hydrogen partial pressure.

Later on, Yui and Standford proposed a kinetic model based on simple first-order reversible reaction for aromatics hydrogenation in middle distillates [127].

\[ -\frac{dC_A}{dt} = k_f P_{H_2}^n C_A^m - k_r (1 - C_A) \]  

(2.3)

where \( m \) = reaction order with respect to aromatic content.

The model was used to calculate kinetic parameters from published catalytic hydrogenation data from different sources. Thanks to the calculated kinetic parameters, the aromatic content in the product was determined at various operating conditions, yielding results that are in good agreement with the experimental data [123] [80] [124].

The research of Yui and Standford was extended to the study of kinetics of bitumen derived oils. In 1991, the same authors used a similar kinetic model to that mentioned above. However, they made the assumption that, stoichiometrically, 0.5 mol of hydrogen is consumed in the conversion of 1 atomic weight of aromatic
carbon, irrespective of the aromatic species, therefore the power term $n$ was equal to 0.5 when the aromatic content was defined as aromatic carbon content [128].

Moreover, they considered the deviations that emerge from the assumption of plug-flow in bench-scale trickle-bed reactors. The results of this kinetic model fit reasonably with experimental data. Additionally, it was concluded that the degree of hydrogenation at equilibrium was lower for the heavier feedstocks.

In 1989, rate equations for aromatic hydrogenation were proposed by Han-
nerup, in which, the equilibrium reactions between mono-aromatics ($mono$) and di-aromatics ($di$) are considered [55].

\[ di \xrightleftharpoons[k_2]{k_1} mono \xrightleftharpoons[k_3]{k_4} AH \]  

(2.4)

where $AH$ stands for hydrogenated aromatic. The rate equations used had the form [55]:

\[- \frac{dC_{di}}{dt} = -k_1 C_{di} P_{H_2}^{aq} + k_2 C_{mono} \]  

(2.5)

\[- \frac{dC_{mono}}{dt} = -k_3 C_{mono} P_{H_2}^{b} + k_1 C_{di} P_{H_2}^{aq} - k_2 C_{mono} + k_4 C_{AH} \]  

(2.6)

\[- \frac{dC_{AH}}{dt} = -k_4 C_{AH} + k_3 C_{mono} P_{H_2}^{b} \]  

(2.7)

In Hannerup’s work, the results of the model fit the experimental data, yet, no values for the kinetic parameters are reported. However, the discussion leads to conclude that the $di \rightarrow mono$ reaction is much faster than the $mono \rightarrow AH$ reaction. Furthermore, Hannerup demonstrates that, in the first part of the reactor, di-aromatics disappear rapidly and the mono-aromatics increase simultaneously, hence, the concentration of total aromatics appears constant. Afterwards, the equi-
librium ratio between di- and mono-aromatics is approached, the fast $di \rightarrow mono$ reaction cannot proceed until mono-aromatics are converted to $AH$ at a low rate. It is worth to point out that none of the kinetic expressions discussed above include adsorption equilibrium constant for reactants, products and the effect of inhibitors such as $H_2S$ and $NH_3$. It means that, the kinetic model does not describe the ad-
sorption mechanisms and the competition between the reactant and products.

### 2.3.3 Thermodynamic aspects

The hydrogenation of aromatics is a reversible reaction with equilibrium limita-
tions. What is more, complete conversion of reactants cannot be achieved at typical hydrotreating conditions.
2.3. Kinetics of hydrotreating

The hydrogen of an aromatic species is given by [114]:

\[ A + nH_2 \rightleftharpoons AH \]  \hspace{1cm} (2.8)

where \( AH \) is the hydrogenated product (napthene).

On the other hand, if the hydrogen activity coefficient and fugacities for \( A \) and \( AH \) are equal, and that the ratio of fugacity to total pressure at hydrotreating conditions are both one, the equilibrium concentration of the aromatic species can be approximated by [52]:

\[ \frac{Y_A}{Y_A + Y_{AH}} = \frac{1}{1 + K_A (P_{H_2})^n} \]  \hspace{1cm} (2.9)

where \( Y_A \) and \( Y_{AH} \) are the mole fractions of aromatic and naphthene respectively, \( K_A \) is the equilibrium constant, and \( P_{H_2} \) the partial pressure of hydrogen.

In Eq.(2.9), high pressures favour equilibrium concentrations of aromatics. Higher conversions are achieved in reactions in which the number of moles of hydrogen, \( n \), required for complete saturation is high. \( K_A \) decreases with increased temperature and, thereby the equilibrium aromatics concentration increases as the temperature is increased. Aromatic hydrogenation reactions are highly exothermic, with heats of reactions typically in range of 63-71 \( \text{kJ/mol}H_2 \) [61] [100].

The Langmuir-Hinshelwood type of rate equation requires many coefficients that need to be determined for a specific feedstock, yet is widely used in modelling kinetics of trickle-bed reactors [114].
PART II:

THE TRICKLE BED REACTOR MODEL
DEVELOPMENT AND IMPLEMENTATION

Prediction is very difficult, especially about the future.

Niels Bohr
In this Chapter, the fundamental dynamic model for a trickle-bed reactor is developed from a control volume. The objective of the acquisition of a comprehensive model that can be implemented for a number of systems with similar characteristics.
Introduction

The objective of this chapter is to present the development of two different dynamic models that are used throughout the thesis to acquaint a trickle-bed reactor. The description and derivation of the models will be given and the models will be presented in the following sections.

The models presented are constructed around different sets of assumptions that represent the physical nature of the trickle-bed reactor used in a hydrotreating process. The trickle-bed reactor models are based on simplifications related to mass and heat transfer, which are the two most important phenomena occurring in the catalyst bed, besides the reactions. In addition, the models are derived in general terms that can be used according to the case study.

In Chapter 2, an overview of the modelling of a trickle-bed reactor has been presented. Nevertheless, only a few models have been oriented to large-scale hydrotreating process for sulfur removal.

Many modelling approaches are based on the film layer proposed by Korsten and Hoffman [70]. In which, the energy balance equations have been excluded. However, in recent contributions, the energy balance is taken into account, and in some cases the dynamic part of the model.

3.1 Modelling of a trickle-bed reactor

In this section, a dynamic model is developed to study the continuous operation on a trickle-bed reactor. The conventional trickle-bed reactor is modelled as a cylinder containing a fixed bed of catalyst through which, a mixture of gas and liquid flows cocurrently downward. Hence, the most common modelling approach is the use of the design equations of a plug-flow tubular reactor (PFTR) and can be considered adiabatic [84] [85], hence, without any radial transport of heat. However, a tubular reactor can be modelled as a series of continuous stirred-tank reactors as well.

Therefore, in order to develop detailed deterministic mathematical models, it is necessary to consider the main phenomena taking place in trickle-bed reactors. First, the trickle-flow occurs in a space, in which, gas and liquid flow through a porous bed of packed catalyst. If the trickle-bed reactor is considered to have a co-current flow, both streams enter to the reactor from the top (Figure 3.1), a liquid film will cover the catalyst particles totally or partially. Some areas of the catalyst particles can remain dry i.e. when the catalyst particles are in direct contact with the gas phase or when stagnant cavities are created.
A common assumption for the modelling of the trickle-bed, is that the catalyst is completely wet, in other words, no dry zones are considered. Therefore, the modelling can be developed in the control volume as shown in (Figure 3.2) defined as $V_{Total}$.

The endpoints of this volume lie at $V$ and $V + \Delta V$ which means that the volume has constant lateral area $S$ and the change in the volume is considered only in direction of $z$, therefore, the length is $\Delta z$. The total control volume can be expressed as $\Delta V = S\Delta z$, see Figure 3.3. Inside the reactor, gas, liquid and solid phase are
The modeling approach comprises a solid phase considered completely wet, which means that the gas is in contact only with the liquid phase as illustrated in Figure 3.3.

![Figure 3.3. Control volume in terms of lateral area S and Δz](image)

The models consist of a set of balance equations of mass and energy that are formulated in general terms with the following assumptions:

- A.1 The reactor operates in dynamic regime.
- A.2 Gas and liquid flows is cocurrent.
- A.3 There are not radial concentration and temperature gradients.
- A.4 Catalyst activity does not change with time.
- A.5 Vaporization and condensation do not take place.
- A.6 Constant pressure.
- A.7 Mass transfer resistance in the gas side of the gas–liquid interface is assumed to be negligible.
- A.8 The catalyst particles are completely wet.

The volume fractions are defined as Gas volume fraction $\varepsilon_G \Delta V$, liquid volume fraction $\varepsilon_L \Delta V$ and the catalyst volume fraction $\varepsilon_S \Delta V$ as shown in Figure 3.4.
3.2 Plug-Flow Tubular reactor model (PFTR)

3.2.1 Mass balance

The continuity equation is obtained by applying the law of conservation of mass to a small element of volume $S\Delta z$ and then allowing the dimensions of the volume to become vanishingly small as $\Delta z \to 0$. The model is constructed around the non-stationary volume element, fixed in space, through which gas and liquid phases are flowing.

**Species balance in the gas phase.** Consider a molar flow rate of species $j$ flowing into the control volume by convection

$$F_j^G \bigg|_{z} \Delta t$$  \hspace{1cm} (3.2)
The molar flow rate of species \( j \) exiting of the control volume is due to convection and mass transfer. In this case the liquid-phase concentration of species \( j \) is expressed as the equilibrium concentration with the bulk in terms of partial pressure represented by the term \( \frac{p^G_j}{H_jv_i} \) where \( p^G_j \) the partial pressure of \( j \) in the gas.

\[ F_j^G \bigg|_{z} \Delta z + k^f_ja_L \left[ \frac{p^G_j}{H_jv_i} - c^L_j \right] S \Delta z \Delta t \]  

Where \( F \) is the total molar flow rate, \( a_L \) is the gas-liquid interfacial area. \( k^f_j \) is the gas-liquid mass-transfer coefficient. The molar rate of generation of species \( j \) within \( S \Delta z \) due chemical reactions

\[ \varepsilon_G S \Delta z \Delta t (r^G_j) \]  

Where \( r^G_j \) is the sum of reaction rates occurring in the gas phase involving species \( j \). In that sense, \( r^G_j \) is considered as the effective reaction rate in the gas phase. Molar rate of accumulation of species \( j \) within \( \Delta z \)

\[ \left( c^G_j \bigg|_{t+\Delta t} - c^G_j \bigg|_{t} \right) \varepsilon_G S \Delta z \]
3.2. Plug-Flow Tubular reactor model (PFTR)

The continuity equation for species \( j \) in the gas phase control volume may be described as:

\[
\left( c_j^G \big|_{t+\Delta t} - c_j^G \big|_t \right) \epsilon_G S \Delta z = \nonumber
\]

\[
F_j^G \big|_z \Delta t - F_j^G \big|_{z+\Delta z \Delta t} - k_j^L a_L \left[ \frac{p_j^G}{H_j v_j} - c_j^L \right] S \Delta z \Delta t + \epsilon_G S \Delta z \Delta t (r_j^G) \nonumber
\]

(3.6)

Dividing by \( S \Delta z \Delta t \) and taking the limit \( \Delta t \to 0 \) and \( \Delta z \to 0 \)

\[
\epsilon_G \frac{\partial c_j^G}{\partial t} = -\frac{1}{S} \frac{\partial F_j^G}{\partial z} - k_j^L a_L \left[ \frac{p_j^G}{H_j v_j} - c_j^L \right] + \epsilon_G r_j^G \nonumber
\]

(3.7)

Where \( a_L \) is the gas-liquid interfacial area per cubic meter volume. Note that \( a_L \) is usually not the geometric surface area of the packing and has to be determined experimentally. Equation (3.7) is a second order PDE and requires the following boundary conditions and initial conditions to be solved:

\[
c_j^G(t,0) = c_{j,in}^G(t) \quad \text{(3.8)}
\]

\[
c_j^G(0,z) = c_{j,0}^G(t) \quad \text{(3.9)}
\]

**Species balance for the liquid phase.** The molar flow rate of species \( j \) into the control volume by convection and mass transfer from the gas phase is

\[
F_j^L \big|_z \Delta t + k_j^L a_L \left[ \frac{p_j^G}{H_j v_j} - c_j^L \right] S \Delta z \Delta t \nonumber
\]

(3.10)

The molar flow rate of species \( j \) out of the liquid phase control volume by convection and mass transfer to the solid phase is

\[
F_j^L \big|_{z+\Delta z} \Delta t + k_j^S a_S \left[ c_j^L - c_j^S \right] S \Delta z \Delta t
\]

(3.11)

Where \( a_S \) is the liquid-solid interfacial area per cubic meter reactor volume and \( k_j^S \) is the liquid-solid mass-transfer coefficient.

The molar rate of generation of species \( j \) within \( S \Delta z \)

\[
\epsilon_L S \Delta z \Delta t (r_j^L) \nonumber
\]

(3.12)

Molar rate of accumulation of species \( j \) within \( S \Delta z \)

\[
\left( c_j^L \big|_{t+\Delta t} - c_j^L \big|_t \right) \epsilon_L S \Delta z
\]

(3.13)
Chapter 3. Fundamental model

The continuity equation in the liquid phase is

\[
\left( c^L_j \bigg|_{t+\Delta t} - c^L_j \bigg|_t \right) \varepsilon_L S \Delta z = \\
F^L_j(z, \Delta t) + k^L_j a_L \left[ \frac{p^G_j}{H_j v_j} - c^L_j \right] S \Delta z \Delta t - F^L_j(z+\Delta z, \Delta t) - k^S_j a_S \left[ c^L_j - c^S_j \right] S \Delta z \Delta t + \varepsilon_L S \Delta z \Delta t (r^L_j)
\]

(3.14)

Dividing by \( S \Delta z \Delta t \) and taking the limit \( \Delta t \to 0 \) and \( \Delta z \to 0 \), the mass balance for the liquid phase is as follows:

\[
\varepsilon_L \frac{\partial c^L_j}{\partial t} = -\frac{1}{S} \frac{\partial F^L_j}{\partial z} + k^L_j a_L \left[ \frac{p^G_j}{H_j v_j} - c^L_j \right] - k^S_j a_S \left[ c^L_j - c^S_j \right] + \varepsilon_L r^L_j
\]

(3.15)

Equation (3.15) is a second order PDE and requires the following boundary and initial conditions to be solved:

\[
c^L_j(t, 0) = c^L_j,_{in}(t)
\]

(3.16)

\[
c^L_j(0, z) = c^L_j,_{0}(t)
\]

(3.17)

**Species balance for the solid phase.** Molar flow rate of species \( j \) into the control volume at \( z \) only by mass transfer

\[
k^S_j a_S [c^S_j - c^L_j] S \Delta z \Delta t
\]

(3.18)

There is no flow defined of species \( j \) out of the solid phase control volume.

Molar rate of generation of species \( j \) within the control volume due to chemical reaction:

\[
\varepsilon_S S \Delta z \Delta t (r^S_j)
\]

(3.19)

Molar rate of accumulation of species \( j \) within \( S \Delta z \)

\[
\left( c^S_j \bigg|_{t+\Delta t} - c^S_j \bigg|_t \right) \varepsilon_S \varepsilon_{pores} S \Delta z
\]

(3.20)

The continuity equation in the solid phase is expressed as follows:

\[
\left( c^S_j \bigg|_{t+\Delta t} - c^S_j \bigg|_t \right) \varepsilon_S \varepsilon_{pores} S \Delta z = k^S_j a_S \left[ c^S_j - c^L_j \right] S \Delta z \Delta t + \varepsilon_S S \Delta z \Delta t (r^S_j)
\]

(3.21)

if we divide by \( S \Delta z \Delta t \)

\[
\varepsilon_S \varepsilon_{pores} \frac{\left( c^S_j \bigg|_{t+\Delta t} - c^S_j \bigg|_t \right)}{\Delta t} = k^S_j a_S \left[ c^L_j - c^S_j \right] + \varepsilon_S r^S_j
\]

(3.22)
3.2. Plug-Flow Tubular reactor model (PFTR)

And taking the limit $\Delta t \to 0$ and $\Delta z \to 0$, the mass balance for the solid phase is as follows:

$$
\varepsilon_S \varepsilon_{\text{pores}} \frac{\partial c^S_j}{\partial t} = k^S_j a^S \left[ c^L_j - c^S_j \right] + \varepsilon_{S\text{r}}^S 
$$

(3.23)

Equation (3.23) is a second order PDE and requires the following boundary and initial conditions to be solved:

$$
c^S_j(t, 0) = c^S_{j, \text{in}}(t) 
$$

(3.24)

$$
c^S_j(0, z) = c^S_{j, 0}(t) 
$$

(3.25)

3.2.2 Energy balance

Analogous to the mass transport phenomenon, the energy is transported from the gas phase to the solid phase passing through the liquid phase and vice versa once the reaction takes place. The equation for the energy balance will be derived based on the non-stationary energy balance equation shown in Figure 3.6.

![Figure 3.6. Energy balance of the PFTR control volume](image)

Before going into detail of the energy balance equations, the definition of enthalpy must be recalled:

$$
H_i = H^S_i(T_R) + \int_{T_R}^{T} C_P_i dT 
$$

(3.26)

and in the differential form

$$
dH_i = C_P_i dT 
$$
Equation (3.26) can be solved according to specific components since the heat capacity is not a constant but a function of temperature that depends on the specific system or components, i.e. polynomial functions in predefined temperature ranges.

**Energy balance of the Gas phase.** The energy flow of each species $j$ into the gas phase control volume by convection is defined as:

$$ \sum_j F_j^G H_j^G \bigg|_z \Delta t $$

(3.27)

Then, the energy flow out by convection and heat transport from the gas to the liquid phase

$$ \sum_j F_j^G H_j^G \bigg|_{z+\Delta z} \Delta t + U_L a_L (T_G - T_L) S \Delta z \Delta t $$

(3.28)

The heat generation rate is implicit in the heat accumulation term as such:

$$ \varepsilon G \Delta z \left( \sum_j c_j^G H_j^G \bigg|_{t+\Delta t} - \sum_j c_j^G H_j^G \bigg|_t \right) $$

(3.29)

Following the continuity equations, the energy balance of the gas phase looks as follows:

$$ \varepsilon G \Delta z \left( \sum_j c_j^G H_j^G \bigg|_{t+\Delta t} - \sum_j c_j^G H_j^G \bigg|_t \right) = \sum_j F_j^G H_j^G \bigg|_z - \sum_j F_j^G H_j^G \bigg|_{z+\Delta z} \Delta t - U_L a_L (T_G - T_L) S \Delta z \Delta t $$

(3.30)

Then, dividing by $S \Delta z \Delta t$ and taking the limit $\Delta t \to 0$ and $\Delta z \to 0$, the following expression is obtained:

$$ \varepsilon G \frac{\partial}{\partial t} \sum_j c_j^G H_j^G = - \frac{1}{S} \sum_j F_j^G H_j^G \frac{\partial}{\partial z} - U_L a_L (T_G - T_L) $$

(3.31)

Expanding the derivative terms:

$$ \varepsilon G \sum_j c_j^G \frac{\partial H_j^G}{\partial t} + \varepsilon G \sum_j H_j^G \frac{\partial c_j^G}{\partial t} = - \frac{1}{S} \sum_j F_j^G \frac{\partial H_j^G}{\partial z} - \frac{1}{S} \sum_j H_j^G \frac{\partial F_j^G}{\partial z} - U_L a_L (T_G - T_L) $$

The previous expression is rearranged to obtain the following equation:

$$ \varepsilon G \sum_j c_j^G \frac{\partial H_j^G}{\partial t} = - \frac{1}{S} \sum_j F_j^G \frac{\partial H_j^G}{\partial z} - \sum_j H_j^G \left( \frac{1}{S} \frac{\partial F_j^G}{\partial z} + \varepsilon G \frac{\partial c_j^G}{\partial t} \right) - U_L a_L (T_G - T_L) $$

(3.32)
At this point, it is necessary to recall the mass balance in the gas phase equation (3.7):

\[ \varepsilon_G \frac{\partial c_j^G}{\partial t} = -\frac{1}{S} \frac{\partial F_j^G}{\partial z} - k_{j}^{G} a_{L} \left[ \frac{p_j^G}{H_{j} v_j} - c_j^L \right] + \varepsilon_{G} r_{j}^G \]

and inserting in equation (3.32)

\[ \varepsilon_G \sum_j c_j^G \frac{\partial H_j^G}{\partial t} = -\frac{1}{S} \sum_j F_j^G \frac{\partial H_j^G}{\partial z} \]
\[ - \sum_j H_j^G \left( \frac{1}{S} \frac{\partial F_j^G}{\partial z} - \frac{1}{S} \frac{\partial F_j^G}{\partial z} - k_{j}^{G} a_{L} \left[ \frac{p_j^G}{H_{j} v_j} - c_j^L \right] + \varepsilon_{G} r_{j}^G \right) \]
\[ - U_{L} a_{L} (T_{G} - T_{L}) \]

For convenience, the previous equation can be re-arranged to obtain:

\[ \varepsilon_G \sum_j c_j^G \frac{\partial H_j^G}{\partial t} = \]
\[ -\frac{1}{S} \sum_j F_j^G \frac{\partial H_j^G}{\partial z} + \sum_j H_j^G k_{j}^{L} a_{L} \left[ \frac{p_j^G}{H_{j} v_j} - c_j^L \right] - \varepsilon_{G} r_{j}^G \sum_j H_j^G - U_{L} a_{L} (T_{G} - T_{L}) \]

(3.33)

An important assumption is made here to simplify the energy equations. The heat transferred to the liquid phase by convection is greater compared to the heat transfer due to mass transport, therefore:

\[ \sum_j H_j^G k_{j}^{L} a_{L} \left[ \frac{p_j^G}{H_{j} v_j} - c_j^L \right] \ll \varepsilon_{G} r_{j}^G \sum_j H_j^G - U_{L} a_{L} (T_{G} - T_{L}) \]

In order to pare the complexity of the energy balance, a common assumption is to conform the terms for all individual species as a lumped term that describes the whole gas bulk [25][17][84][58][24][5]:

\[ \sum_j c_j^G \frac{\partial H_j^G}{\partial t} = \rho_{G} \frac{\partial H_{G}}{\partial t} \]
\[ \frac{1}{S} \sum_j F_j^G \frac{\partial H_j^G}{\partial z} = \frac{1}{S} F_{G} \frac{\partial H_{G}}{\partial t} \]
\[ \sum_j r_j^G H_j^G = r_{G} H_{G} \]

In that sense, when recalling equation 3.26, the energy balance of the gas phase in a trickle-bed reactor is obtained as follows:

\[ \varepsilon_G \rho_G C_p G \frac{\partial T_G}{\partial t} = -\frac{1}{S} F_{G} C_p G \frac{\partial T_G}{\partial z} - U_{L} a_{L} (T_{G} - T_{L}) - \varepsilon_{G} (-\Delta H_{G}) r_{G} \] (3.34)
With \((-\Delta H_G)\) defined as the effective reaction enthalpy in the gas phase.

Equation (3.34) is a second order PDE and requires the following boundary and initial conditions to be solved:

\[
T_G(t, 0) = T_{G,0}(t) \tag{3.35}
\]

\[
T_G(0, z) = T_{G,in}(t) \tag{3.36}
\]

**Energy balance of the Liquid phase.** Energy flow into the liquid phase control volume by convection and heat transfer

\[
\sum_j F_j^L H_j^L \bigg|_{z} \Delta t + U_L a_L (T_G - T_L) S \Delta z \Delta t \tag{3.37}
\]

Energy flow out of the liquid phase control volume by convection and heat transfer

\[
\sum_j F_j^L H_j^L \bigg|_{z+\Delta z} \Delta t + U_S a_S (T_L - T_S) S \Delta z \Delta t \tag{3.38}
\]

Heat accumulated within the liquid phase control volume

\[
\varepsilon_L S \Delta z \left( \sum_j c_j^L H_j^L \bigg|_{t} - \sum_j c_j^L H_j^L \bigg|_{t+\Delta t} \right) \tag{3.39}
\]

The heat balance of the liquid phase can be expressed as follows

\[
\varepsilon_L S \Delta z \left( \sum_j c_j^L H_j^L \bigg|_{t} - \sum_j c_j^L H_j^L \bigg|_{t+\Delta t} \right) = \sum_j F_j^L H_j^L \bigg|_{z+\Delta z} \Delta t - \sum_j F_j^L H_j^L \bigg|_{z} \Delta t - U_L a_L (T_G - T_L) S \Delta z \Delta t - U_S a_S (T_L - T_S) S \Delta z \Delta t \tag{3.40}
\]

When dividing by \(S \Delta z \Delta t\) and taking the limit \(\Delta t \to 0\) and \(\Delta z \to 0\):

\[
\varepsilon_L \frac{\partial}{\partial t} \sum_j c_j^L H_j^L = - \frac{1}{S} \frac{\partial}{\partial z} \sum_j F_j^L H_j^L + U_L a_L (T_G - T_L) - U_S a_S (T_L - T_S) \tag{3.41}
\]

and expanding the derivative terms we obtain:

\[
\varepsilon_L \sum_j c_j^L \frac{\partial H_j^L}{\partial t} + \varepsilon_L \sum_j H_j^L \frac{\partial c_j^L}{\partial t} = - \frac{1}{S} \sum_j F_j^L \frac{\partial H_j^L}{\partial z} - \frac{1}{S} \sum_j H_j^L \frac{\partial F_j^L}{\partial z} + U_L a_L (T_G - T_L) - U_S a_S (T_L - T_S) \tag{3.42}
\]
and rearranging the following expression is obtained:

\[
\varepsilon_L \sum_j c^L_j \frac{\partial \bar{H}_j^L}{\partial t} = -\frac{1}{S} \sum_j F^L_j \frac{\partial \bar{H}_j^L}{\partial z} - \sum_j H_j^L \left( \frac{1}{S} \frac{\partial F^L_j}{\partial z} + \varepsilon_L \frac{\partial c^L_j}{\partial t} \right) + U_{LA} (T_G - T_L) - U_{SA} (T_L - T_S)
\]  

(3.43)

From the mass balance in the liquid phase in equation (3.15)

\[
\varepsilon_L \sum_j c^L_j \frac{\partial \bar{H}_j^L}{\partial t} = -\frac{1}{S} \sum_j F^L_j \frac{\partial \bar{H}_j^L}{\partial z} - \sum_j H_j^L \left( k^L_j a_L \left[ \frac{\rho^G_j}{H_j} - c^L_j \right] - k^S_j a_S \left[ c^L_j - c^S_j \right] + \varepsilon_L r_j^L \right) + U_{LA} (T_G - T_L) - U_{SA} (T_L - T_S)
\]

The assumption of heat transfer by convection is greater that the heat transfer by mass transport is also taken into account

\[
\sum_j H_j^L k^L_j a_L \left[ \frac{\rho^G_j}{H_j} - c^L_j \right] \ll U_{LA} (T_G - T_L)
\]

\[
\sum_j H_j^L k^S_j a_S \left[ c^L_j - c^S_j \right] \ll U_{SA} (T_L - T_S)
\]

The previous equation is reduced to

\[
\varepsilon_L \sum_j c^L_j \frac{\partial \bar{H}_j^L}{\partial t} = -\frac{1}{S} \sum_j F^L_j \frac{\partial \bar{H}_j^L}{\partial z} + U_{LA} (T_G - T_L) - U_{SA} (T_L - T_S) + \varepsilon_L r_j^L \sum_j H_j^L
\]

(3.44)

It is also a common assumption that the terms for individual species are lumped together in order to describe the liquid bulk, in other words:

\[
\sum_j c^L_j \frac{\partial \bar{H}_j^L}{\partial t} = \rho_L \frac{\partial \bar{H}_L}{\partial t}
\]

\[
\frac{1}{S} \sum_j F^L_j \frac{\partial \bar{H}_j^L}{\partial z} = \frac{1}{S} F^L \frac{\partial \bar{H}_L}{\partial t}
\]

\[
\sum_j r_j^L H_j^L = r_L \bar{H}_L
\]

When recalling equation (3.26) the energy equation of the liquid phase for a trickle-bed reactor

\[
\varepsilon_L \rho_L C_p L \frac{\partial T_L}{\partial t} = -\frac{1}{S} F_L C_p L \frac{\partial T_L}{\partial z} + U_{LA} (T_G - T_L) - U_{SA} (T_L - T_S) + \varepsilon_L (\Delta H_L) r_L
\]

(3.45)
Equation (3.45) is a second order PDE and requires the following boundary and initial conditions to be solved:

\[ T_L(t,0) = T_{L,0}(t) \]  
\[ T_L(0,z) = T_{L,in}(t) \]  
\[ (3.46) \]

**Energy balance of the Solid phase.** Recalling assumption A.8, the energy flow into the control volume by heat transfer from the liquid phase is:

\[ U_{SA_S} (T_L - T_S) S \Delta z \Delta t \]  
\[ (3.48) \]

The heat generation rate is implicit in the heat accumulation term, as follows:

\[ \varepsilon_S S \Delta z \left( \sum_j c_j S H_j^S \big|_{t+\Delta t} - \sum_j c_j S H_j^S \big|_t \right) \]  
\[ (3.49) \]

The continuity equations, lead to:

\[ \varepsilon_S S \Delta z \left( \sum_j c_j S H_j^S \big|_{t+\Delta t} - \sum_j c_j S H_j^S \big|_t \right) = U_{SA_S} (T_L - T_S) S \Delta z \Delta t \]  
\[ (3.50) \]

Then, dividing by \( \Delta t \) and taking the limit \( \Delta t \to 0 \), the following expression is obtained:

\[ \varepsilon_S \frac{\partial \sum_j c_j S H_j^S}{\partial t} = U_{SA_S} (T_L - T_S) \]  
\[ (3.51) \]

expanding the derivative term:

\[ \varepsilon_S \sum_j c_j S \frac{\partial H_j^S}{\partial t} + \varepsilon_S \sum_j H_j^S \frac{\partial c_j S}{\partial t} = U_{SA_S} (T_L - T_S) \]  
\[ (3.52) \]

Then, recalling the mass balance in equation (3.23) is necessary:

\[ \varepsilon_S \frac{\partial c_j S}{\partial t} = \frac{1}{\varepsilon_{pores}} k_j a_S (c_j^S - c_j^L) + \frac{\varepsilon_S}{\varepsilon_{pores}} r_j^S \]

When equation (3.23) is incorporated, the following expression is obtained:

\[ \varepsilon_S \sum_j c_j S \frac{\partial H_j^S}{\partial t} = \sum_j H_j^S \left( \frac{1}{\varepsilon_{pores}} k_j a_S (c_j^S - c_j^L) + \frac{\varepsilon_S}{\varepsilon_{pores}} r_j^S \right) + U_{SA_S} (T_L - T_S) \]  
\[ (3.53) \]

The individual components in the solid phase are lumped together as such:

\[ \sum_j c_j S \frac{\partial H_j^S}{\partial t} = \rho_S \frac{\partial H_S}{\partial t} \]  
\[ (3.54) \]
The heat generated and transferred from the liquid phase by convection is much higher than the heat transported by mass transfer, in other words:

\[ \sum_j r_j^S H_j^S \left( \frac{1}{\varepsilon_{\text{pores}}} k_j^a S_j^S (c_j^S - c_j^L) \right) \ll \sum_j H_j^S \left( \frac{\varepsilon_S}{\varepsilon_{\text{pores}}} r_j^S \right) + U_S a_S (T_L - T_S) \]

After this simplification, the energy balance of the solid phase is expressed as follows:

\[ \varepsilon_S \rho_S C_p S \frac{\partial T_S}{\partial t} = U_S a_S (T_L - T_S) - \frac{\varepsilon_S}{\varepsilon_{\text{pores}}} (-\Delta H_S) r_S \]  

Equation (3.56) is a second order PDE and requires the following boundary and initial conditions to be solved:

\[ T_S(t, 0) = T_{S,0}(t) \]  
\[ T_S(0, z) = T_{S,\text{in}}(t) \]

### 3.3 Summary of the PFTR model

To conclude this section, a summary of the PFTR model for a trickle-bed reactor provides an overview to the reader about the set of equations, boundary conditions and initial conditions.

\[ \varepsilon_G \frac{\partial c_j^G}{\partial t} = -\frac{1}{S} \frac{\partial F_j^G}{\partial z} - k_j^L a_L \left[ \frac{p_j^G}{H_j v_j} - c_j^L \right] + \varepsilon_G r_j^G \]  

\[ \varepsilon_L \frac{\partial c_j^L}{\partial t} = -\frac{1}{S} \frac{\partial F_j^L}{\partial z} + k_j^L a_L \left[ \frac{p_j^G}{H_j v_j} - c_j^L \right] - k_j^S a_S \left[ c_j^L - c_j^S \right] + \varepsilon_L r_j^L \]  

\[ \varepsilon_S \varepsilon_{\text{pores}} \frac{\partial c_j^S}{\partial t} = k_j^S a_S \left[ c_j^L - c_j^S \right] + \varepsilon_S r_j^S \]  

\[ \varepsilon_G \rho_G C_p G \frac{\partial T_G}{\partial t} = -\frac{1}{S} F_G C_p G \frac{\partial T_G}{\partial z} - U_L a_L (T_G - T_L) - \varepsilon_G (-\Delta H_G) r_G \]  

\[ \varepsilon_L \rho_L C_p L \frac{\partial T_L}{\partial t} = -\frac{1}{S} F_L C_p L \frac{\partial T_L}{\partial z} + U_L a_L (T_G - T_L) - U_S a_S (T_L - T_S) + \varepsilon_L (-\Delta H_L) r_L \]  

\[ \varepsilon_S \rho_S C_p S \frac{\partial T_S}{\partial t} = U_S a_S (T_L - T_S) - \frac{\varepsilon_S}{\varepsilon_{\text{pores}}} (-\Delta H_S) r_S \]
3.4 Continuous Stirred-Tank Reactor Model (CSTR)

A different approach can be used to simulate a trickle-bed reactor. Conceptually, a tubular reactor can be modelled as a series of continuous stirred-tank reactors. The model of a Continuous Stirred-tank Reactors (CSTR) can be constructed with the same approach of continuity equations on the control volume. In this section, the trickle-bed reactor is modelled as a CSTR that can be used in series.

3.4.1 Mass Balance

From the generic control volume definition in Figure 3.2, the definition of the mass balance equations for the CSTR model will be constructed (Figure 3.7).

![Figure 3.7. Mass balance in the CSTR control volume](image)

Species balance in the gas phase. The rate of species $j$ flowing into the gas-phase control volume by convection are defined as:

$$F_{j,0}^G \Delta t$$

(3.77)
Similarly, the rate of species $j$ flowing out of the gas-phase control volume by convection are defined as:

$$F^*_j \Delta t + k^L_j a_L \left[ \frac{p^G_j}{H_j} - c^L_j \right] S \Delta z \Delta t \quad (3.78)$$

The rate of generation of species $j$ by chemical reactions is given by:

$$\epsilon^G_S \Delta z \Delta t r^G_j \quad (3.79)$$

The rate of accumulation of species $j$ within $\Delta z$ is defined as:

$$\left( c^G_j \bigg|_{t+\Delta t} - c^G_j \bigg|_t \right) \epsilon^G_S \Delta z \quad (3.80)$$

Therefore, the expression of the continuity equation has the following structure:

$$\epsilon^G_S \Delta z \left( c^G_j \bigg|_{t+\Delta t} - c^G_j \bigg|_t \right) = F^*_G^G_j \Delta t - F^*_G^G_j \Delta t - k^L_j a_L \left[ \frac{p^G_j}{H_j} - c^L_j S \Delta z \right] S \Delta z \Delta t + \epsilon^G_S \Delta z \Delta t r^G_j \quad (3.81)$$

Then, dividing by $\Delta t$ Taking the limit $\Delta t \to 0$ the general mass balance equation for the gas phase is obtained:

$$\epsilon^G_S \Delta z \frac{\partial c^G_j}{\partial t} = F^*_G^G_j - F^*_G^G_j - k^L_j a_L \left[ \frac{p^G_j}{H_j} - c^L_j \right] S \Delta z \Delta t + \epsilon^G_S \Delta z \Delta t r^G_j \quad (3.82)$$

Equation (3.82) is a first order ODE and requires the following initial condition to be solved:

$$c^G_j(0) = c^G_j,_{in} \quad (3.83)$$

**Species balance in the liquid phase.** The species rate flowing into the liquid phase by convection and mass transfer from the gas phase takes into account the mass that is transported from the gas phase:

$$F^L_j \Delta t + k^L_j a_L \left[ \frac{p^G_j}{H_j} - c^L_j \right] S \Delta z \Delta t \quad (3.84)$$

The rate of species $j$ flowing out of the liquid phase control volume:

$$F^L_j \Delta t + k^S_j a_S \left[ c^S_j - c^L_j \right] S \Delta z \Delta t \quad (3.85)$$

Then, the rate of generation of species $j$ by chemical reactions in the liquid phase is expressed as follows:

$$r^L_j \epsilon^S_L S \Delta z \Delta t \quad (3.86)$$
The term of accumulation of species $j$ in the liquid phase control volume is:

$$
\left. \left( c_j^L \right|_{t+\Delta t} - c_j^L \right|_t \right) \varepsilon_L S \Delta z \tag{3.87}
$$

Then, the complete expression of the continuity equation in the liquid phase in the control volume is:

$$
\left. \left( c_j^L \right|_{t+\Delta t} - c_j^L \right|_t \right) \varepsilon_L S \Delta z = F_{j,0}^L \Delta t + k_j^L a_L \left[ \frac{p_j^G}{H_j} - c_j^L \right] S \Delta z \Delta t - F_j^L \Delta t
$$

$$
- k_j^S a_S \left[ c_j^S - c_j^L \right] S \Delta z \Delta t + \varepsilon_L S \Delta z r_j^L \tag{3.88}
$$

Then, dividing by $\Delta t$ and taking the limit $t \to 0$ the general mass balance equation for the liquid phase is obtained:

$$
\varepsilon_L S \Delta z \frac{\partial c_j^L}{\partial t} = F_{j,0}^L - F_j^L + k_j^L a_L \left[ \frac{p_j^G}{H_j} - c_j^L \right] S \Delta z - k_j^S a_S \left[ c_j^S - c_j^L \right] S \Delta z + \varepsilon_L S \Delta z r_j^L \tag{3.89}
$$

Equation (3.89) is a first order ODE and requires the following initial condition to be solved:

$$
c_j^L(0) = c_{j, in} \tag{3.90}
$$

**Species balance in the solid phase.** The mass of species $j$ is transported into the solid phase in by mass transfer only, therefore;

$$
k_j^S a_S \left[ c_j^S - c_j^L \right] S \Delta z \Delta t \tag{3.91}
$$

The rate of generation of species $j$ in the solid phase control volume is expressed as follows:

$$
r_j^S \varepsilon_S S \Delta z \Delta t \tag{3.92}
$$

The rate of accumulation of species $j$ within the liquid phase control volume is as such:

$$
\left. \left( c_j^S \right|_{t+\Delta t} - c_j^S \right|_t \right) \varepsilon_S S_{pores} S \Delta z \tag{3.93}
$$

The complete expression for the continuity equations over the the solid phase is described as follows:

$$
\varepsilon_S S_{pores} S \Delta z \frac{\left( c_j^S \right|_{t+\Delta t} - c_j^S \right|_t}{\Delta t} = k_j^S a_S \left( c_j^S - c_j^L \right) S \Delta z + \varepsilon_S S \Delta z r_j^S \tag{3.94}
$$

Then, dividing by $S \Delta z \Delta t$ and taking the limit $\Delta t \to 0$, the general expression of mass balance of the solid phase is obtained:

$$
\varepsilon_S S_{pores} \frac{\partial c_j^S}{\partial t} = k_j^S a_S \left( c_j^S - c_j^L \right) + \varepsilon_S r_j^S \tag{3.95}
$$

Equation (3.95) is a first order ODE and requires the following initial condition to be solved:

$$
c_j^S(0) = c_{j, in} \tag{3.96}$$
3.4.2 Energy balance

Similarly to the mass balance, the energy balance is performed over the control volume:

**Energy balance in gas phase.** Energy flow into the control volume by convection

\[ \sum_j F_j^G H_j^G \Delta t \]  
(3.97)

Energy flow out the control volume by convection and heat transfer

\[ \sum_j F_j^G H_j^G \Delta t + U_L a_L (T_G - T_L) S \Delta z \Delta t \]  
(3.98)

Heat accumulated within the gas phase control volume

\[
\varepsilon_G S \Delta z \left( \sum_j c_j^G H_j^G \bigg|_{\Delta t} - \sum_j c_j^G H_j^G \right) = \sum_j F_j^G H_j^G \Delta t - \sum_j F_j^G H_j^G \Delta t - U_L a_L (T_G - T_L) S \Delta z \Delta t 
\]  
(3.99)

Then the energy balance of the gas phase is as follows

\[
\varepsilon_G S \Delta z \left( \sum_j c_j^G H_j^G \bigg|_{\Delta t} - \sum_j c_j^G H_j^G \right) = \sum_j F_j^G H_j^G \Delta t - \sum_j F_j^G H_j^G \Delta t - U_L a_L (T_G - T_L) S \Delta z \Delta t 
\]  
(3.100)

Dividing by \( \Delta t \) and taking the limit \( \Delta t \to 0 \)

\[
\varepsilon_G S \Delta z \frac{\partial}{\partial t} \sum_j c_j^G H_j^G = \sum_j F_j^G H_j^G \bigg|_0 - \sum_j F_j^G H_j^G - U_L a_L (T_G - T_L) S \Delta z 
\]  
(3.101)
Expanding the derivative term, to obtain

$$
\varepsilon_G S\Delta z \left( \sum_j c_j^G \frac{\partial H_j^G}{\partial t} + \sum_j H_j^G \frac{\partial c_j^G}{\partial t} \right) = \sum_j F_j^G \gamma_0 H_j^G - \sum_j F_j^G H_j^G - U_{L} a_{L} (T_{G} - T_{L}) S\Delta z
$$

(3.102)

Rearranging to finally get

$$
\varepsilon_G S\Delta z \sum_j c_j^G \frac{\partial H_j^G}{\partial t} = \sum_j F_j^G \gamma_0 H_j^G - \sum_j F_j^G H_j^G - \varepsilon_G S\Delta z \sum_j H_j^G \frac{\partial c_j^G}{\partial t} - U_{L} a_{L} (T_{G} - T_{L}) S\Delta z
$$

(3.103)

From the mass balance 3.82

$$
\varepsilon_G S\Delta z \sum_j c_j^G \frac{\partial H_j^G}{\partial t} = \sum_j F_j^G \gamma_0 H_j^G - \sum_j F_j^G H_j^G
$$

$$
- \sum_j H_j^G \left( F_j^G - F_j^G - k_j^L a_L \left[ \frac{p_j^G}{H_j v_L} - c_j^L \right] \right) S\Delta z + S\Delta z r_j^G
$$

$$
- U_{L} a_{L} (T_{G} - T_{L}) S\Delta z
$$

(3.104)

rearranging

$$
\varepsilon_G S\Delta z \sum_j c_j^G \frac{\partial H_j^G}{\partial t} = \sum_j F_j^G \gamma_0 \left( H_j^G \gamma_0 - H_j^G \right) + \sum_j H_j^G k_j^L a_L \left[ \frac{p_j^G}{H_j v_L} - c_j^L \right] S\Delta z
$$

$$
- S\Delta z r_j^G \sum_j H_j^G - U_{L} a_{L} (T_{G} - T_{L}) S\Delta z
$$

(3.105)

And if we assume that the heat transferred to the liquid phase by convection is greater compared to the heat transfer due to mass transport

$$
\sum_j H_j^G k_j^L a_L \left[ \frac{p_j^G}{H_j v_L} - c_j^L \right] \ll \varepsilon_G r_j^G \sum_j H_j^G + U_{L} a_{L} (T_{G} - T_{L})
$$

Lumping the components together into a single gas phase

$$
\sum_j c_j^G \frac{\partial H_j^G}{\partial t} = \rho_G \frac{\partial H_G}{\partial t}
$$

(3.106)

$$
\sum_j F_j^G \gamma_0 \left( H_j^G \gamma_0 - H_j^G \right) = F_0^G \left( H_0^G - H_G \right)
$$

(3.107)

$$
\sum_j r_j^G H_j^G = r_G H_G
$$

(3.108)
from the definition of enthalpy the energy balance equation in the gas phase is obtained
\[
\varepsilon_G S \Delta z \rho_G C_p G \frac{dT_G}{dt} = C_p G F_0^G (T_G^0 - T_G) - U_L a_L (T_G - T_L) S \Delta z - S \Delta z (-\Delta H_{GR})
\] (3.109)

Equation (3.109) is a first order ODE and requires the following initial condition to be solved:
\[
T_G(0) = T_{G,\text{in}}
\] (3.110)

**Energy balance of the liquid phase.** Energy flow into the control volume by convection and heat transfer from the gas phase
\[
\sum_j F_j^L j^L_j \Delta t + U_L a_L (T_G - T_L) S \Delta z \Delta t
\] (3.111)

Energy flow out the control volume by convection and heat transfer into the solid phase
\[
\sum_j F_j^G H_j^G \Delta t + U_S a_S (T_L - T_S) S \Delta z \Delta t
\] (3.112)

The heat generation rate is implicit in the heat accumulation term
\[
\varepsilon_L S \Delta z \left( \sum_j c_j^L H_j^L |_{t+\Delta t} - \sum_j c_j^L H_j^L |_t \right)
\] (3.113)

Then, the energy balance of the gas phase is as follows
\[
\varepsilon_L S \Delta z \left( \sum_j c_j^L H_j^L |_{t+\Delta t} - \sum_j c_j^L H_j^L |_t \right) = \sum_j F_j^L j^L_j \Delta t + \sum_j F_j^G H_j^G \Delta t + U_L a_L (T_G - T_L) S \Delta z \Delta t
\] (3.114)

Dividing by \(\Delta t\) and taking the limit \(\Delta t \to 0\)
\[
\varepsilon_L S \Delta z \frac{\partial \sum_j c_j^L H_j^L}{\partial t} = \sum_j F_j^L j^L_j - \sum_j F_j^G H_j^G + U_L a_L (T_G - T_L) S \Delta z - U_S a_S (T_L - T_S) S \Delta z
\] (3.115)

Expanding the derivative term to obtain
\[
\varepsilon_L S \Delta z \left( \sum_j c_j^L \frac{\partial H_j^L}{\partial t} + \sum_j H_j^L \frac{\partial c_j^L}{\partial t} \right) = \sum_j F_j^L j^L_j - \sum_j F_j^G H_j^G + U_L a_L (T_G - T_L) S \Delta z - U_S a_S (T_L - T_S) S \Delta z
\] (3.116)
From the mass balance in equation (3.89)

\[
\varepsilon_L S \Delta z \sum_j c_j^L \frac{\partial H_j^L}{\partial t} = \sum_j F_j^{L \rightarrow 0} H_j^{L \rightarrow 0} - \sum_j F_j^L H_j^L \\
- \sum_j H_j^L \left( F_j^{L \rightarrow 0} - F_j^L + k_j^L a_L \left[ \frac{p_{jG}}{H_j} - c_j^L \right] S \Delta z - k_j^S a_S \left[ c_j^L - c_j^S \right] S \Delta z + \varepsilon_L S \Delta z r_j^L \right) \\
+ U_L a_L (T_G - T_L) S \Delta z - U_S a_S (T_L - T_S) S \Delta z
\]

(3.117)

The previous expression can be reduced to:

\[
\varepsilon_L S \Delta z \sum_j c_j^L \frac{\partial H_j^L}{\partial t} = \sum_j F_j^{L \rightarrow 0} \left( H_j^{L \rightarrow 0} - H_j^L \right) + U_L a_L (T_G - T_L) S \Delta z \\
- U_S a_S (T_L - T_S) S \Delta z - \varepsilon_L S \Delta z r_j^L \sum_j H_j^L
\]

(3.118)

The assumption of heat transfer by convection is greater than the heat transfer by mass transport is also taken into account as such:

\[
\sum_j H_j^L k_j^L a_L \left[ \frac{p_{jG}}{H_j} - c_j^L \right] \ll U_L a_L (T_G - T_L)
\]

\[
\sum_j H_j^L k_j^S a_S \left[ c_j^L - c_j^S \right] \ll U_S a_S (T_L - T_S)
\]

Here, a lump of species considered:

\[
\sum_j c_j^L \frac{\partial H_j^L}{\partial t} = \rho L \frac{\partial H_L}{\partial t}
\]

(3.119)

\[
\sum_j F_j^{L \rightarrow 0} \left( H_j^{L \rightarrow 0} - H_j^L \right) = F_0^L (H_0^L - H_L)
\]

(3.120)

\[
\sum_j r_j^L H_j^L = r_L H_L
\]

(3.121)

When recalling the enthalpy definition equation (3.26), the energy general energy balance equation of the liquid phase is obtained:

\[
\varepsilon_L S \Delta z \rho_L C_p L \frac{\partial T_L}{\partial t} = C_p L F_0^L (T_0^L - T_L) + U_L a_L (T_G - T_L) S \Delta z \\
- U_S a_S (T_L - T_S) S \Delta z - \varepsilon_L S \Delta z (\Delta H_L r_L)
\]

(3.122)

Equation (3.122) is a first order ODE and requires the following initial condition to be solved:

\[
T_L(0) = T_{L,in}
\]

(3.123)
3.4. Continuous Stirred-Tank Reactor Model (CSTR)

Energy balance of the solid phase. The energy flow into the control volume by heat transfer from the liquid phase is:

\[ U_{sa_s} (T_L - T_S) S \Delta z \Delta t \]  

(3.124)

The heat generation rate is implicit in the heat accumulation term as follows:

\[ \varepsilon_s S \Delta z \left( \sum_j c_j^S H_j^S \bigg|_{t+\Delta t} - \sum_j c_j^S H_j^S \bigg|_t \right) \]  

(3.125)

Then, the overall energy balance equation is:

\[ \varepsilon_s S \Delta z \left( \sum_j c_j^S H_j^S \bigg|_{t+\Delta t} - \sum_j c_j^S H_j^S \bigg|_t \right) = U_{sa_s} (T_L - T_S) S \Delta z \Delta t \]  

(3.126)

Then, dividing by \( \Delta t \) and taking the limit \( \Delta t \to 0 \), the following expression is obtained:

\[ \varepsilon_s \frac{\partial \sum_j c_j^S H_j^S}{\partial t} = U_{sa_s} (T_L - T_S) \]  

(3.127)

Expanding the derivative term:

\[ \varepsilon_s \sum_j c_j^S \frac{\partial H_j^S}{\partial t} + \varepsilon_s \sum_j H_j^S \frac{\partial c_j^S}{\partial t} = U_{sa_s} (T_L - T_S) \]  

(3.128)

The mass balance given in equation (3.95) must be recalled at this point:

\[ \varepsilon_s \frac{\partial c_j^S}{\partial t} = \frac{1}{\varepsilon_{pores}} k_j^S a_S (c_j^S - c_j^L) + \frac{\varepsilon_s}{\varepsilon_{pores}} r_j^S \]  

When equation (3.95) is inserted in equation (3.128), the following expression is obtained

\[ \varepsilon_s \sum_j c_j^S \frac{\partial H_j^S}{\partial t} = - \sum_j H_j^S \left( \frac{1}{\varepsilon_{pores}} k_j^S a_S (c_j^S - c_j^L) + \frac{\varepsilon_s}{\varepsilon_{pores}} r_j^S \right) + U_{sa_s} (T_L - T_S) \]  

(3.129)

The components are lumped as follows:

\[ \sum_j c_j^S \frac{\partial H_j^S}{\partial t} = \rho S \frac{\partial H_S}{\partial t} \]  

(3.130)

\[ \sum_j r_j^S H_j^S = r_S H_S \]  

(3.131)

The heat generated and transferred from the liquid phase by convection is quantitatively higher that the heat transported by mass transfer, in other words:

\[ \sum_j H_j^S \left( \frac{1}{\varepsilon_{pores}} k_j^S a_S (c_j^S - c_j^L) \right) \ll \sum_j H_j^S \left( \frac{\varepsilon_s}{\varepsilon_{pores}} r_j^S \right) + U_{sa_s} (T_L - T_S) \]
Finally, after recalling the enthalpy equation, the general energy balance equation of the solid phase is obtained:

\[
\varepsilon_S \rho_S C_P S \frac{\partial T_S}{\partial t} = U_S a_S (T_L - T_S) S \Delta z - \frac{\varepsilon_S}{\varepsilon_{pores}} S \Delta z (-\Delta H_S) r_j^S \tag{3.132}
\]

Equation (3.132) is a first order ODE and requires the following initial condition to be solved:

\[T_S(0) = T_{S,in} \tag{3.133}\]

### 3.5 Summary of the CSTR model

This summary has the purpose of providing an overview of the set of equations and boundary and initial conditions that comprise the CSTR model.

\[
\varepsilon_G S \Delta z \frac{\partial c_j^G}{\partial t} = F_{j,0}^G - F_j^G - k^G_j a_L \left[ \frac{p_j^G}{H_j^G} - c_j^L \right] S \Delta z - \varepsilon_G S \Delta z r_j^G \tag{3.134}
\]

\[
\varepsilon_L S \Delta z \frac{\partial c_j^L}{\partial t} = F_{j,0}^L - F_j^L + k^L_j a_L \left[ \frac{p_j^G}{H_j^L} - c_j^L \right] S \Delta z - \varepsilon_L S \Delta z r_j^L \tag{3.135}
\]

\[
\varepsilon_S \varepsilon_{pores} \frac{\partial c_j^S}{\partial t} = k^S_j a_S \left( c_j^S - c_j^L \right) + \varepsilon_S r_j^S \tag{3.136}
\]

\[
\varepsilon_G S \Delta z \rho_G C_P G \frac{\partial T_G}{\partial t} = C_p G F_{G,0}^G (T_G^0 - T_G) - U_L a_L (T_G - T_L) S \Delta z - S \Delta z (-\Delta H_G) r_G \tag{3.137}
\]

\[
\varepsilon_L S \Delta z \rho_L C_P L \frac{\partial T_L}{\partial t} = C_p L F_{L,0}^G (T_L^0 - T_L) + U_L a_L (T_G - T_L) S \Delta z - U_S a_S (T_L - T_S) S \Delta z - \varepsilon_L S \Delta z (-\Delta H_L) r_L \tag{3.138}
\]

\[
\varepsilon_S \rho_S C_P S \frac{\partial T_S}{\partial t} = U_S a_S (T_L - T_S) S \Delta z - \frac{\varepsilon_S}{\varepsilon_{pores}} S \Delta z (-\Delta H_S) r_j^S \tag{3.139}
\]

\[c_j^G(0) = c_{j,in}^G \tag{3.140}\]

\[c_j^L(0) = c_{j,in}^L \tag{3.141}\]

\[c_j^S(0) = c_{j,in}^S \tag{3.142}\]

\[T_G(0) = T_{G,in} \tag{3.143}\]

\[T_L(0) = T_{L,in} \tag{3.144}\]

\[T_S(0) = T_{S,in} \tag{3.145}\]
3.6 Feedstock reconstruction

In industry, the information of the feedstock is typically presented as data based on Boiling Point or cutpoint ranges on the true boiling point (TBP) distillation for the feedstock (i.e. Table 3.1). If one plots the information, we obtain Boiling Point Curve of the Feedstock (Figure 3.9). The initial boiling point is denoted by IBP. The analysis commonly provides information about concentration of monoaromatics, diaromatics and polyaromatics, total Nitrogen and Sulfur. However, in order to utilise the information of the feedstock in conjunction with a trickle-bed reactor model, a process simulator such as ProII, is a powerful tool. ProII allows multiple compounds sets (cutpoints) to be used in any problem to define various blends of pseudo-components.

Table 3.1. Example of typical boiling data for a Feedstock [31]

<table>
<thead>
<tr>
<th>IBP</th>
<th>°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>221.2</td>
</tr>
<tr>
<td>10%</td>
<td>236.5</td>
</tr>
<tr>
<td>30%</td>
<td>251.1</td>
</tr>
<tr>
<td>50%</td>
<td>264.8</td>
</tr>
<tr>
<td>70%</td>
<td>288.7</td>
</tr>
<tr>
<td>90%</td>
<td>310.0</td>
</tr>
<tr>
<td>95%</td>
<td>319.8</td>
</tr>
<tr>
<td>End Point</td>
<td>333.1</td>
</tr>
<tr>
<td>Sulfur</td>
<td>352.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoaromatics</td>
<td>2.339</td>
</tr>
<tr>
<td>Diaromatics</td>
<td>21.2</td>
</tr>
<tr>
<td>Polyaromatics</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
</tr>
</tbody>
</table>

A pseudo-component is a virtual compound defined by the user for which, the necessary physical and thermodynamic properties have to be estimated. Using ProII, one can take advantage of the numerous procedures to translate petroleum stream laboratory assay data into pseudo-components.

In hydrotreating applications, partitioning the feedstock by boiling point into a finite number of pseudo-components is a common approach. But, a natural simplification is to use real compounds to represent specific hydrocarbon groups, such as mono-, di- and polyaromatics [31].

First, one must define the Boiling Point ranges for each of the compound groups of interest, where the number of components is defined for one or more temperature intervals on the boiling point curve. In this case, for example, we take the following cutpoints for aromatics in the feedstock (see Figure 3.10):
Figure 3.9. Boiling point curve of a typical Feedstock

Table 3.2. Selection of cutpoints and number of pseudo-components

<table>
<thead>
<tr>
<th>Cutpoint set name</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MONO</td>
<td>220-270</td>
</tr>
<tr>
<td>DI</td>
<td>270-310</td>
</tr>
<tr>
<td>POLY</td>
<td>310-370</td>
</tr>
</tbody>
</table>

Figure 3.10. Definition of the cutpoints of aromatic by Boiling Point.
3.6. Feedstock reconstruction

Next we select the representative compound for each group of aromatic. For illustration purposes, we can select 2-ethylanthracene ($C_{16}H_{14}$) as representative of polyaromatics, the same for 2-ethyl-1,2,3,4-tetrahydroanthracene ($C_{16}H_{18}$) as representative of diaromatics and 2-ethyl-1,2,3,4,4a,9,9a,10-octahydroanthracene ($C_{16}H_{22}$) as monoaromatic (Figure 3.11):

![Boiling point curve of a Feedstock](image)

**Figure 3.11.** Definition of the cutpoints of aromatic by Boiling Point using representative real compounds.

With this practice, the concentrations, and the physical and thermodynamic properties can be implemented in the model since the compound lumps include overall chemical classes, i.e. organic sulfur and organic nitrogen compounds, and aromatics. However, this approach is drastic because each lump must contain a disperse sample of molecules in order to reflect reality. Therefore, the approach of modelling with lumps of real components is detached from the factual chemistry of the process. The information such as molecular structure and reaction paths, is hidden in the lumps. One of the main drawbacks of this modelling approach is that the kinetic model is significantly feedstock-specific. This approach allows the quantitative prediction for practical interests with a small range of process conditions, nonetheless.

As a step further in this practice, we take advantage of the pseudo-components. One can apply the same approach of dividing the petroleum stream into cutpoints of the Boiling Points, which at the same time are divided into their own sets of components blends based on boiling-point cutpoints. Using ProII, a default petroleum assay is generated with the Boiling Point data of the Feedstock. This will serve as
a bulk stream that we must use the in order to satisfy the mass balance since we know the the concentration of aromatics in the feedstock.

Next, the number of pseudo-components must be selected:

![Boiling point curve of a Feedstock](image)

**Figure 3.12.** Definition of the cutpoints of aromatic compounds by Boiling Point using pseudo-components.

The boiling point curves of each aromatic pseudo-component assay must be determined in such way that the final blend of the bulk stream and aromatics resemble the original boiling point curve of the original Feedstock (Figure 3.13). This can be done by a number of methods. In literature, systematic methods using algorithms have been explored [4], which can be useful if a large number of pseudo-components is necessary. However, a manual definition of the aromatic pseudo-component assays can be performed for a small number of pseudo-components.

Once the aromatics assays are obtained, the properties of the simulated Feedstock, i.e. molecular weights of aromatic pseudo-components, molar volumes, densities of gas and liquid, can be easily obtained from the process simulator and the reaction path can be established in order to solve the model.

### 3.7 Kinetic model

The development of a kinetic model is fundamental for the design of chemical processes. In the field of petroleum refining, one of the biggest challenges is the prediction of the vast product distribution. The difficulty implied to petroleum feedstock lies on the complex composition and intricate molecular structures. The number of compounds in an oil fraction depends on the boiling point range, and it may be
from a few hundred to several thousands. The modelling of such system implies a huge number of interconnected reactions network with a significant distribution of reactivities. Therefore, the modelling of hydrocarbon conversion processes is challenging and is a whole topic. However, for practical purposes, the kinetic model is based on the lumping approach. In other words, the feedstock is represented in terms of chemical lumps or pseudo-components that can be delimited according to the focus of the modelling. This representation is useful because the lumps are derived from standard petroleum analyses.

### 3.7.1 Langmuir-Hinshelwood Kinetic model

Throughout this work, the kinetic model takes into account the following reactions:

- \[2H_2 + Ar \rightarrow \text{aromatic} + H_2S\] (R.1)
- \[5H_2 + Ar \rightarrow \text{aromatic} + NH_3\] (R.2)
- \[aH_2 + b\text{Mono} \rightleftharpoons c\text{Naph}\] (R.4)
- \[dH_2 + e\text{Di} \rightleftharpoons f\text{Mono}\] (R.5)
- \[gH_2 + h\text{Poly} \rightleftharpoons i\text{Di}\] (R.6)

Where \(Ar\) stands for aromatic, and equation (R.1) and (R.2) are the HDS and HDN reactions respectively. The following Langmuir-Hinshelwood type kinetic equations are used to model the rate of HDS reactions [70][24][25]:

![Figure 3.13. Final blend of the bulk stream and the simulated pseudo-components resembling the original Boiling Point curve of the real Feed.](image)
Chapter 3. Fundamental model

\[ r_{Ar-S} = -\frac{k_{Ar-S}c_{Ar-S}m_1c_{H_2}^{m_2}}{1 + K_{ads}c_{H_2}S} \]  (3.146)

Where \( m_1, m_2 \) are the reaction orders, \( k_{Ar-S} \) is the reaction rate constant and the adsorption constant is denoted by \( K_{ads} \).

Reaction (R.2) is the HDN reaction and is modelled as a first order reaction [6]:

\[ r_{Ar-N} = -k_{Ar-N}c_{Ar-N} \]  (3.147)

where \( k_{Ar-N} \) is the reaction rate constant of aromatic nitrogen.

(R.4), (R.5) and (R.6) are the HDA reactions. The HDA reactions saturate ring by ring of each aromatic group and are reversible. The following rate equations have been used to describe the hydrogenation of aromatics [70][24][25][84].

\[ r_{naph} = k_{f,mono}c_{mono}P_{H_2}^{n_{mono}} - k_{r,mono}c_{naph} \]  (3.148)

\[ r_{mono} = -k_{f,mono}c_{mono}P_{H_2}^{n_{mono}} + k_{r,mono}c_{naph} \]  (3.149)

\[ r_{di} = -k_{f,di}c_{di}P_{H_2}^{n_{di}} + k_{r,di}c_{mono} \]  (3.150)

\[ r_{poly} = -k_{f,poly}c_{poly}P_{H_2}^{n_{poly}} + k_{r,poly}c_{di} \]  (3.151)

Where \( k_f \) and \( k_r \) denote the forward and reverse kinetic constants. The backwards reaction rates are determined as follows:

\[ K_{mono} = \frac{k_{f,mono}P_{H_2}^{n_{mono}}}{k_{r,mono}} \]  (3.152)

\[ K_{di} = \frac{k_{f,di}P_{H_2}^{n_{di}}}{k_{r,di}} \]  (3.153)

\[ K_{poly} = \frac{k_{f,poly}P_{H_2}^{n_{poly}}}{k_{r,poly}} \]  (3.154)

Therefore:

\[ k_{r,mono} = \frac{k_{f,mono}P_{H_2}^{n_{mono}}}{K_{mono}} \]  (3.155)

\[ k_{r,di} = \frac{k_{f,di}P_{H_2}^{n_{di}}}{K_{di}} \]  (3.156)

\[ k_{r,poly} = \frac{k_{f,poly}P_{H_2}^{n_{poly}}}{K_{poly}} \]  (3.157)

Where \( K_{mono/di/poly} \) are the equilibrium constants of aromatics respectively. The temperature dependencies of all the reaction rate constants and forward reactions are considered to be described by the Arrhenius law.
3.8 Model parameters

This section describes the equations used to obtain different model parameters.

Mass transfer coefficient. The mass transfer coefficients are calculated using the following correlations for gas-liquid mass transfer coefficient [48].

\[ k^L_{jA} = 1.11 \times 10^4 D_{AB} \left( \frac{G_L}{\mu_L} \right)^{0.4} \left( \frac{\mu_L}{\rho_L G_L} \right)^{0.5} \]  
(3.158)

Where \( k^L_{jA} \) is the specific mass transfer coefficient of solute A, over the liquid-solid interphase, \( D_{AB} \) is the diffusion coefficient of solute A in solvent B. \( G_L \) is the liquid mass flux, \( \mu_L \) and \( \rho_L \) are the viscosity and the density of the liquid at given temperature and pressure.

The liquid-solid mass transfer coefficients are calculated by Van Krevelen and Krekels correlation [22]:

\[ k^S_{jA} = 1.8 D_{AB} a_s^2 \left( \frac{G_L}{\mu_L} \right)^{0.5} \left( \frac{\mu_L}{\rho_L G_L} \right)^{1/3} \]  
(3.159)

Where \( k^S_{jA} \) is the mass transfer coefficient of solute A, over the liquid-solid interphase, \( a_s \). The diffusion coefficients are obtained from the Tyn-Calus correlation [70]:

\[ D_{AB} = \frac{8.93 \times 10^{-8} V_B^{0.267} T}{V_A^{0.433} \mu_B} \]  
(3.160)

Where \( \mu_B \) is the viscosity of the solvent B, \( V_B \) is the molecular volume of the solute, and \( T \) is the temperature.

The heat transfer coefficient. The heat transfer coefficient can be obtained with the following equations [22]:

\[ U_S = \frac{C_{PL} j_H}{\left( \frac{C_{PL} \mu_L}{k_L} \right)^{2/3}} \]  
(3.161)

Where \( \mu_L \) is the viscosity of the liquid, \( k_L \) is the thermal conductivity of the liquid and \( j_H \) is the \( j \) factor of heat transfer that can be obtained by [22]:

\[ j_H = k_{AB} \frac{\mu_A}{\rho_A D_{AB}} \]  
(3.162)

Where \( k_{AB} \) is the mass transfer coefficient from phase A to phase B. The same correlation is used to calculate \( U_L \) by replacing the properties of the gas in equation (3.162).
The gas velocity calculation  In practice, the molar flows are calculated using the following expression:

$$\frac{1}{S} F_j^G = u_s c_j^G$$  \hspace{1cm} (3.163)

Therefore, taking into account the mass and energy balances, the following equation is used to calculate the gas velocity:

$$\frac{\partial u_G}{\partial z} = \frac{RT}{P} \left( \frac{\varepsilon_G P}{RT^2} \frac{\partial T}{\partial t} - \sum_j k_{j}^{L} a_{L} \left( \frac{p_{j}^{G}}{H_{j} v_{j}} - c_{j}^{L} \right) \right) + \frac{u_G}{T} \frac{\partial T}{\partial z}$$  \hspace{1cm} (3.164)
This section describes the methodology that has been used to implement the trickle-bed reactor models. The mathematical model is solved using the finite difference scheme. The implementation is demonstrated using an example taken from literature.
Introduction

The overall purpose of a trickle-bed reactor model, in basic words, is to describe the process of converting reactant A to product B in a three-phase chemical reactor with mass and heat transfer phenomena considered. The simulation using numerical methods has proven to be a suitable tool to evaluate and solve mass and heat transfer problems amongst several other engineering problems [104] [78] [18].

If we take the steady-state process, the equations system results in a first-order ordinary differential equations (ODE) system subject to boundary conditions at two ends. Whenever our problem requires the specification of boundary conditions at two points, it is often called a two point boundary value problem. The Runge-Kutta method, is broadly used to numerically solve ODEs systems with boundary value problems commonly associated with hydrotreating reactors [70][25][84][36][87]. If we take into account the dynamic part of the model, we have an additional initial value problem because the initial conditions of the dependent variables must be known to determine how the dependent variables change over time. The system becomes a partial differential equations system (PDE). In order to solve it, different numerical methods are needed.

In literature, many different numerical methods are available to solve PDEs systems. The most recurrent examples are finite differences and orthogonal collocation [49][37][104]. Each one with different characteristics.

The orthogonal collocation method is implemented by selecting collocation points where the residual of the differential equation must be zero. The collocation points are defined by the roots of the Jacobi Polynomial. The polynomial solution can be expressed in the Lagrange Polynomial form. This procedure of involving collocation points and numerical resolution with polynomials, provides a quick coherent and accurate problem solution with a low number of discretizations [104].

On the other hand, the finite differences method, is a popular method used by researchers. It allows us to solve initial value problems comprised by ODEs or PDEs. Mass and heat transfer problems are common examples of such systems. Yet, the method requires inevitably a high number of discretization points due to a low accuracy of the finite difference approximation, which, is computationally demanding.

Nevertheless, the orthogonal collocation method is not always known for being the best solution because of its likelihood to produce unstable solutions with a larger number of discretizations [60]. Conversely, a higher discretization in the finite differences method is acknowledged for bringing more stability to the numerical evaluation and moreover, is easy to program and systematize. This makes it the
preferred choice for many initial development and analysis purposes.

Knowing the advantages of the finite differences method, we now study how to solve the model equations. In order to implement the finite difference scheme, first, all the equations shown previously in Sections 3.3 and 3.4.2 are PDEs and ODEs. The PDEs require discretization in space and integration in time to be solved. This section presents the programming structure of the solution of the equations that comprise the model.

### 4.1 The finite differences scheme

The finite differences method was one of the first discretization methods ever developed, yet, is the easiest to implement. Its principle lies on the representation of derivatives in a model, in terms of a finite Taylor expansion [60]. For a function $u(x)$, the derivative at point $x$ is defined by the relationship:

$$\frac{\partial u}{\partial x} = \lim_{\Delta x \to 0} \frac{u(x + \Delta x) - u(x)}{\Delta x},$$

(4.1)

where $\Delta x$ must be small enough for the above expression to tend towards a finite limit. However, this is only an approximation and an error subsists with regard to the derivative value. The truncation error committed by the approximation can be estimated using a Taylor expansion around the point $x$.

The majority of physical problems can be modelled in the form of a system of PDEs. Take for example the following equation to describe the linear advection of a compound in water. The concentration of the compound denoted by $C$. The compound is convected at a constant velocity $u$ in one space dimension. The variable $C$ is a function of two variables $t$ and $x$, hence, unsteady. If $t \in [0; t_f]$, and the initial conditions for this problem are $u(0, x) = u_0(x)$, the equation for a constant advection velocity is given by:

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = 0$$

(4.2)

where the exact solution is $C(t, x) = C_0(x - ut)$, however, in order to numerically solve the equation using the finite difference method, the points of interest must be selected i.e. $x_i = h \times i$, where $h$ is a distance between equal-spaced points. The objective is to obtain approximations of $C$ at the points $x_i$. Usually, unsteady state problems are solved advancing in time. In other words, approximations at all of the points $x_i$ at successive instants are computed.

If the value of the solution $C$ with $x = x_i$ at $t = 0$, then the initial conditions are given as: $C_0(x_i)$. The time step is defined as $\Delta t$. Then, the values of $C_i^n$ are approximated by the values of $C$ at $x = x_i$ and $t = t^n \equiv n\Delta t$. The finite differences
scheme is constructed by replacing the partial derivatives with the differences of the values $C^n_i$ using the Taylor developments, for example:

$$\frac{\partial C}{\partial t}(t^n, x_i) \sim \frac{C(t^{n+1}, x_i) - C(t^n, x_i)}{\Delta t} \sim \frac{C_{i+1}^n - C_i^n}{\Delta t}$$ (4.3)

$$\frac{\partial C}{\partial x}(t^n, x_i) \sim \frac{C(t^n, x_{i+1}) - C(t^n, x_{i-1})}{2h} \sim \frac{C_{i+1}^n - C_{i-1}^n}{2h}$$ (4.4)

Then, the finite difference scheme for Eq(4.2) is as follows:

$$\frac{C_{i+1}^n - C_i^n}{\Delta t} + u \frac{C_{i+1}^n - C_{i-1}^n}{2h} = 0$$ (4.5)

This scheme allows us to compute the approximations $C^n_i$ of $C$ with $x = x_i$ at $t = t^n$ by advancing in time. The finite differences scheme obtained, depends on the model equations and the choice of approaching the partial derivatives.

The accuracy of the method depends on the choice of the approximations of the partial derivatives to give a smooth solution. The scheme obtained in equation (4.5) is usually referred as centred difference scheme (equation (4.6)). However it is also possible to formulate forward (equation (4.7)) or backward (equation (4.8)) schemes.

$$\frac{\partial C}{\partial x}(t^n, x_i) = \frac{C_{i+1}^n - C_{i-1}^n}{2h} + O(h^2)$$ (4.6)

$$\frac{\partial C}{\partial x}(t^n, x_i) = \frac{C_{i+1}^n - C_{i}^n}{h} + O(h)$$ (4.7)

$$\frac{\partial C}{\partial x}(t^n, x_i) = \frac{C_{i}^n - C_{i-1}^n}{h} + O(h)$$ (4.8)

Where $O(h)$ is the error of the approximation compared to the ideal solution as a function of the selected step size.

The stability of the method, on the other hand, benefits when $h$ and $\Delta t$ tend towards 0. The centered and backward schemes are generally more stable. The forward scheme usually has a stability limit dependent on $h$ and the physical parameters of the PDE, beyond which, the scheme becomes unstable.

### 4.2 Program structure

Once we know how to solve PDE and ODE systems, we need a program to solve the model. The model was solved in Matlab© using a coding structure constructed in such was that every part of the model can be easily understood and modified according to the user’s needs. Figure 4.1 shows a schematic overview of the program structure.
4.3 Example - Hydrodesulfuration process to obtain ultra low sulfur diesel.

To illustrate the solution of a trickle-bed reactor model using the Finite Difference Method, an example is presented. Consider the hydrodesulfuration process of a feedstock [31]. In which, it was made use of gasoils from two refineries of Latin America to study the hydrodesulfuration process at standard industrial conditions, such as straight run gasoil (SGO), light cracked gasoil (LCGO), light cycle oil (LCO). The study is carried out in a pilot plant using different blends listed in Table 4.1. The pilot plant is operated at trickle-flow, isothermally with a fresh load of catalyst for each feed.

Table 4.1. Feedstock properties [31].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Feed 1</th>
<th>Feed 2</th>
<th>Feed 3</th>
<th>Feed 4</th>
<th>Feed 5</th>
<th>Feed 6</th>
<th>Feed 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP (°C)</td>
<td>278.1</td>
<td>250.8</td>
<td>211.2</td>
<td>176.5</td>
<td>211.8</td>
<td>192.4</td>
<td>177.9</td>
</tr>
<tr>
<td>10</td>
<td>293.9</td>
<td>274.4</td>
<td>236.5</td>
<td>216.9</td>
<td>270.6</td>
<td>225.6</td>
<td>221.5</td>
</tr>
<tr>
<td>20</td>
<td>300.1</td>
<td>282.6</td>
<td>251.1</td>
<td>236.3</td>
<td>281.0</td>
<td>246.4</td>
<td>237.6</td>
</tr>
<tr>
<td>30</td>
<td>305.3</td>
<td>289.3</td>
<td>264.8</td>
<td>252.5</td>
<td>287.2</td>
<td>253.7</td>
<td>252.1</td>
</tr>
<tr>
<td>50</td>
<td>315.6</td>
<td>302.0</td>
<td>288.7</td>
<td>283.6</td>
<td>295.7</td>
<td>276.0</td>
<td>274.8</td>
</tr>
<tr>
<td>70</td>
<td>327.3</td>
<td>316.5</td>
<td>310.0</td>
<td>308.0</td>
<td>304.4</td>
<td>293.7</td>
<td>292.4</td>
</tr>
<tr>
<td>80</td>
<td>334.3</td>
<td>325.6</td>
<td>319.8</td>
<td>319.1</td>
<td>309.9</td>
<td>302.6</td>
<td>300.5</td>
</tr>
<tr>
<td>90</td>
<td>343.4</td>
<td>337.5</td>
<td>333.1</td>
<td>333.0</td>
<td>317.9</td>
<td>312.8</td>
<td>311.0</td>
</tr>
<tr>
<td>100 (°C)</td>
<td>358.3</td>
<td>355.5</td>
<td>352.0</td>
<td>351.8</td>
<td>333.0</td>
<td>331.8</td>
<td>329.8</td>
</tr>
<tr>
<td>Specific gravity at 20/4 °C</td>
<td>0.8876</td>
<td>0.8987</td>
<td>0.8651</td>
<td>0.8487</td>
<td>0.8479</td>
<td>0.8549</td>
<td>0.8394</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>260.0</td>
<td>240.1</td>
<td>227.3</td>
<td>230.0</td>
<td>250.0</td>
<td>222.2</td>
<td>222.2</td>
</tr>
<tr>
<td>Total sulfur (wt.%)</td>
<td>1.9574</td>
<td>2.0232</td>
<td>2.339</td>
<td>1.021</td>
<td>0.9722</td>
<td>1.7833</td>
<td>0.6703</td>
</tr>
<tr>
<td>DBTs/total sulfur ratio</td>
<td>0.9858</td>
<td>0.9862</td>
<td>0.9853</td>
<td>0.9723</td>
<td>0.9864</td>
<td>0.9852</td>
<td>0.9723</td>
</tr>
<tr>
<td>Bromine number (gBr/100g)</td>
<td>3.9</td>
<td>2.3</td>
<td>17.62</td>
<td>3.28</td>
<td>1.96</td>
<td>11.16</td>
<td>3.26</td>
</tr>
<tr>
<td>Monoaromatics (wt.%)</td>
<td>20.1</td>
<td>16.9</td>
<td>21.2</td>
<td>23.6</td>
<td>19.5</td>
<td>19.6</td>
<td>22.9</td>
</tr>
<tr>
<td>Di-aromatics (wt.%)</td>
<td>10.7</td>
<td>28.5</td>
<td>13.1</td>
<td>8.5</td>
<td>13.6</td>
<td>11.7</td>
<td>7.1</td>
</tr>
<tr>
<td>Tri-aromatics (wt.%)</td>
<td>2.7</td>
<td>3.8</td>
<td>1.9</td>
<td>1.2</td>
<td>3.7</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Nitrogen (mg N/kg)</td>
<td>497</td>
<td>349</td>
<td>531</td>
<td>611</td>
<td>133</td>
<td>422</td>
<td>408</td>
</tr>
</tbody>
</table>

In order to obtain the model of the hydrodesulfuration (HDS) trickle-bed re-
actor, we need to recall the set of assumptions are presented in Chapter 2, which include plug flow, gas and liquid on one-dimensional flow, mass transfer performance estimated by the film theory. The heterogeneous model is used to describe the sulfur removal following two different HDS pathways: (1) Direct hydrogenolysis and (2) Hydrogenation. The direct hydrogenolysis acts on most of the sulfur compounds easy to desulfurize, i.e, dibenzothiophene (DBT). In The hydrogenation pathway, the DBT compunds are subject to partial hydrogenation of the aromatic rings before the sulfur removal. The liquid is comprised by paraffinic, naphthenic, monoaromatic, polyaromatic and sulfur compounds. The gas phase is $\text{H}_2$ and $\text{H}_2\text{S}$. All the compounds are represented as a set of specific reactants and products (Table 4.2).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>$\text{H}_2\text{S}$</td>
<td>Hydrogen sulfide</td>
</tr>
<tr>
<td>DBT</td>
<td>Dibenzothiophene, Very reactive sulfur compounds</td>
</tr>
<tr>
<td>46dmDBT</td>
<td>4,6-Dimethyl dibenzothiophene. Sulfur compounds difficult to convert.</td>
</tr>
<tr>
<td>BPH</td>
<td>Biphenyl. Polyaromatics at the inlet and derived from HDS of DBT.</td>
</tr>
<tr>
<td>33dmBPH</td>
<td>3,3-Dimethyl biphenyl. Polyaromatics derived from HDS of 46dmDBT.</td>
</tr>
<tr>
<td>CHB</td>
<td>Cyclohexylbenzene. Monoaromatics in the inlet and derived from HDS of DBT</td>
</tr>
<tr>
<td>3mCHT</td>
<td>3-Methylcyclohexyltoluene. Monoaromatics derived from HDS of 46dmDBT.</td>
</tr>
<tr>
<td>BCH</td>
<td>Bicyclohexyl. Naphthenic compounds in the inlet and outlet</td>
</tr>
<tr>
<td>nC28</td>
<td>Octacosane, Paraffinic compounds in the inlet and outlet</td>
</tr>
</tbody>
</table>

This example takes into account two different types of sulfur compounds, (1) Very reactive sulfur compounds and (2) sulfur compounds difficult to convert.

The very reactive sulfur compounds, i.e. mercaptans, sulfides, disulfides, thio-phenes, benzothiophenes, and dibenzothiophenes (DBTs), have similar reaction rates to the non-substituted DBT, hence used as the representative compound.

Other sulfur compounds, i.e. 4-methyl dibenzothiophene (4mDBT), 4,6-dimethyl dibenzothiophene (46dmDBT), 4,6-methyl-ethyl-dibenzothiophene (46meDBT), are isomers of alkyl-DBTs that contain alkyl groups close to the sulfur atom which are known to be very difficult to convert [31]. These compounds have similar reaction rates to the 4,6-substituted DBT and therefore used as the representative compound.
4.4 Implementation of the example case using a PFTR modelling approach

In order to obtain the HDS reactor model, first, we need to refer back to equations (3.59) to (3.61), where \( j \) is each of the ten compounds considered in Table 4.2, giving a total of 30 mass balance equations. The reaction terms \( r_j^G = r_j^L = 0 \), since the reaction takes place in the solid phase exclusively. To obtain the reaction term in the solid phase \( r_j^S \), one must consider the reactions pathways for the sulfur compounds and the saturation reactions given in Figure 4.2.

\[
\begin{align*}
\text{Figure 4.2. Hydrodesulfuration reaction pathway of DBT and 46dmDBT.}
\end{align*}
\]

The kinetic model was constructed according to the Langmuir-Hinshelwood-Hougen-Watson model, and includes kinetic and adsorption parameters for each compound of the reaction network are given in Tables 4.5 and 4.6. The kinetic model is given in equations (4.9)- (4.14).

\[
\begin{align*}
\text{(4.9)} \\
\text{(4.10)} \\
\text{(4.11)} \\
\text{(4.12)}
\end{align*}
\]
Chapter 4. Model implementation

\[ r_5 = \frac{k_{46dmDBT, \sigma} K_{46dmDBT, \sigma} K_{H_2, \sigma} C_{46dmDBT} C_{H_2}}{(1 + K_{DBT, \sigma} C_{DBT} + \sqrt{K_{H_2, \sigma} C_{H_2} + K_{BPB, \sigma} C_{BPB} + K_{46dmDBT, \sigma} C_{46dmDBT} + K_{33dmBPB, \sigma} C_{33dmBPB}})^3 } \]

\[ r_6 = \frac{k_{46dmDBT, \tau} K_{46dmDBT, \tau} K_{H_2, \tau} C_{46dmDBT} C_{H_2}}{(1 + K_{DBT, \tau} C_{DBT} + \sqrt{K_{H_2, \tau} C_{H_2} + K_{BPB, \tau} C_{BPB} + K_{46dmDBT, \tau} C_{46dmDBT} + K_{33dmBPB, \tau} C_{33dmBPB}})^3 } \]

Recalling equations (3.62) to (3.64), the energy balance equations for each phase can be obtained. Similarly to the mass balance equations, \( r_G = r_L = 0 \). The term \( r_s \) in equation (3.64) accounts for all the reactions taking place \( r_1 \) to \( r_6 \) and their respective heat of reaction \( \Delta H \), in other words:

\[ (-\Delta H_s) r_s = \sum_{i=1}^{6} (-\Delta H_i) r_i \]

The PFTR model for the example is obtained with a total of 33 equations for mass balances of reactants and products as well as energy balances for each phase. For illustration purposes, the equations for very reactive sulfur compounds are shown below:

Gas:

\[ \varepsilon_G \frac{\partial C_{DBT}^G}{\partial t} = -u_G \frac{\partial C_{DBT}^G}{\partial z} - k_{DBT}^L a_L \left[ \frac{p_{DBT}^G}{H_{DBT} v_{DBT}} - C_{DBT}^L \right] \]  

Liquid:

\[ \varepsilon_L \frac{\partial C_{DBT}^L}{\partial t} = -u_L \frac{\partial C_{DBT}^L}{\partial z} - k_{DBT}^S a_S \left[ C_{DBT}^L - C_{DBT}^S \right] \]

Solid:

\[ \varepsilon_S \varepsilon_{pores} \frac{\partial C_{DBT}^S}{\partial t} = k_{DBT}^S a_S \left[ C_{j}^L - C_{j}^S \right] + \varepsilon_S [r_1 + r_2] \]

Then, using the backward finite differences scheme the model equations for \( DBT \) are discretized in position as follows:

Gas:

\[ \varepsilon_G \frac{\partial C_{DBT}^G}{\partial t} = -u_G \frac{C_{DBT,j}^G - C_{DBT,j-1}^G}{h} - k_{DBT}^L a_L \left[ \frac{p_{DBT}^G}{H_{DBT} v_{DBT}} - C_{DBT}^L \right] \]
4.4. Implementation of the example case using a PFTR modelling approach

Liquid:

\[ \varepsilon_L \frac{\partial C_{DBT}^L}{\partial t} = -u_L \frac{C_{DBT,i}^L - C_{DBT,i-1}^L}{h} - k_{DBT}^S a_S [C_{DBT}^L - C_{DBT}^S] \tag{4.19} \]

The equation for the solid phase remains unchanged as there is no position component.

Solid:

\[ \varepsilon_S \varepsilon_{\text{pores}} \frac{\partial C_{DBT}^S}{\partial t} = k_{DBT}^S a_S [C_{DBT}^L - C_{DBT}^S] + \varepsilon_S [r_1 + r_2] \tag{4.20} \]

The time component is left without discretization in order to be solved by means of the built-in function \textit{ODE15s} in Matlab using the inlet properties given in Tables 4.4 and 4.3.

### Table 4.3. Properties of the oil species in the example case [31].

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SG (20/4°C)</td>
<td>0.8676</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP</td>
<td>D86</td>
<td>°C</td>
<td>278.1</td>
</tr>
<tr>
<td>10%</td>
<td>D86</td>
<td>°C</td>
<td>293.9</td>
</tr>
<tr>
<td>20%</td>
<td>D86</td>
<td>°C</td>
<td>300.1</td>
</tr>
<tr>
<td>30%</td>
<td>D86</td>
<td>°C</td>
<td>305.3</td>
</tr>
<tr>
<td>50%</td>
<td>D86</td>
<td>°C</td>
<td>315.6</td>
</tr>
<tr>
<td>70%</td>
<td>D86</td>
<td>°C</td>
<td>327.3</td>
</tr>
<tr>
<td>80%</td>
<td>D86</td>
<td>°C</td>
<td>334.3</td>
</tr>
<tr>
<td>90%</td>
<td>D86</td>
<td>°C</td>
<td>343.4</td>
</tr>
<tr>
<td>End Point</td>
<td>D86</td>
<td>°C</td>
<td>358.3</td>
</tr>
</tbody>
</table>

| Sulfur | wt%  | 1.9574 |
| Nitrogen | wt%  | 0.0497 |
| Monoaromatics | wt%  | 20.1  |
| Polyaromatics  | wt%  | 13.4  |

### Table 4.5. Kinetic parameters for the example case [92][2][21][34].

<table>
<thead>
<tr>
<th>Expression</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{DBT, \sigma} )</td>
<td>( 6.7871 \times 10^6 \exp(-122770/RT) )</td>
</tr>
<tr>
<td>( k_{DBT, \tau} )</td>
<td>( 7.9655 \times 10^{12} \exp(-186190/RT) )</td>
</tr>
<tr>
<td>( k_{BPH, \tau} )</td>
<td>( 3.44112 \times 10^{19} \exp(-255714/RT) )</td>
</tr>
<tr>
<td>( k_{46dmDBT, \sigma} )</td>
<td>( 1.7904 \times 10^4 \exp(-106223/RT) )</td>
</tr>
<tr>
<td>( k_{46dmDBT, \tau} )</td>
<td>( 1.0228 \times 10^{24} \exp(-299042/RT) )</td>
</tr>
<tr>
<td>( K_{DBT, \sigma} )</td>
<td>( 7.56868 \times 10^{11} )</td>
</tr>
<tr>
<td>( K_{DBT, \tau} )</td>
<td>( 2.50395 \times 10^{-6} \exp(76840/RT) )</td>
</tr>
<tr>
<td>( K_{BPH, \sigma} )</td>
<td>( 3.84984 \times 10^{-3} \exp(48214/RT) )</td>
</tr>
<tr>
<td>( K_{BPH, \tau} )</td>
<td>( 4.96685 \times 10^{-3} \exp(37989/RT) )</td>
</tr>
<tr>
<td>( K_{H_2, \sigma} )</td>
<td>( 3.36312 \times 10^{-10} \exp(113232/RT) )</td>
</tr>
<tr>
<td>( K_{H_2,S, \sigma} )</td>
<td>( 1.47118 \times 10^{-7} \exp(105670/RT) )</td>
</tr>
<tr>
<td>( K_{H_2, \tau} )</td>
<td>( 1.40255 \times 10^{-14} \exp(142693/RT) )</td>
</tr>
<tr>
<td>( K_{46dmDBT, \sigma} )</td>
<td>( 18.0397 \times 10^3 )</td>
</tr>
<tr>
<td>( K_{46dmDBT, \tau} )</td>
<td>( 1.58733 \times 10^{-7} \exp(90485/RT) )</td>
</tr>
</tbody>
</table>
Table 4.4. Process input parameters and specifications [31][84]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{\text{inlet}} )</td>
<td>644 K</td>
</tr>
<tr>
<td>( a )</td>
<td>7.21 cm(^{-1}) [70]</td>
</tr>
<tr>
<td>( \rho_{\text{cat}} )</td>
<td>875 kg/m(^3)</td>
</tr>
<tr>
<td>( P )</td>
<td>7.8 MPa</td>
</tr>
<tr>
<td>( \text{LHSV} )</td>
<td>0.7 h(^{-1})</td>
</tr>
<tr>
<td>( \rho_L )</td>
<td>0.762 g/cm(^3)</td>
</tr>
<tr>
<td>( H_j )</td>
<td>( \text{H}_2 ) 16,230 MPa/cm(^3)mol</td>
</tr>
<tr>
<td></td>
<td>( \text{H}_2\text{S} ) 25,350 MPa/cm(^3)mol</td>
</tr>
<tr>
<td></td>
<td>( \text{NH}_3 ) 4,693 MPa/cm(^3)mol</td>
</tr>
<tr>
<td>( H_2/\text{oil} )</td>
<td>446</td>
</tr>
<tr>
<td>( C_p^G )</td>
<td>14.5 J/gK [30]</td>
</tr>
<tr>
<td>( C_p^L )</td>
<td>3.19 J/gK [30]</td>
</tr>
<tr>
<td>( D_j )</td>
<td>( \text{H}_2 ) 1.492\times10^{-4} cm(^2)/s</td>
</tr>
<tr>
<td></td>
<td>( \text{H}_2\text{S} ) 1.233\times10^{-4} cm(^2)/s</td>
</tr>
<tr>
<td></td>
<td>( \text{NH}_3 ) 1.425\times10^{-4} cm(^2)/s</td>
</tr>
<tr>
<td>( \lambda_j )</td>
<td>( \text{H}_2 ) 22.6 NL/g</td>
</tr>
<tr>
<td></td>
<td>( \text{H}_2\text{S} ) 35.2 NL/g</td>
</tr>
<tr>
<td></td>
<td>( \text{NH}_3 ) 25.2 NL/g</td>
</tr>
</tbody>
</table>

Inlet partial pressures (Pa)

| \( \text{H}_2 \) | 0.998\times10^6 |
| \( \text{H}_2\text{S} \) | 0.002\times10^2 |

Table 4.6. Reaction enthalpies for the example case [121].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H_r ) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_1 )</td>
<td>DBT + 2H(_2) → BPH + H(_2\text{S})</td>
</tr>
<tr>
<td>( r_2 )</td>
<td>DBT + 5H(_2) → CHB + H(_2\text{S})</td>
</tr>
<tr>
<td>( r_3 )</td>
<td>BPH + 3H(_2) → CHB</td>
</tr>
<tr>
<td>( r_4 )</td>
<td>CHB + 3H(_2) → BCH</td>
</tr>
<tr>
<td>( r_5 )</td>
<td>46dmDBT + 2H(_2) → 33dmBPH + H(_2\text{S})</td>
</tr>
<tr>
<td>( r_6 )</td>
<td>46dmDBT + 5H(_2) → 3mCHT + H(_2\text{S})</td>
</tr>
</tbody>
</table>

4.5 Model implementation analysis

A key element for the implementation is to determine the number of nodes in which the solution is obtained. The numerical solution using the finite differences scheme requires a number of nodes to be solved. The number of nodes depends significantly of the application. In principle, higher number of nodes increase the accuracy of the solution [110]. However, the number of nodes has a significant impact in the computational load.

At the steady-state conditions, the number of nodes in position is more relevant. In order to determine the appropriate number of nodes in position, the solution of
4.5. Model implementation analysis

Figure 4.3. Concentration profiles of total sulfur- compounds at steady state with different number of nodes in position.

The model is obtained using 10, 20, 50, 100, 150 and 200 nodes. The solution with different number of nodes is compared graphically against each other (Figure 4.3). The computation time, in which all the equations are solved simultaneously, is an important factor, especially if real-time simulation for e.g. monitoring or control is a priority.

The computation time varies from a few seconds to hours according to the chosen number of nodes. Table 4.7 illustrates the time to obtain the solution using different number of nodes for the example case.

Table 4.7. Computation time of the model solution using different number of nodes.

<table>
<thead>
<tr>
<th>Number of nodes</th>
<th>Computation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>25.00 seconds</td>
</tr>
<tr>
<td>20</td>
<td>63.14 seconds</td>
</tr>
<tr>
<td>50</td>
<td>375.07 seconds</td>
</tr>
<tr>
<td>100</td>
<td>1034.25 seconds (17 mins. approx.)</td>
</tr>
<tr>
<td>150</td>
<td>2520.31 seconds (42 mins. approx.)</td>
</tr>
<tr>
<td>200</td>
<td>5969.71 seconds (99 mins. approx.)</td>
</tr>
</tbody>
</table>

The highlight of the model is to describe the hydrotreating process to obtain low-sulfur diesel. Therefore, using the selected number of nodes, the steady-state solutions for the concentration of total sulfur- compounds are obtained and plotted in Figure 4.3.
The solutions in Figure 4.3 are seemingly different, but follow the same trend nonetheless. The concentration Sulfur-compounds stabilizes around 3.5 cm in every solution. If one focuses in the region for 0 to 2.5 cm, the difference between the solutions becomes more evident (Figure 4.4).

In order to quantify the difference in the solutions with changed number of nodes, the absolute error between the two solutions is calculated as follows:

\[ \varepsilon = \text{abs}(x - y) \quad (4.21) \]

where \( x \) and \( y \) are solution points for two different number of nodes at the same position.

Figure 4.5 shows the magnitude of the absolute error between two different solutions in \( \text{mol/cm}^3 \) of Sulfur-compound, i.e. the absolute error between the solutions with 10 nodes and 20 nodes and denoted by \( \varepsilon_{(20|10)} \).

A decrease in the magnitude of the absolute error is anticipated as the number of nodes increase. In Figure 4.5, one can observe that the maximum error is obtained when the solutions with 10 and 20 nodes are compared obtaining a magnitude of \( 4.3 \times 10^{-7} \text{mol/cm}^3 \). This means that the solutions differ expressively, and serve as the reference for the rest of the study. Once again, a higher number of nodes is required for a more consistent solution. The difference decreases to \( 1.3 \times 10^{-7} \text{mol/cm}^3 \) when one grasps the error of 50 and 20 nodes. Moreover, the absolute error shrinks significantly to \( 0.45 \times 10^{-7} \text{mol/cm}^3 \) when comparing 50 and 100 nodes, meaning...
that these two solutions are more consistent with each other. The error of the solution with 100 and 150 nodes has a magnitude of $0.31 \times 10^{-7}\text{mol/cm}^3$, while 150 and 200 nodes produces an error of $0.21 \times 10^{-7}\text{mol/cm}^3$.

The extent of the error when using more than 100 nodes remains fairly consistent as the solutions linger in the same order of magnitude. Therefore it can be concluded that using more than 100 nodes in position, does not increase significantly the accuracy of the solution, especially if one takes into consideration the cost of the computation time. This can explain why solutions with 100 nodes in position are usually found in literature for similar hydrotreating models [84][24][5][3][25].

The solution of the model for hydrodesulfuration process to obtain ultra low sulfur dieses, using the PFTR modelling approach, is obtained using 100 nodes in position. Figure 4.6 shows the concentration profiles of $\text{H}_2$ in the gas and the liquid phases, in which a drop in the hydrogen concentration in the gas phase can be appreciated. The hydrogen is transported to the liquid phase, and therefore to the solid phase where the reaction occurs. During the reaction, $\text{H}_2\text{S}$ is released as a product and is transported to the liquid phase and, subsequently to the gas phase 4.7. The HDS reaction rate decays significantly after 4 cm, approaching zero towards the end of the reactor. This causes a consistent transport of $\text{H}_2\text{S}$ to the gas phase until the equilibrium is reached. The behaviour of the $\text{H}_2\text{S}$ is consistent with the behaviour of the sulfur- compounds in the liquid phase shown in Figure 4.8.
Figure 4.6. Concentration profiles of H₂ in the gas and liquid phases across the length of the reactor.

The sulfur- compounds easy to react (C_DBT) are consumed faster, as expected. The rate of hydrodesulfuration reaction for sulfur- compounds difficult to convert (C_{46dmDBT}) approaches zero after 4 cm. The maximum concentration of H₂S in the liquid phase is reached around 1.8 cm, which is the region where most of the sulfur- compounds are consumed. Beyond this point, the rate of HDS reaction decreases significantly causing a faster transport of H₂ than it is consumed.

Figure 4.9 shows the concentration profiles of aromatic compounds. The products of the HDS reaction of DBT are BPH (polyaromatic) and CHB (monoaromatic). The products of the HDS reaction of 46dmDBT are 33dmBPH (polyaromatic) and 3mCHT (monoaromatic). The profiles of the aromatic compounds in Figure 4.9 are the outcome of the saturation reactions of all the organic compounds. Overall, the concentration of monoaromatic and naphthenic compounds(BCH) increases towards the end of the reactor as a consequence of saturation of polyaromatics.

Figure 4.10 shows the temperature profiles for gas, liquid and solid phases. The profiles are almost identical between each other. This can be explained by a high heat transfer amid the phases assuming the solid phase is completely wetted. Close to the inlet, the temperature of the solid is slightly higher than the other two because is where the reaction takes place. However, the small differences in the temperature profiles shrink and, as the reaction rates approach zero towards the end of the reactor, the same outlet value of 681 K is achieved.
Figure 4.7. Concentration profiles of $\text{H}_2\text{S}$ in the gas and liquid phases across the length of the reactor.

Figure 4.8. Concentration profiles of sulfur- compounds easy to convert ($C_{\text{DBT}}$) and difficult to react ($C_{46\text{dmDBT}}$) in the liquid phases across the length of the reactor.
Figure 4.9. Concentration profiles of aromatic compounds in the liquid phases across the length of the reactor.

Figure 4.10. Temperature profiles of the gas, liquid and solid phases across the length of the reactor.
In this section, an additional implementation analysis is performed with the objective of using a CSTR model to simulate the hydrotreating unit. The CSTR model developed in Chapter 3, is constructed with a simulation in series in mind. The simulation in series is performed by drawing the results from one reactor and use it as the input for the next one until equal volume of the hydrotreating reactor is attained. This method is not reported in literature for simulation of hydrotreating reactors. However, it can be useful to contemplate different process attributes such as inter-bed quench zones.

The study of the simulation of CSTR in series is carried out as follows. Six simulations of CSTRs in series are carried out to simulate the example case study with different numbers of equal-size CSTRS that vary from 1 to 100. The simulations are compared to the simulation using the PFTR model with 100 nodes and the absolute error is calculated using equation (4.21) just as in the previous section.

The first instance of the CSTR simulation is with one single reactor. In order to determine the steady-state, the dynamic sulfur- concentration in the liquid is plotted in Figure 4.11.

Figure 4.11 serves as a reference for the simulation time in which the steady state is reached at around 150 seconds. The simulation time is used for the subsequent simulations.
Figure 4.12. Steady-state profile of sulfur- compounds in the liquid phase of one CSTR used to represent the hydrotreating reactor.

Figure 4.12, shows the inlet and outlet concentrations sulfur- compounds in the liquid phase at steady state. The outlet concentration coincides with the performance of the PFTR simulation with 100 nodes. However, the information of the concentration across the length of the reactor is absent with this approach.

In order to investigate the number of reactors that achieve comparable results to the PFTR simulation with 100 nodes, the absolute error is calculated using equation (4.21). The evaluation of the error of 3, 5, 10, 20, 50 and 100 CSTRs in series is compared to the PFTR solution with 100 nodes. The results are presented in Figure 4.13.

As expected, Figure 4.13 shows that with one CSTR, the error at the outlet of the reactor is zero. However, due to the lack of information across the reactor due to the nature of the CSTR, the magnitude of the error is predominantly high. As the number of CSTRs increase, the region, in which the error is larger, shrinks towards the inlet of the hydrotreating reactor.

The simulation with 10 equal-size CSTRs in series is the simulation that has the overall lowest error compared to the PFTR with 100 nodes. However, it is worth pointing out that close to 2 cm, the error goes to zero for for 10, 20, 50 and 100. In the region from 0 to 2 cm, the error grows as the number of CSTRs in series increase. This phenomena leads to the resolution in which variable-sized CSTRs is the avenue that one must follow if the goal is to obtain the minimum error possible.
4.5. Model implementation analysis

Figure 4.13. Absolute error between the simulation of the hydrotreating reactor with different number of CSTRs in series and the solution of the PFTR with 100 nodes. The magnitude of the error is measured in $mol/cm^3$. 
This chapter presents the application of the trickle-bed reactor model and its implementation to a real large-scale hydrotreating unit using the PFTR modelling approach. The simulations are performed in order to evaluate the behaviour of the system under different conditions and assumptions e.g. related to the linear gas velocity. A study of the dynamics is carried out to investigate the behaviour of the system with a change in the sulfur compound concentration of the feed. Furthermore, a sensitivity analysis of the most relevant model parameters is performed.
Chapter 5. Case Study: Part I

Introduction

The case study selected, is a real large-scale industrial hydrotreating reactor. The process operates continuously. Industrial hydrotreating units have several catalytic beds with quench zones in between. Gas and liquid flow cocurrently into the reactor from the top. A layer of falling liquid covers the catalyst particles in the reaction zone. The gas phase is mostly hydrogen; however, recycle gas contains other gaseous compounds such as H\(_2\), NH\(_3\) and organic sulfur compounds in low amounts. The liquid phase is composed of aromatic and aliphatic compounds, as well as, sulfur- and nitrogen-organic compounds. Benzothiophene (BT) and dibenzothiophene (DBT) are used as representative organic sulfur compounds in the model, as they are easy and difficult to desulfurize respectively. Carbazole is used to represent organic-nitrogen compounds and, for simplicity in the notation, will be denoted by \( N \). The reaction kinetics is based on the Langmuir–Hinshelwood model with partial pressures for gas phase and concentrations for the liquid and solid phases [25], which includes kinetic and adsorption parameters for each active compound of the reaction network. Hydrotreating reactions are lumped into kinetic expressions for sulfur-, nitrogen- and aromatic compounds. The following reactions are considered.

Hydrodesulfuration of sulfur containing species (benzothiophene (BT) and dibenzothiophene (DBT)):

\[
3H_2 + C_8H_6S \rightarrow C_8H_{10} + H_2S
\]

\[
5H_2 + C_{12}H_8S \rightarrow C_{12}H_{16} + H_2S
\]

Hydrogenation of organic-nitrogen containing species (N):

\[
5H_2 + C_{12}H_9N \rightarrow C_{12}H_{16} + NH_3
\]

The hydrodearomatization (HDA) reaction is conveyed by the consecutive saturation of mono-, di- and poly-aromatic compounds:

Expressed as follows:

\[
aH_2 + bMono \leftrightarrow cNaphthene
\]
5.1 The trickle-bed reactor model for the large-scale hydrotreating unit.

The equilibrium concentration in the film layer of species $j$ in the gas phase are expressed in terms of partial pressure ($p_G^j$), the Henry coefficient ($H_j$) and $v_j$ is the molar volume of species $j$ [70]. With the molar flow given as $\frac{1}{S_A}F_G^j = u_Gc_j^G$ for the phase $j$, the following mole balance equations are obtained:

with $j = H_2, H_2S, NH_3, BT, DBT$ and $S_A$ is the cross-sectional area of the bed.

The industrial reactor can be considered adiabatic and, in common practice, without any radial transport of heat [84][4]. The plug-flow trickle-bed reactor model from the mass and energy balance equations based on the set of assumptions (A.1)-(A.8) in Chapter 3 and the following equations are obtained:

$$dH_2 + eDi \leftrightarrow fMono$$

$$gH_2 + hPoly \leftrightarrow iDi$$

(5.5)

(5.6)

Where $a, b, c, d, e, f, g, h, i$ are stoichiometric coefficients. The stoichiometric coefficients are characteristic of the feed and can be obtained by experiments.
5.1.1 Kinetic model of the large-scale hydrotreating unit.

The kinetic model highlights the reaction of HDS and HDA reactions of petroleum feedstock to produce commercial diesel, however, HDN reaction is also considered. HDS reactions are lumped into kinetic expressions for BT, DBT, nitrogen and aromatic compounds. The following Langmuir-Hinshelwood type kinetic equations are used based on partial pressures for the gas phase and concentrations for the solid and liquid phases for a heterogeneous reaction. All the concentrations, given in all rate expressions, refer to concentrations in the liquid trapped in the pores of the solid phase, \( c_j^S \)

The superscript \( S \) has been omitted in the rate expressions to give room for the exponents and is worth remembering that \( N \) stands for carbazole, which is the representative nitrogen organic compound. The reaction rate expression in the equations (5.13)-(5.18) [25] comprise the hydrodesulfurization reaction of BT and DBT at \( p^0 = 4 \) Mpa and are corrected to the pressure of the process \( P \). HDN reaction is represented by a first order kinetic expression. Both the HDN and HDS reactions are considered irreversible.

\[
\begin{align*}
    r_{BT} &= -k_{BT}c_{BT}^{1.6}c_{H_2}^{0.56} \\
    &= - \frac{k_{BT}c_{BT}^{1.6}c_{H_2}^{0.56}}{1 + K_{H_2S}c_{H_2S}} \quad (5.13) \\
    r_{DBT} &= -k_{DBT}c_{DBT}^{1.6}c_{H_2}^{0.56} \\
    &= - \frac{k_{DBT}c_{DBT}^{1.6}c_{H_2}^{0.56}}{1 + K_{H_2S}c_{H_2S}} \quad (5.14) \\
    r_{mono} &= -k_{f,mono}c_{mono} \left( \frac{P}{P^0} \right)^{n_{mono}} + \frac{k_{f,mono}}{K_{eq,mono}}c_{Naph} \quad (5.15) \\
    r_{Di} &= -k_{f,Di}c_{Di} \left( \frac{P}{P^0} \right)^{n_{di}} + \frac{k_{f,Di}}{K_{eq,Di}}c_{Mono} \quad (5.16) \\
    r_{Poly} &= -k_{f,Poly}c_{Poly} \left( \frac{P}{P^0} \right)^{n_{poly}} + \frac{k_{f,Poly}}{K_{eq,Poly}}c_{Di} \quad (5.17) \\
    r_N &= -k_Nc_N \quad (5.18)
\end{align*}
\]

5.1.2 Characterization of the Feed

The reactor feed is an oil feedstock identified as combined feed. The following data are available from the reactor:

- Combined Feed mass flowrate: 233313.96 kg/h
- Hydrogen: 4045.67 kg/h
The combined feed is a mixture of diverse components. However, it is possible
to quantify the sulfur- and nitrogen- content in the feed, as well as certain types of
aromatic compounds. A boiling point curve is also available from the feedstock:

**Table 5.1.** Properties of the oil feed. API stands for American Petroleum Institute
gravity and IBP for initial boiling point.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Average API Gravity</td>
<td>32.9</td>
<td></td>
</tr>
<tr>
<td>IBP D86 °C</td>
<td>5% 221</td>
<td>10% 248</td>
</tr>
<tr>
<td>30% 256</td>
<td>50% 287</td>
<td>70% 307</td>
</tr>
<tr>
<td>90% 342</td>
<td>95% 361</td>
<td>End Point 378</td>
</tr>
<tr>
<td>Total Nitrogen wt ppm</td>
<td>181</td>
<td></td>
</tr>
<tr>
<td>Sulfur wt%</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>Monoaromatics wt%</td>
<td>17.6</td>
<td></td>
</tr>
<tr>
<td>Diaromatics wt%</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Polyaromatics wt%</td>
<td>3.4</td>
<td></td>
</tr>
</tbody>
</table>

Using the data from Table 5.3, the corresponding boiling point curve of the
combined Feed is generated.

![Boiling Point Curve of the process Feed](image)

**Figure 5.1.** Boiling point curve of the process feed.
Using the boiling point curve of the Feed as a reference, a mixture of petroleum assays is created in ProII. Aromatic compounds are defined by boiling point: temperature ranges:

<table>
<thead>
<tr>
<th>Cutpoint set name</th>
<th>Temperature (°C)</th>
<th>Number of Pseudocomponents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono</td>
<td>220-270</td>
<td>3</td>
</tr>
<tr>
<td>Di</td>
<td>270-310</td>
<td>3</td>
</tr>
<tr>
<td>Poly</td>
<td>310-370</td>
<td>3</td>
</tr>
</tbody>
</table>

Using ProII, a mixture of simulated compounds is generated and is defined as a mixture of petroleum assays with assumed cutpoints that will be considered as Monoaromatics, Diaromatics and Polyaromatics. The objective is to generate a simulated feed with the same characteristics of the feed stream to the hydrotreating unit. The simulated monoaromatics, diaromatics and polyaromatics are defined as a set of pseudocomponents with the boiling point curves shown in Table 5.3.

<table>
<thead>
<tr>
<th>Cutpoint</th>
<th>Temperature (°C)</th>
<th>Number of Pseudocomponents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono</td>
<td>220-270</td>
<td>3</td>
</tr>
<tr>
<td>Di</td>
<td>270-310</td>
<td>3</td>
</tr>
<tr>
<td>Poly</td>
<td>310-370</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 5.3. Properties of the oil feed. API stands for American Petroleum Institute gravity and IBP for initial boiling point. Total density at D86

<table>
<thead>
<tr>
<th></th>
<th>Monoaromatics</th>
<th>Diaromatics</th>
<th>Polyaromatics</th>
<th>Naphtha</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total density</td>
<td>860.06</td>
<td>867.53</td>
<td>866.02</td>
<td>778</td>
</tr>
<tr>
<td>IBP</td>
<td>220</td>
<td>270</td>
<td>310</td>
<td>89</td>
</tr>
<tr>
<td>5%</td>
<td>227</td>
<td>274</td>
<td>312</td>
<td>101</td>
</tr>
<tr>
<td>10%</td>
<td>235</td>
<td>275</td>
<td>315</td>
<td>104</td>
</tr>
<tr>
<td>30%</td>
<td>240</td>
<td>276</td>
<td>327</td>
<td>114</td>
</tr>
<tr>
<td>50%</td>
<td>255</td>
<td>278</td>
<td>338</td>
<td>127</td>
</tr>
<tr>
<td>70%</td>
<td>265</td>
<td>291</td>
<td>350</td>
<td>142</td>
</tr>
<tr>
<td>90%</td>
<td>268</td>
<td>305</td>
<td>364</td>
<td>159</td>
</tr>
<tr>
<td>95%</td>
<td>269</td>
<td>308</td>
<td>368</td>
<td>164</td>
</tr>
<tr>
<td>End Point</td>
<td>270</td>
<td>310</td>
<td>370</td>
<td>180</td>
</tr>
<tr>
<td>Average molecular weight</td>
<td>194.75</td>
<td>230.29</td>
<td>286.73</td>
<td>113.59</td>
</tr>
<tr>
<td>Average molar volume</td>
<td>0.26</td>
<td>0.33</td>
<td>0.18</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The reconstructed feed using the lumps of aromatics is obtained (Figure 5.2). The pseudo-components are then assigned to their respective representative compound, which is used in the model.
Characterization of the bulk stream  To satisfy the mass balance, a bulk stream is created to represent the mixture of all unidentified compounds and do not play a role in the selected kinetic model. This stream is assumed to be comprised by components that are not identifiable in the analyses, yet, they contribute to the physical properties of a specific feedstock. The bulk stream can be simulated using pseudocomponents. In ProII, the Default Cutpoint set is used to generate the pseudocomponents in the feed that are not considered Monoaromatics, Diaromatics, nor Polyaromatics, but almost certainly having boiling points in common with the Feed pseudocomponents nonetheless.

Table 5.4. Pseudocomponents defined for the bulk using the Default Cutpoint in ProII. The minimum temperature for first component 37.7°C.

<table>
<thead>
<tr>
<th>Maximum Temperature (°C)</th>
<th>Number of Pseudocomponents</th>
</tr>
</thead>
<tbody>
<tr>
<td>426.67</td>
<td>28</td>
</tr>
<tr>
<td>648.89</td>
<td>8</td>
</tr>
<tr>
<td>871.11</td>
<td>4</td>
</tr>
</tbody>
</table>

5.1.3 Product properties

The product stream out of the reactor is diesel. However, naphtha is also generated from the saturation reactions taking place inside the reactor, for which, the BPC
is available as well. Similarly to the Feed, the following data are available for the Product stream:

**Table 5.5.** Properties of the Naphtha. API stands for American Petroleum Institute gravity and IBP for initial boiling point

<table>
<thead>
<tr>
<th>API @15.6°C</th>
<th>50.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP</td>
<td>D86  °C</td>
</tr>
<tr>
<td>5%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>10%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>30%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>50%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>70%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>90%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>95%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>End Point</td>
<td>D86  °C</td>
</tr>
<tr>
<td>Sulfur</td>
<td>wt ppm</td>
</tr>
</tbody>
</table>

**Table 5.6.** Boiling point curve of the Product from the hydrotreating unit available from the hydrotreating unit.

<table>
<thead>
<tr>
<th>API @ 15.6°C</th>
<th>37.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP</td>
<td>D86  °C</td>
</tr>
<tr>
<td>5%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>10%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>30%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>50%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>70%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>90%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>95%</td>
<td>D86  °C</td>
</tr>
<tr>
<td>End Point</td>
<td>D86  °C</td>
</tr>
<tr>
<td>Sulfur</td>
<td>wt ppm</td>
</tr>
<tr>
<td>Monoaromatics</td>
<td>wt%</td>
</tr>
<tr>
<td>Diaromatics</td>
<td>wt%</td>
</tr>
<tr>
<td>Polyaromatics</td>
<td>wt%</td>
</tr>
</tbody>
</table>

Using the data from Tables 5.5 and 5.5, the corresponding boiling point curve of the blend of Naphtha and Product is generated.
5.2 Implementation of the hydrotreating unit model solution.

At the inlet, the gas and liquid feeds are assumed to be in phase equilibrium. Industrial hydrotreating units have several catalytic beds with quench zones in between, however, in this Chapter the reactor is simulated as a single catalytic bed of 30 meters long without quench zones. This simplification from the real hydrotreating plant allows us to reduce the complexity of the model and study the extent of reactions at adiabatic conditions through a long bed. The hydrogen that would have been supplied in the quench zones has been added to the reactor gas feed instead. Therefore, the results of the simulation will differ from the actual industrial case; nevertheless, the behaviour of the system remains consistent. In addition, the reactor is long enough such that all reaction rates approach zero towards the reactor outlet.

In this Case study, the aromatics yielded from the reactions are assumed the same as the ones defined in the feed characterization initially. The naphthenes are considered to be in the naphtha pool. The amount of hydrogen in the feed is approximately 5 times more than that stoichiometrically required. It is common practice to use a significant hydrogen excess in order to ensure sufficient hydrogen available at the catalyst surface, minimize formation of coke and facilitate removal of the generated heat. The inlet conditions are given in Table 5.7. The stoichiometric coefficients for the reactions (5.4) to (5.6) are: \( a = 3, b = 1, c = 1, d = 2, e = 1, f = 1, g = 2, h = 1, i = 1 \).
Table 5.7. Process input parameters and specifications. Values marked with $^a$ are taken from Pro/II

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T, Gas inlet</td>
<td>330 °C</td>
</tr>
<tr>
<td>T, Liquid inlet</td>
<td>330 °C</td>
</tr>
<tr>
<td>T, Solid inlet</td>
<td>330 °C</td>
</tr>
<tr>
<td>$a_s, a_L$</td>
<td>3540 m$^2$/m$^3$</td>
</tr>
<tr>
<td>$\rho_{cat}$</td>
<td>875 kg/m$^3$</td>
</tr>
<tr>
<td>P</td>
<td>8.4 MPa</td>
</tr>
<tr>
<td>Inlet gas flowrate</td>
<td>$76 \times 10^4$ kg/h</td>
</tr>
<tr>
<td>Inlet liquid flowrate</td>
<td>$237 \times 10^4$ kg/h</td>
</tr>
<tr>
<td>$C_{pG}^a$</td>
<td>0.917 kcal/kg °C</td>
</tr>
<tr>
<td>$C_{pL}^a$</td>
<td>0.722 kcal/kg °C</td>
</tr>
</tbody>
</table>

Inlet partial pressures (Pa)

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>$7.12 \times 10^6$ Pa</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>$4.8 \times 10^2$ Pa</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>29.8 Pa</td>
</tr>
<tr>
<td>BT</td>
<td>$2.96 \times 10^3$ Pa</td>
</tr>
<tr>
<td>DBT</td>
<td>$5.38 \times 10^2$ Pa</td>
</tr>
</tbody>
</table>

Inlet concentration of bulk liquid, kgmol/m$^3$

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>$3.37 \times 10^{-1}$ kgmol/m$^3$</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>$2.25 \times 10^{-5}$ kgmol/m$^3$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>$1.07 \times 10^{-1}$ kgmol/m$^3$</td>
</tr>
<tr>
<td>BT</td>
<td>$5.21 \times 10^{-3}$ kgmol/m$^3$</td>
</tr>
<tr>
<td>DBT</td>
<td>$5.07 \times 10^{-2}$ kgmol/m$^3$</td>
</tr>
<tr>
<td>N</td>
<td>$1.14 \times 10^{-3}$ kgmol/m$^3$</td>
</tr>
<tr>
<td>Monoaromatics</td>
<td>$7.88 \times 10^{-1}$ kgmol/m$^3$</td>
</tr>
<tr>
<td>Diaromatics</td>
<td>$6.12 \times 10^{-1}$ kgmol/m$^3$</td>
</tr>
<tr>
<td>Polyaromatics</td>
<td>$1.27 \times 10^{-1}$ kgmol/m$^3$</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>$8.68 \times 10^{-1}$ kgmol/m$^3$</td>
</tr>
</tbody>
</table>

Henry constants (Pa m$^3$/kgmol)

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{H_2}V_{H_2}$</td>
<td>$1.81 \times 10^7$ Pa m$^3$/kgmol</td>
</tr>
<tr>
<td>$H_{H_2S}V_{H_2S}$</td>
<td>$3.61 \times 10^7$ Pa m$^3$/kgmol</td>
</tr>
<tr>
<td>$H_{NH_3}V_{NH_3}$</td>
<td>$3.61 \times 10^7$ Pa m$^3$/kgmol</td>
</tr>
<tr>
<td>$H_{BT}V_{BT}$</td>
<td>$5.69 \times 10^5$ Pa m$^3$/kgmol</td>
</tr>
<tr>
<td>$H_{DBT}V_{DBT}$</td>
<td>$1.06 \times 10^5$ Pa m$^3$/kgmol</td>
</tr>
</tbody>
</table>

The constants for the rate of reaction expressions (5.13) - (5.17) are given in Table 5.8 and 5.9. It is worth pointing out that the kinetic constants are taken from different sources [116][23][25][4].
5.2. Implementation of the hydrotreating unit model solution

Table 5.9. Heats of reaction for the reactions in HDT process given in equations (5.4) to (5.6).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H_R$ (J/mol$H_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDS</td>
<td>-60 400 [23]</td>
</tr>
<tr>
<td>HDN</td>
<td>-64 850 [116]</td>
</tr>
<tr>
<td>HDA$_{\text{mono}}$</td>
<td>-100 000 [5]</td>
</tr>
<tr>
<td>HDA$_{\text{di}}$</td>
<td>-62 000 [5]</td>
</tr>
<tr>
<td>HDA$_{\text{poly}}$</td>
<td>-32 000 [5]</td>
</tr>
</tbody>
</table>

Table 5.8. Kinetic parameters, equilibrium constants and exponents for pressure corrections for hydrotreating reactions in equations (5.13)-(5.18). Data reported by $^a$[25] and $^b$[4].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDS</td>
<td>$k_{\text{ads}, \text{H}_2\text{S}}$=50,000 $^a$</td>
</tr>
<tr>
<td></td>
<td>$k_{\text{HDS}}$=2.50\times10^{12}\exp(-19384/T)$^a$</td>
</tr>
<tr>
<td>HDN</td>
<td>$k_{\text{HDN}}$=110\exp(-105000/(RT))</td>
</tr>
<tr>
<td>HDA$_{\text{mono}}$</td>
<td>$k_{f,\text{mono}}$=604\exp(-12414/T)$^a$</td>
</tr>
<tr>
<td></td>
<td>$K_{\text{mono}}$=7.49E-17\exp(24070/T)$^b$</td>
</tr>
<tr>
<td></td>
<td>$n_{\text{mono}}$=1$^b$</td>
</tr>
<tr>
<td>HDA$_{\text{di}}$</td>
<td>$k_{f,\text{di}}$=850\exp(-12140/T)$^a$</td>
</tr>
<tr>
<td></td>
<td>$K_{\text{di}}$=5.56E-11\exp(15741/T)$^b$</td>
</tr>
<tr>
<td></td>
<td>$n_{\text{di}}$=0.5$^b$</td>
</tr>
<tr>
<td>HDA$_{\text{poly}}$</td>
<td>$k_{f,\text{poly}}$=2.66\times10^5\exp(-15170/T)$^a$</td>
</tr>
<tr>
<td></td>
<td>$K_{\text{poly}}$=1.05E-5\exp(8308/T)$^b$</td>
</tr>
<tr>
<td></td>
<td>$n_{\text{poly}}$=0.5$^b$</td>
</tr>
</tbody>
</table>

5.2.1 Model evaluation

In this section, the model equations are solved using the numerical solution finite differences scheme with 100 nodes, described in Chapter 4. The axial profiles for $H_2$, $H_2S$, $\text{NH}_3$, BT, DBT, N and the aromatics, as well as temperature profiles are obtained. In this context, the sulfur conversion ($x_{\text{Ar-S}}$) is defined as the conversion of total organic-sulfur compounds, BT and DBT combined, considering both the gas and liquid phases and as a function of the reactor length. Let the molar flowrates of the mixture of BT and DBT be $F_{\text{Ar-S}}^{\text{Total}}$, then the sulfur conversion is calculated as follows:

$$x_{\text{Ar-S}}(\text{Length}) = \frac{F_{\text{Ar-S,inlet}}^{\text{Total}} - F_{\text{Ar-S}}^{\text{Total}}(\text{Length})}{F_{\text{Ar-S,inlet}}^{\text{Total}}} \quad (5.19)$$

The simulation is performed employing pseudocomponents. The used kinetic expressions are taken from literature [23][84][114][25]. The steady state solution of the model for the case study provides the profiles of the components across the length of the reactor, as shown in Figure 5.4. The hydrogen profiles in the gas phase and liquid phase are shown in Figure 5.4A. The concentration of dissolved hydrogen decays significantly within the first meters of the reactor where all the reactions take place simultaneously as soon as the feed gets in contact with the catalyst bed. This is also reflected in the temperature increase shown in Figure
5.4H and the significant increase in concentration of $\text{H}_2\text{S}$ (Figure 5.4B). However, as the rates of reactions slow down, an increase in the hydrogen concentration in the liquid phase is observed.

The excess of hydrogen in the gas phase acts as a driving force that favors the transport of the hydrogen into the liquid by mass transfer. Therefore, a consistent drop in the concentration of hydrogen in the gas phase is observed towards the outlet. Figure 5.4B shows the profiles of $\text{H}_2\text{S}$ in the gas and liquid phases, where the $\text{H}_2\text{S}$ is produced as soon as the feed gets in contact with the catalyst bed and it is then transported to the gas phase. The rapid conversion of BT and DBT (Figures 5.4C and 5.4D) results in an equally rapid production of $\text{H}_2\text{S}$ at a higher rate than the mass transfer in the initial part of the bed, which explains the peak in the dissolved $\text{H}_2\text{S}$ concentration.

The $\text{H}_2\text{S}$ concentration in the liquid stabilizes after 10 to 15 meters of the reactor, meaning that the rate at which it is produced equals the rate it is transported to the gas phase. Figure 5.4E shows the concentration of $\text{NH}_3$ in the gas phase and the concentration of organic nitrogen in the liquid phase. It can be observed that the organic-nitrogen is removed from the liquid phase throughout the length of the reactor. The profiles of BT are shown in Figure 5.4C, where one can observe that the easy-to-desulfurize organic sulfur compounds react predominantly in the first 2 to 3 meters. However, the concentration decays throughout the reactor, meaning that the reaction rate is slower towards the outlet as the reactants are depleted. Whilst both BT and DBT profiles show that the HDS reaction occurs predominantly within the first 3 to 5 meters of the reactor, it is necessary to reach very low concentrations in the liquid phase to fulfil diesel specifications, e.g., overall sulfur content < 10 wt ppm in the liquid. Figure 5.4F shows the profile of the organic sulfur content in the liquid phase, in which 10 wt ppm is reached around 5 meters of the reactor.

The profiles of mono-, di-, and polyaromatics in the liquid are shown in Figure 5.4G. The monoaromatics profile is constant in the first meters due to an equal conversion of diaromatics compared to the conversion of monoaromatics that lead to an increase in the concentration of naphthenes. For the rest of the reactor, HDA reactions continues at a much slower rate.
5.2. Implementation of the hydrotreating unit model solution.

Figure 5.4. Concentration profiles of H$_2$, H$_2$S, BT, DBT, N (A)-(E). Organic sulfur content across the length of the reactor (F) and aromatic compounds across the length of the reactor (G). and Temperature profile of gas, liquid and solid phases (H) at steady-state.
Figure 5.4H shows the temperature profiles for gas, liquid and solid phases. The solid phase is assumed completely wetted, therefore, the heat transfer rate between solid and liquid is high, generating almost identical temperature profiles for solid and liquid phases. The temperature of the gas is clearly lower than the other two and responds slower to the generated heat from the reactions. The heat transfer resistance between the liquid and the gas phase results in a maximum temperature difference of just above 50°C at these conditions. However, the temperatures of all phases converge towards the same outlet value as the reaction rates approach zero. Therefore, the heat transfer catches up to equal out the difference, which implies that a thermal equilibrium is reached.

The results of the model are evaluated by comparison to the actual plant results. However, it is important to note that the results can only be compared qualitatively as the quench zones are not included in the model, where all hydrogen is introduced to the system at the reactor inlet.

The analysis of feed and product streams is displayed in Table 5.10, which shows the concentration in weight percent (wt%) of the key components in the feed and the product to compare the model and the plant. It is evident that the model is not able to accurately predict the concentration of all the aromatics in the product.

The conversion of the polyaromatics is clearly under predicted and the concentration of diaromatics is also too high while that of the monoaromatics is very close to the data. The conversion of organic sulfur is slightly overestimated by the model. All in all, the model behaves as expected and a better fit can hardly be expected from a purely predictive model where all the reaction and transport coefficients are taken from literature [25][23]. It is known that the kinetics expressions from the literature in general do not predict adequately the high conversion in the HDA reactions from the plant data.

<table>
<thead>
<tr>
<th>Table 5.10. Concentration of aromatics in the feed and the product of the real plant and the simulation.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feed</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Sulfur wt%</td>
</tr>
<tr>
<td>Mono wt%</td>
</tr>
<tr>
<td>Di wt%</td>
</tr>
<tr>
<td>Poly wt%</td>
</tr>
</tbody>
</table>

The boiling point curve of the product from the model and the actual boiling point curve of the real product is displayed in Figure 7. The main difference between the model and actual distillation curves is observed in the region of 0 to 40% distilled. The model predicts a higher concentration of more volatile compounds.
This difference can be attributed to the use of pseudo-components to represent the naphthenes generated from the monoaromatics reaction.

 Figure 5.5. Comparison of the boiling point curve of the original blend of product and the boiling point curve for the product obtained from the model.

The results of the simulations follow the trend of previous works [23][4] in which three aromatic lumps, i.e., polyaromatics, diaromatics and monoaromatics, are converted. However, these studies were used to account for the vaporization of aromatics in models of hydrotreating reactors and a detailed study of the aromatics concentration of the product is missing. The prediction of the concentration of aromatics throughout the reactor is determined by the selection of the HDA kinetic model. Hence, with the available kinetic model, it is challenging to reproduce the behavior of the real large-scale plant. In addition, there is a lack of experimental kinetic data of hydrogenation of complex mixtures of aromatics in literature. Therefore, a sensitivity analysis on kinetic parameters on the model is performed in Section 5.5.

5.2.2 Dynamic response

In this section, the dynamic response of the model is evaluated. In practice, the HDT unit might be subject to changes in the feed. Depending on the source of the feedstock, the concentration of total sulfur compounds will change accordingly. Hence, in this section, a change in the concentration in the difficult-to-desulfurize sulfur compounds is simulated to study the dynamic behavior of the proposed model.
At time $t = 0$, a change in the concentration of difficult-to-desulfurize sulfur compounds in the liquid phase is implemented. Figure 5.6 shows the transient concentration profiles of DBT in the liquid phase at nine specific lengths down the reactor. These profiles display how the change in the inlet conditions propagate down through the reactor and show both the delay in the response of the system towards the outlet of the reactor and how the step change is being smoothed on the way. It is seen that it takes almost an hour before a steady outlet conditions are obtained for the sulfur content in the product.

![Figure 5.6. Dynamic profiles of concentration of DBT with a change of +10% in the feed at time t=0 at different positions in the reactor.](image)

### 5.3 Comparison of a variable and constant axial gas velocity.

Considering the large excess of hydrogen to the reactor, a constant gas velocity has often been assumed in the literature [84]. However, the gaseous species are consumed at different stoichiometric ratio than they are produced. Furthermore, changes in temperature and pressure along the reactor influence the gas velocity and should be taken into account. This is most conveniently done by using molar flow rates as dependent variables rather than concentrations and applying an equation of state to account for the specific gas volume. Therefore, in this model implementation, we have evaluated both, a constant axial gas velocity, equal to the inlet value, as well as variable axial gas velocity as accounted for in equation (5.7). The latter implementation is the one used in the case study simulation displayed in
5.3. Comparison of a variable and constant axial gas velocity.

Figure 5.4. The impact of a constant linear velocity is evaluated and the results are displayed in Table 5.11.

Table 5.11. Error of the mass balance closure due to the numerical solution of the model with variable gas velocity and constant gas velocity

<table>
<thead>
<tr>
<th>Mass Balance Error</th>
<th>Constant $u_G$</th>
<th>Variable $u_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No reaction</td>
<td>9.3×10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>HDS + HDN Reactions</td>
<td>0.172%</td>
<td>0.169%</td>
</tr>
<tr>
<td>HDS + HDN + HDA reactions</td>
<td>4.08%</td>
<td>4.03%</td>
</tr>
</tbody>
</table>

In this work, the simulation has been tested in order to identify the error of the numerical solution. The error in the numerical solution is performed in the overall mass balance and is defined as:

$$\text{Error} = \frac{\text{mass}_{\text{in}} - \text{mass}_{\text{out}}}{\text{mass}_{\text{in}}}$$  \hspace{1cm} (5.20)

The numerical solution is performed first with no reactions, i.e., only the gas-liquid equilibrium is achieved. Since the incoming species are already in gas-liquid equilibrium, the error with no reaction is 9.3×10$^{-4}$%, which can be considered as the simulation accuracy using the proposed finite difference scheme. Then, the solution of the model considering only HDS and HDN reactions, as well as including all the reactions for the assumption of both constant and variable gas velocity. The error of the different solutions is compared in Table 5.11. It can be observed that the error increases when HDS and HDN are taken into account compared to the case with no reactions. One source of error can be attributed to the use of correlations and parameters taken from different sources for similar but not identical cases available in literature. Finally, when the HDA reactions are included in the solution the error in the mass balance closure increased up to 4%.

The considerable growth in the error is due to the definition of the pseudo-components. The pseudo-components that are obtained from the process simulator have characteristic properties such as molecular weights (Table 5.3) that do not necessarily reflect the aromatic hydrogenation path similar to the example in Section 5.1. Therefore, the use of pseudocomponents generates an error that is significantly larger than the error of the numerical solution of the implementation of a constant gas velocity in contrast with a variable gas velocity. The use of pseudocomponents is, however, the practical approach of simulating the properties of a real feed. The use of a variable gas velocity might be critical for other applications where the operation regime is close to stoichiometric values such as laboratory and kinetic studies.
At large-scale operation, the assumption of a constant gas velocity can be useful since the gas is already in significant excess; however, it is conceptually wrong and including a variable gas velocity equation does not increase the complexity of the model itself. Therefore, a variable axial gas velocity will be used in this work.

5.4 Sensitivity analysis on the model parameters

In industry, temperature control of trickle-bed reactors is crucial, not only for safety reasons, but also to ensure the quality of the products. There are many variables or physical parameters involved in the process that may affect the overall performance. Therefore, it is important to understand which are the key process variables and parameters which are most influential and which do not change the performance significantly. However, predictions using simulations are an affordable way to identify effectively the most critical variables and parameters in a process. In the case of hydrotreating, reactor temperature and sulfur content in the liquid product are the key output variables of interest.

Publicly available HDA kinetic models reported in literature do not adequately predict the plant performance in this work. Therefore, it is important to study the effect of the selection of the kinetic parameters used in HDA reactions including the effect on the HDS reaction scheme.

Sensitivity analyses are advantageous to identify the most influential parameters in complex systems on given process outputs. The Morris screening method [88] is generally used to perform computational experiments to determine which process variables and parameters may be considered to have effects on specific model outputs that are (a) negligible, (b) linear and additive, and (c) nonlinear or involved in interactions with other parameters. This method is often used as an efficient screening method with low computational requirements to identify the most influential parameters of a model. From a practical standpoint, it allows to make a visual representation of the importance of particular values in context of the variable of interest. In this work, the model analysis includes the model parameters, which are referred to as factors. The method relies on estimating the distribution of the elementary effects (EE) of each factor on the \( k^{th} \) model output called \( EE_{jk} \). Let us take a model of the form:

\[
\frac{dx}{dt} = f(x, \theta, u, t); \quad x(0) = x_0
\]

\[
y = g(x, \theta, u, t)
\]
The elementary effect of the $i_{th}$ input factor, $\theta_i$, in a point $\theta_0$ (input space):

$$EE_i^0 = \frac{y(\theta_0^0, \theta_0^1, \theta_0^2, \theta_0^i + \Delta, \ldots \theta_0^m) - y(\theta_0)}{\Delta}$$

Morris suggests calculations of $EE_i$ at randomly selected points in the input space (m-dimensional p-level grid). To this end, Morris performs $EE_i$ calculations $r$ times following an efficient randomized sampling scheme [88].

$$EE_i^r = \frac{y(\theta_r^0, \theta_r^1, \theta_r^2, \theta_r^i + \Delta, \ldots \theta_r^m) - y(\theta_r)}{\Delta}$$

The data analysis is based on examination of the finite distributions of elementary effects. From each $\theta_i$, a random sample of size $r = 8$ has been collected.

First, a range for each parameter is specified. Then the sampling number is defined (e.g. 50, 100, etc.) and samples are drawn from the parameter space using an appropriate sampling technique. Two of the most common sampling techniques are random sampling and Latin Hypercube sampling. In this work, Latin Hypercube sampling is used. The output from each step is a sampling matrix with $N$ number of samples and $m$ number of parameters. Then the model is evaluated for each of the elements in the sample matrix. Finally, the parameters are ranked according to the mean $\mu_i$ of the output and the standard deviation $\sigma_i$ [88].

In this trickle-bed reactor model, the selection of the kinetic parameters of HDA reactions has a great impact in the reaction rates, which in turn influences the prediction of the concentration profiles. Similarly, the heat of reaction of HDS, HDN and HDA reactions, as well as the mass flows of gas and liquid, influence the temperature rise and therefore also the reaction rates. These are therefore considered as the parameters of interest in the sensitivity analysis with a sampling range shown in Table 5.12. Particularly, for the value of $\Delta H_{pol}$, there is considerably uncertainty. In this case study, a value reported for similar hydrogenation systems of $\Delta H_{pol} = -32kJ/molH_2$ was used [23][4](see Table 5.9). However, this value is significantly lower compared to the values for common polyaromatic compounds. For instance, in the reaction scheme given in the example in Section 5.1, the value of $\Delta H_{pol}$ for phenanthrene is $\Delta H_{pol} = -60kJ/molH_2$. Therefore, the sampling of the value of $\Delta H_{pol}$ is performed in the range of $-32kJ/molH_2$ to $-60kJ/molH_2$.

The value of the pressure corrections $n_{mono/di/poly}$ is an important parameter in the model performance because the kinetic models are usually obtained from experimental data at controlled conditions that might not translate directly to a large-scale process. In addition, the pre exponential factor $A$ of the HDA forward reactions are also subject to a specific case and catalyst used, hence, included in the sensitivity analysis. From Table 5.8, these were found to be $A_{mono} = 604m^3/kgs$, $A_{di} = 850m^3/kgs$, $A_{poly} = 2.66 \times 10^5m^3/kgs$. 


Table 5.12. Model parameters considered in the sensitivity analysis and range of sampling.

<table>
<thead>
<tr>
<th>Model parameter</th>
<th>Range</th>
<th>Model parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{in}$</td>
<td>±20%</td>
<td>$n_{mono}$</td>
<td>±50%</td>
</tr>
<tr>
<td>$m_G$</td>
<td>±10%</td>
<td>$n_{di}$</td>
<td>±50%</td>
</tr>
<tr>
<td>$m_L$</td>
<td>±10%</td>
<td>$n_{poly}$</td>
<td>±50%</td>
</tr>
<tr>
<td>$\Delta H_{mono}$</td>
<td>±5%</td>
<td>$A_{mono}$</td>
<td>±25%</td>
</tr>
<tr>
<td>$\Delta H_{di}$</td>
<td>±5%</td>
<td>$A_{di}$</td>
<td>±25%</td>
</tr>
<tr>
<td>$\Delta H_{poly}$</td>
<td>[-32, -60] kJ/mol</td>
<td>$A_{poly}$</td>
<td>±25%</td>
</tr>
</tbody>
</table>

The results of the Morris analysis are shown in Figures 5.7 to 5.11. According to Morris, if a model parameter (+) lies inside the wedge (∨), then, it indicates that its effect on the variable of interest [88], i.e. outlet temperature, sulfur concentration, etc., is negligible. On the contrary, if the model parameter lies outside the wedge, it has a significant effect on variable of interest. The Morris screening method provides an overview of the most significant parameters with respect to the following variables: (1) Outlet temperature of the reactor (Figure 5.7), (2) organic-sulfur concentration in the liquid phase (Figure 5.8), (3) Concentration of monoaromatics in the liquid phase (Figure 5.9), (4) Concentration of di-aromatics (Figure 5.10) and (5) Concentration of polyaromatics (Figure 5.11). In order to make the plots clear, only the most significant parameters (+) are labeled.

In Figure 5.7, the Morris sensitivity analysis reveals that the critical model parameter on the outlet reactor temperature given by $T_L$, is the inlet temperature ($T_{in}$) since it is significantly outside the wedge because the set of hydrotreating reactions are highly temperature dependent and release a significant amount of energy, explaining why the wedge looks like a single line. However, a closer look reveals that $\Delta H_{mono}$, $\Delta H_{di}$ and $n_{mono}$ also have a significant effect. The reaction path of monoaromatic compounds reacting to produce naphthenes has the highest $\Delta H$, therefore a higher contribution to the temperature rise. In addition, $n_{mono}$ affects directly the hydrogen pressure in the expression of the reaction rate of monoaromatics. At higher hydrogen pressures, the hydrogenation to naphthenes is favored. On the other hand, the value of $\Delta H_{di}$ contributes to the temperature rise because the polyaromatics generate diaromatics. These diaromatics generate monoaromatics and subsequently naphthenes increasing the temperature.

The Morris screening method reveals that, the organic sulfur concentration in the liquid phase is not sensitive to any of the considered parameters. The inlet temperature plays an important role in the outlet concentration of organic sulfur because HDS reaction is exothermic. However, the reactor is long enough to ensure a low-sulfur concentration in the liquid at the outlet regardless of variations in
concentration of BT and DBT-type compounds in the feed. Because of this, all of the parameters included in the Morris screening method remain inside the wedge.

Figure 5.9 shows the sensitivity analysis of the outlet value of the concentration of monoaromatics in the liquid phase. The Morris screening method reveals that the value of $T_{in}$ and $n_{mono}$ are significant parameters as expected. However, the screening method portraits $n_{mono}$ as a significant parameter to the concentration of monoaromatics in the outlet. This can be explained by the relationship between the excess of hydrogen and the saturation of the aromatic rings in the monoaromatics that effects the equilibrium composition. When the equilibrium of monoaromatics is shifted, it has an effect in the equilibrium of di- and polyaromatics. In addition, the outlet concentration of diaromatics is sensitive to the value of $\Delta H_{di}$ and $n_{di}$ as expected (Figure 5.10). It is important to note that $T_{in}$ is not an influential parameter to the outlet concentrations of aromatics. If one observes Figure 5.4H, the maximum temperature is reached within the first 3m of the reactor, which coincides with reaching the equilibrium concentrations of aromatics.

### 5.5 Model performance analysis

In this section, the performance of the prediction acquired from the model solution is studied by evaluating the effect of the most significant parameters documented in Section 5.5. The focus is on the value of the heat of HDA reaction of polyaromatics, the effect of the inlet temperature, the gas flowrate and the values of $n_{mono/di/poly}$. 

![Figure 5.7](image)

**Figure 5.7.** Morris screening method results (1). The most significant parameters to the temperature of the liquid ($T_L$) at the outlet of the reactor. The labeled parameters outside the wedge are the most significant.
Figure 5.8. Morris screening method results (2). The parameters that have a significant effect on the concentration of organic-sulfur in the liquid phase at the outlet are the labelled parameters outside the wedge.

Figure 5.9. Morris screening method results (3). The most significant parameters to the concentration of monoaromatics in the liquid phase at the outlet are the labelled parameters outside the wedge.
Figure 5.10. Morris screening method results (4). The most significant parameters to the concentration of diaromatics in the liquid phase at the outlet are the labeled parameters outside the wedge.

Figure 5.11. Morris screening method results (5). The most significant parameters to the concentration of monoaromatics in the liquid phase at the outlet are the labeled parameters outside the wedge.
Chapter 5. Case Study: Part I

Table 5.13. Concentration of aromatics in the feed and the product of the real plant and the simulation.

<table>
<thead>
<tr>
<th></th>
<th>Product$_{(\text{Plant})}$</th>
<th>Product$_{(\text{Model})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{\text{in}}+20^\circ\text{C}$</td>
<td>$T_{\text{in}}=330^\circ\text{C} (\text{Case Study})$</td>
</tr>
<tr>
<td>Sulfur wppm</td>
<td>3.4</td>
<td>0.12</td>
</tr>
<tr>
<td>Mono wt%</td>
<td>18.6</td>
<td>15.6</td>
</tr>
<tr>
<td>Di wt%</td>
<td>3.0</td>
<td>14.9</td>
</tr>
<tr>
<td>Poly wt%</td>
<td>0.4</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Effect of inlet temperature  In this section, results of the influence of the inlet temperature on the outlet concentrations of sulfur and aromatics is evaluated in three cases: 1) Inlet temperature of the case study $T_{\text{in}}=330^\circ\text{C}$, 2) $T_{\text{in}}+20^\circ\text{C}$ and 3) $T_{\text{in}}-20^\circ\text{C}$ and the results are summarized in Table 5.13. The results show that at higher inlet temperature, the sulfur content at the outlet of the reactor is the same as the case study. However, the concentrations of aromatics changes depending on the value of $T_{\text{in}}$. For instance, at higher $T_{\text{in}}$, the monoaromatics produce more naphthenes and at the same time, diaromatics produce less monoaromatics. In Figure 5.12A, the concentration profiles of aromatics show that the equilibrium of polyaromatics is only slightly affected by a higher value of the inlet temperature. However, the saturation reaction of monoaromatics to naphthenes is clearly promoted.

A rather small difference in the sulfur concentration profile is also observed (Figure 14B). Therefore, lower values of inlet temperature have less influence in the equilibrium of aromatics and in the saturation reactions in general with the current kinetic model.

Sensitivity analysis of the correction for pressure  The Morris screening method suggests that the value of the pressure correction has a significant impact on the concentration profiles of aromatics. In this section, the sensitivity to the value of the pressure correction in equations (5.15)(5.17) on the outlet stream of the model simulation is presented. Since the kinetic model found in the literature predicts a lower conversion of aromatics compared to actual plant data, the analysis is performed with two cases: (a) the main case study ($n_{\text{mono}}=1, n_{\text{di}}=0.5$ and $n_{\text{poly}}=0.5$), and (b) the solution of the model with the following values: $n_{\text{mono}}=2, n_{\text{di}}=1$ and $n_{\text{poly}}=1$. The results of the simulations are summarized in Table 5.14.

The results of the simulations show that the value of the correction of pressure affects the outlet concentration of aromatics. This is explained by the structure of the rate expressions. In equations (5.15)(5.17), the pressure correction is related to the availability of hydrogen in terms of partial pressure. Therefore, a higher
Figure 5.12. Sensitivity to inlet temperature. Simulations of (A) Concentration profiles of aromatics throughout the reactor with a variation of ±20°C in the inlet temperature, (B) Sulfur concentration profiles throughout the reactor with a variation of ±20°C in the inlet temperature.
Table 5.14. Concentration of aromatics in the feed and the product of the real plant and the simulation.

<table>
<thead>
<tr>
<th></th>
<th>Product (Plant)</th>
<th>Product (Model)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Case (a)</td>
<td>Case (b)</td>
</tr>
<tr>
<td></td>
<td>Case (study)</td>
<td></td>
</tr>
<tr>
<td>n\text{mono}</td>
<td>n_{\text{mono}} = 1, n_{\text{di}} = 0.5, n_{\text{poly}} = 0.5</td>
<td>n_{\text{mono}} = 2, n_{\text{di}} = 1, n_{\text{poly}} = 1</td>
</tr>
<tr>
<td>Sulfur wppm</td>
<td>3.4</td>
<td>0.12</td>
</tr>
<tr>
<td>Mono wt%</td>
<td>18.6</td>
<td>18.9</td>
</tr>
<tr>
<td>Di wt%</td>
<td>3.0</td>
<td>12.1</td>
</tr>
<tr>
<td>Poly wt%</td>
<td>0.4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

value of the pressure correction affects the rate of reaction that favours the forward reactions. This can be observed in Figure 5.13A. In Case (b), the concentration of poly- and di- is lower at the outlet compared to Case (a), this causes an increase in concentration of mono-. However, the concentration of naphthenes is similar in both cases. Even though the kinetic model falls short to represent the plant data in terms of mono-, di- and poly-, selecting a higher value of pressure correction brings the results of the simulation closer to the real data. This is also reflected in the temperature which is considerably higher for case b, because more heat is released (Figure 5.13B). The effect is propagated to the HDS reaction, which is promoted (Figure 5.13C) across the reactor.

**Inlet gas flowrate** In this section, the model is evaluated using 1) the standard value of inlet gas flowrate ($m_G$) which corresponds to 5 times the stoichiometric amount of hydrogen, 2) an intermediate value of 4.0 times the stoichiometric hydrogen and 3) 3.5 the stoichiometric hydrogen, which is a suggested lowest value to use in practice. The importance of this investigation lies on the fact that the gas is mainly composed of $H_2$, which reacts with the liquid oil to reduce the concentration of undesired compounds such as sulfur and nitrogen. In industry, excess gas is used to ensure the required sulfur removal from the petroleum feedstock without catalyst deactivation. The recovery of unreacted hydrogen is expensive and a large recycle gas flow requires a high compression work and large equipment volumes; therefore, we investigate the influence of the hydrogen flow. Nevertheless, the model performance evaluation can be an aid for the investigation of the behaviour of the system under different inlet-gas flowrate conditions. The results of the simulations for the three different flowrates mentioned earlier are summarized in Table 5.15. The value of the $H_2$/oil ratio has an effect in the organic sulfur concentration as expected. At higher $H_2$/oil ratio, the concentration of sulfur is affected predominantly after 5 to 6 meters of the reactor (Figure 5.14). On the other hand, the behaviour of the aromatics is affected to a lesser degree. However, the results are still far from
Figure 5.13. Sensitivity to pressure correction. (A) Concentration profiles of aromatics for case (a) and case (b) across the length of the reactor. (B) Organic sulfur content in the liquid phase across the length of the reactor. (C) Temperature profiles of Cases (a) and (b).
Table 5.15. Concentration of aromatics in the feed and the product of the real plant and the simulation.

<table>
<thead>
<tr>
<th></th>
<th>Product_{Plant}</th>
<th>Product_{Model}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.5 (H_2) excess</td>
<td>4.0 (H_2) excess</td>
</tr>
<tr>
<td>Sulfur wppm</td>
<td>3.4</td>
<td>0.21</td>
</tr>
<tr>
<td>Mono wt%</td>
<td>18.6</td>
<td>19.4</td>
</tr>
<tr>
<td>Di wt%</td>
<td>3.0</td>
<td>12.6</td>
</tr>
<tr>
<td>Poly wt%</td>
<td>0.4</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Figure 5.14. Sulfur content in the liquid phase across the length of the reactor (ppm) with three different \(H_2\)/oil ratios: 1) 3.5 times the stoichiometric \(H_2\), 2) 4.0 times the stoichiometric \(H_2\) and 3) 5.0 times the stoichiometric \(H_2\) (Case study).

Effect of heat of reaction of aromatics

In this subsection, the effect of the value \(\Delta H_{poly}\) is investigated. The study consists of the model evaluation using 1) the standard value of \(\Delta H_{poly}\) (-30 kJ/mol\(H_2\)) shown in Table 5.10 for the case study, 2) A value of \(\Delta H_{poly} = -60\) kJ/mol\(H_2\), which is the expected value in commonly used polyaromatics in the hydrotreating reaction path, and 3) and intermediate value of \(\Delta H_{poly} = -45\) kJ/mol\(H_2\). The model is solved for each case and the results of the concentrations of aromatics in the liquid phase are summarized in Table 5.16.

It is evident from Table 5.16 that the value of \(\Delta H_{poly}\) has a big impact on the concentrations of polyaromatics. A higher value of \(\Delta H_{poly}\) causes a significant shift in the equilibrium, promoting the hydrogenation of the polyaromatics (forward reaction in equation (5.17)). The predicted concentration of sulfur in the outlet remains
Table 5.16. Concentration of aromatics in the feed and the product of the real plant and the simulation.

<table>
<thead>
<tr>
<th></th>
<th>Product (Plant)</th>
<th>Product (Model)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_{poly} = -30 \text{ kJ/mol} \text{H}_2$ (case study)</td>
<td>$\Delta H_{poly} = -45 \text{ kJ/mol} \text{H}_2$</td>
</tr>
<tr>
<td>Sulfur wppm</td>
<td>3.4</td>
<td>0.14</td>
</tr>
<tr>
<td>Mono wt%</td>
<td>18.6</td>
<td>18.9</td>
</tr>
<tr>
<td>Di wt%</td>
<td>3.0</td>
<td>12.1</td>
</tr>
<tr>
<td>Poly wt%</td>
<td>0.4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

slightly lower (Figure 5.15A) compared to the industrial case. On the other hand, the temperature profiles with higher values of $\Delta H_{poly}$ remain consistent and higher than the temperature profile of the case study, as expected (Figure 5.15B). This explains the higher concentration of di- and consequently monoaromatics (Figure 5.15C). The slightly smaller value compared to the case study is explained by the higher temperature caused by the saturation of di- and monoaromatics. However, with the available kinetic model, the concentration of polyaromatics decreases to unrealistic levels. Therefore, in order to achieve accurate predictions of concentrations of aromatics in the product, the value of $\Delta H_{poly}$ and the kinetic model must be addressed carefully.

Even though the simulations follow the trend of previous works, it is evident that more elaborate qualitative studies on the kinetics of the aromatics are missing in literature; hence, the predictive simulation is not able to reflect the actual HDA conversions of an industrial reactor. Experimental data are required to develop kinetics models that reflect more accurately the characteristics of the products of the hydrotreating unit. In addition to the kinetic studies and for further investigations, accounting for vaporization of the pseudo-components and quench zones would likely be important steps to obtain predictions closer to the industrial reality.

5.5.1 Case study: conclusions and discussion.

In this chapter, a model for a trickle-bed reactor has been developed and its application is demonstrated on an industrial hydrotreating unit using a practical definition of lumps of aromatic groups in terms of pseudo-components with their own boiling point curves. Two different modelling approaches (i) assuming constant gas velocity and (ii) variable gas velocity were evaluated. From a modelling consistency point of view, a variable gas velocity should always be used. However, the use of pseudo-components to simulate a petroleum stream is a source of error in the mass balance bigger than the error of using a variable gas velocity as opposed to a constant one. Furthermore, the available kinetic models found in literature lead
Figure 5.15. Simulations of (A) temperature profile of the liquid with a three different values of $\Delta H_{\text{poly}}$: 1) $\Delta H_{\text{poly}} = -30 \text{ kJ/mol}_\text{H}_2$ (case study) $\Delta H_{\text{poly}} = -45 \text{ kJ/mol}_\text{H}_2$, and 3) $\Delta H_{\text{poly}} = -60 \text{ kJ/mol}_\text{H}_2$. (B) Organic sulfur content in the liquid phase across the length of the reactor with the three different values of $\Delta H_{\text{poly}}$. (C) Concentration profiles of aromatics throughout the reactor.
to a slight over prediction in the concentration of organic sulfur at the outlet of the reactor. On the other hand, the prediction of the concentration of each group of aromatics is over predicted when comparing to the data of the plant, however, the trends on the behaviour of reactants is consistent with cases studied in literature. Nevertheless, the kinetic model must be improved to be able describe the saturation reactions and should be considered for further investigations.

In order to identify the most sensitive model parameters and input variables, a sensitivity analysis using the Morris-screening method was carried out. When focusing on the outlet temperature of the liquid and the outlet concentration of organic sulfur, mono-, di-, and polyaromatics as the variables of interest, the Morris screening method shows that the most sensitive parameters and input variables are the inlet temperature, and the pressure correction of the kinetic model for aromatics saturation. Therefore, a set of model evaluations were carried out to investigate the effect of different values associated with the inlet temperature, the pressure correction of the kinetic model of aromatics saturation.

The inlet temperature dictates how fast the reactions take place and the aromatics reach equilibrium. Unsurprisingly, the inlet temperature has also an effect on the outlet concentration of organic sulfur with lower values obtained at higher temperatures. The correction for pressure of the kinetic model of aromatic saturation has an effect on both the outlet temperature and the organic sulfur concentration due to the rate and magnitude of the heat released by the saturation reactions. The equilibrium concentration of each of the aromatics is also affected and it can be a fine-tuning parameter in order to describe more accurately the outlet concentration of aromatics. Preferably, an adequate aromatics saturation kinetics model should be used and/or developed.

A model performance study was performed to observe the effect of the excess of hydrogen on the organic sulfur concentration of the outlet. At higher \( \frac{H_2}{oil} \) ratios, higher conversions of BT and DBT-type compounds is obtained as expected. Finally, a model performance study was carried out to investigate the effect of the value of \( \Delta H_{poly} \). The kinetic model of polyaromatics is not able to predict realistic values of concentration of polyaromatics when using typical values of \( \Delta H_{poly} \) available in literature, because higher values of \( \Delta H_{poly} \) cause the concentration of polyaromatics go to zero. Therefore, a more accurate kinetic model of aromatic saturation is needed to predict qualitatively the outlet stream of a real large-scale hydrotreating unit.

This Chapter discloses the most influential parameters of the operation of a hydrotreating unit. The outcome of this simulation work can be beneficial for hydrotreating units that are currently operating. However, there are different vari-
ables that are a source of uncertainties and might be addressed in future work. For instance, the liquid maldistribution is a characteristic of the reactor design. Liquid maldistribution usually leads to unpredictable and uncontrollable reactor performance at large scale. Therefore, different variables must be taken into account, such as catalyst packing, number, size and location of the reactor beds.
In this Chapter, the solution scheme of a trickle-bed reactor model is extended to include phase change of species using a simulation framework that harnesses the practicality and widespread use of a process simulator and the flexibility of a reactor model developed according to the needs.
Chapter 6. Vaporization effects in hydrotreating processes

Introduction

The conditions in which the hydrotreating process is carried out are typically at temperatures between 320 to 420°C and pressures ranging from 30 to 120 atm [54][5]. These reactor conditions suggest that the model assumption in Chapter 4, which postulates that the hydrocarbons are non-volatile, is controversial. It is undeniable that a share of the hydrocarbons in the liquid vaporize causing a development in the gas and liquid phases that ultimately affects both, the mass and energy balance.

As the exothermic reactions take place, the temperature increases causing more hydrocarbons to vaporize. This causes an undeniable change in the fluids flow rates and the hydrodynamics of the system, which influence the concentrations of the diverse reacting and non-reacting species in the two phases that fundamentally effects the reactor performance. The main problem is to manage the complexity of modelling and solving vapor-liquid equilibrium (VLE) in a trickle-bed reactor in order to obtain realistic process simulations.

The VLE investigation is paramount specially for pilot-scale studies. At smaller scale, any divergence from the ideal operating regime such as plug-flow or full catalyst wetting, can cause inaccurate data that could potentially conflict with the behaviour of a large-scale commercial unit, or generate deviant kinetic studies. Additionally, by its own nature, it is difficult to obtain, characterize and analyse samples experimentally. For this reason, flash experiments were conducted to obtain VLE data with a variety of gas-oil feeds.

These circumstances makes VLE in hydrotreating processes difficult to address for commercial large-scale units in open literature. Furthermore, no correlations are available in literature that deal with pseudo-components without treating them as real compounds.

Various authors, however, ventured to study the effects of vaporization in hydrotreating trickle-bed reactors with two major approaches: 1) experimental studies and 2) simulation-based studies.

In literature, experimental research convey the study of the distribution of species in the two phases in a hydrotreating pilot-plant. The VLE flash experiments were fulfilled in a continuous-flow unit with a number of petroleum middle distillates and hydrogen at typical hydrotreating conditions [24]. The experimental data served as a reference to assess interaction coefficients for further simulation studies of VLE flash calculations. This study extends to predict flow hydrodynamics that suggests operating conditions under which the desired operating regimes could be maintained.
Supplementary research, focused on the modelling and simulation of rigorous VLE calculations to develop a model and simulate a commercial light-cycle-oil (LCO) hydrotreater [5]. The proposed model is a one-dimensional plug-flow adiabatic reactor model contemplating quench zones between beds. The VLE calculations were performed with a program of their own authoring specifically constructed for hydrogen-petroleum systems. This study exhibits the differences in reactor temperature profiles, hydrotreating conversions, fluid rates, and phase compositions between simulations with and without VLE.

In the pursuance of bridging the gap between in-house built programs and commercial tools available to simulate hydrotreating units, in this Chapter, a simulation framework of a hydrotreating reactor is proposed. Using the database from ProII for petroleum streams, the utility to manage flash calculations of simulated pseudo-compounds is coupled with a dynamic model of a trickle-bed reactor, solved in Matlab. This approach reduces the complexity of the numerical solution and extends its application to industrial and commercial practice.

6.1 The simulation with VLE calculation

The underlying idea behind the approach of the extended simulation approach, is that, using the model established in this thesis and, in principle, any model developed in-house) can be coupled with existing process simulators to utilize all the tools that are commercially available and widespread used outside the academic community (Figure 6.1).

![Figure 6.1. Fundamental concept of the upgraded simulation scheme.](image)

The intention is, more specifically, to exploit the capabilities of ProII to handle petroleum properties and, consequentially pseudo-compounds. At the same time, using a reactor model to dictate the most fitting reaction scheme for the needs. In this case, is the reaction of real and simulated organic compounds carried out in a discretized tubular reactor model. The proposed simulation arrangement consists
of sequentially solving the model in MatLab and feed the output data into ProII for further VLE calculation.

### 6.2 Simulation Framework

A couple of possible configurations, A and B, can serve the purpose of the simulation coupled with an external VLE calculation. These configurations are solved one after the other. In configuration A, the VLE calculation is solved at the beginning of the simulation and the output of the VLE calculation is then used as an input for the model. In configuration B, the reactor model is solved before the VLE calculation (Figure 6.2).

**Configuration A:**

![Configuration A](image)

**Configuration B:**

![Configuration B](image)

**Figure 6.2.** Two different arrangements for the simulation coupled with a VLE calculation.

Configuration A is used to obtain the gas-liquid equilibrium conditions for the Feed. Using Configuration A exclusively is inconsequential to the rest of the simulation with VLE, as no further VLE calculations are performed. Working with configuration B exclusively can be used only if the inlet conditions are known to be in gas-liquid equilibrium. Once the inlet is in gas-liquid equilibrium, then the model solution can provide the conditions and the conversion of species and therefore, perform a VLE calculation afterwards. Furthermore, this process can be repeated in sequence for any number of reactor segments.

#### 6.2.1 Framework structure

The proposed configuration for the simulation framework with a coupled VLE calculation is merging both configurations into the discretized reactor model. In this way,
the VLE calculation aids the estimation of gas and liquid concentration of species and pseudo-components throughout the reactor length and not only at the outlet.

Figure 6.3. Proposed simulation scheme of a trickle-bed reactor model coupled with a VLE calculation.

6.3 Implementation of the simulation framework

In order to implement the simulation framework, the initial and boundary conditions must be defined, i.e. rate of species, temperature, pressure, etc. Assuming that the inlet conditions are in gas-phase equilibrium, then, the inputs of the model include gas and liquid flowrates, concentration of species, inlet pressure, inlet temperature, densities, among others. Otherwise, a VLE calculation must be performed to ensure that the inlet is in gas-liquid equilibrium conditions. The length of the hydrotreating reactor is divided into segments. The segments in this chapter are considered equal-size, however, the size can, in principle, be determined based on a specific system or behaviour, in which certain regions of the reactor have a more significant response.

A full-functioning ProII file must be created, in which all the species and pseudo-components in the system are defined and the operation conditions of the hydrotreating reactor are used. The bulk has the same boiling point curve of the Feedstock and must be used to satisfy the mass balance. The bulk has a direct effect on the overall energy balance, hence influencing the chemical reactions. ProII offers different types of flash calculation, such as adiabatic flash, isothermic flash, isoentropic flash, among others. It is also possible to use duty, dew point and bubble point as an input to the flash calculation. In order to fulfil the objectives of this chapter, isothermic and isoentheopic flash can be discarded, as a change in temperature is expected due to vaporization of hydrocarbons. The adiabatic flash is the appropriate VLE calculation path because the heat released during the reaction increases the temperature of the fluids, which, plays the role of the duty input for the flash.

The ProII file must contain an adiabatic Flash unit operation (Figure 6.4). A number of equations of state are available, in this chapter, the Soave-Redlich-Kwong Equation (SRK) of State is used.

Once the ProII file is created and the size of each reactor section is determined,
the reactor model is solved for the first segment. The output is logged and transferred to the ProII file, which is then, executed. The output of the ProII file is recorded into a new set of data that are used as inlet conditions of the next reactor segment, as shown in Figure 6.3. The link between Matlab and ProII is carried out in Excel using VBA-code, which extracts, writes and stores the relevant data throughout the simulation course.

It is worth pointing out that achieving a completely automated algorithm that links Matlab and ProII is difficult through VBA-code due to licence-clearing hindrances. To alleviate this situation, every step in the simulation is hand-operated, causing the work flow to pause in order to save the data and then input it to the ProII file manually, leading to unattainable dynamic simulations. A dynamic simulation requires the execution of the simulation framework for every time-step. However, the proposed simulation framework can still be fulfilled using the example case in Chapter 4.

Figure 6.4. Schematic example of the ProII file used in the simulation framework. Poly, Di and Mono are replaced by any number of pseudo-components and each one of them treated the same way as the real component during the information transfer.
6.3. Implementation of the simulation framework

6.3.1 Example - Hydrodesulfuration process to obtain ultra low sulfur diesel (PFTR model).

In this section, the implementation of the simulation framework is performed the example simulation given in Chapter 4. A previous study dealt with the example case, in which, the reactor is divided into 5 and 10 segments with a VLE calculation in-between [41]. Additionally a study with configuration A (Figure 6.2) is implemented to serve as a reference (Figures 6.6 to 6.8).

In Figure 6.6, one can observe that the inlet temperature to the reactor model is 26 K lower than the original example case. This can be explained by the given inlet gas and liquid not being in gas-phase equilibrium. The VLE calculation at the beginning of the reactor corrects the inlet gas and liquid flowrates that are conveyed to the reactor model, which undoubtedly effects the overall performance of the reactor system.

Figure 6.7 shows the concentration of DBT in the liquid. The inclusion of the VLE calculations show an increase concentration of DBT close to 3 cm and 13 cm
for the case of 5 segments. A similar trend is observed for the case of 10 segments. The results suggest that the flash calculation causes the DBT present in the gas, to be transported to the liquid to achieve the gas-liquid equilibrium again, and subsequently to the solid phase where it reacts. However, the three cases indicate that all of the Sulfur-compounds easy to desulfurize are predominantly converted.

A similar trend is observed in the concentration profile of 46mDBT in the liquid, although the difference in the concentration is considerable (Figure 6.8). It is interesting to note that the flash calculation promotes the condensation of 46mDBT to the liquid at a higher rate than the mass transfer entails. In the case of a single flash at the inlet of the reactor, the simulation suggests that virtually all of the 46mDBT is converted. However, when the VLE calculation is included across the length of the reactor, the results differ. The concentration 46mDBT in the liquid across the length of the reactor is, to some extend, higher when more VLE calculations are performed due to vaporization of a portion of the liquid. This also explains the higher temperatures close to the outlet of the reactor observed in Figure 6.8.

Complete disregard of the VLE calculation in the trickle-bed reactor model solution, compromises the performance of the simulation outcome, hence, the prediction of the behaviour of the system. Clearly, considering VLE compensates for a possible overprediction of the conversion of Sulfur-compounds, especially compounds difficult to desulfurize.
Figure 6.7. DBT concentration profiles of the liquid with 1, 5 and 10 flashes.

Figure 6.8. 46mDBT concentration profiles of the liquid with 1, 5 and 10 flashes.
This Chapter presents the simulation framework implementation. The data for a large-scale hydrotreating unit is used as a reference, i.e. dimensions and inlet and outlet temperatures of each of three beds. Two sets of experimental data are available, the operation design as well as data for a test run. The simulation framework is implemented first as one plug-flow reactor coupled with a VLE calculation per bed and accounting for quench zones. The results show that the inclusion of phase change in the calculations have a substantial effect on the overall temperature profile, thus effecting the behaviour of the reaction system.
Introduction

In the previous chapter, the concept of the simulation framework is presented and implemented for the example case found in literature. One of the main outcomes of the implementation of the simulation framework, is that the results obtained from the model is that the VLE calculation has a remarkable effect compared to the reactor model alone. The temperature profiles are noticeably different. Even though the results follow a similar trend, the distinctive behaviour has an effect on the results at a qualitative level.

In this Chapter, the reactor model is partitioned into sections that represent different zones of the real large-scale hydrotreating unit with a VLE calculation in between. The results of the implementation of the simulation framework are studied side by side with the available information from the real large-scale hydrotreating unit. The plug-flow modelling approach to simulate hydrotreating reactors is widely used with functional results that aid the analyst and the operator to understand the behaviour of the reactor. However, a more thorough simulation that accounts e.g. the number of beds and the location of quench zones could bring a more comprehensive insight for the operation of existing hydrotreating units and the design of new equipment.

In this Chapter, the implementation of simulation framework is presented using the plug-flow model coupled with flash calculations to represent the reactor beds and the quench zones at first. Secondly, the simulation is elaborated to incorporate the vaporization effects inside the beds. The beds are simulated as segments with VLE calculations in between that represent an individual reactor bed.

The simulation framework proposed in this work is advantageous to analyse the behaviour of the reactor equipment, and might be useful for the development of process optimization tools.

7.1 Extensive description of the industrial Hydrotreating unit

In Chapter 6, the VLE calculation inserted between sections of the example plug-flow reactor demonstrated the performance of the segmented simulation. As a follow-up to our research on VLE in the large-scale trickle-bed hydrotreating reactor presented in Chapter 5, the simulation approach is further developed to include phase change without increasing the complexity of the mathematical model. Fundamental information, such as the arrangement of the hydrotreating unit, inlet and outlet flows, temperature and quenching, of each bed is available (Figure 7.1). The data is for standard operation of one specific hydrotreating unit. The hydrotreat-
7.1. Extensive description of the industrial Hydrotreating unit

Figure 7.1. Schematic representation of the data available as operation design for the large-scale hydrotreating unit.

ing unit studied in this chapter, is a rather common configuration of hydrotreating reactors and one can expect similar behaviour for similar hydrotreating systems.

In Chapter 5, the total length of the reactor is 30 m in which the solution was obtained. The plug-flow model alone does not consider quench zones. It takes into account the hydrogen introduced in the quench as a single gas inlet flowing into the reactor at the top. Following the typical approach found in literature, the plug-flow model in Chapter 5 considers the entire length of the reactor as a single bed. A more in-depth simulation of the hydrotreating reactor for industrial purposes requires to look upon to a more realistic configuration of the reactor.

In this chapter, a hydrotreating unit consisting of three catalytic beds will be studied. The first bed, which is the closer to the inlet, has a length of 3.3 m, and it is where most of the reaction takes place. The other two beds are of similar length, the second bed is 7.8 m and the third is 7.9. Two quench zones are located between the beds. With this configuration in mind, the reaction takes place effectively throughout 19 m of bed, assuming that the reaction occurs on the solid
A simulation using the plug-flow model to represent each one of the beds individually accounting for quench zones in locations that resemble the real reactor can provide more realistic results.

Figure 7.1 presents the layout of the hydrotreating unit. A mix of oil and a hydrogen-rich gas stream heated to 335°C and is introduced at the top of the reactor. The mixture trickles through the fixed bed packed with catalyst. At the outlet of the fixed bed, a quench stream is injected to the reactor to counteract the heat release. In this case, the quench is comprised predominantly by hydrogen at 88.8°C. The fresh hydrogen from the quench interacts with the gas an liquid stream affecting the distribution of species in the system. The premise is that the mixing in the quench zone is so efficient that the equilibrium between the two phases is achieved before the mixture enters the next bed. After the first quench, the mixture trickles through the second bed. With the extra hydrogen, the reaction continues to take effect. At the outlet of the second bed, another quench is injected to deal with the heat released by the second bed. The supplementary hydrogen aids the third bed to ensure the maximum removal of sulfur from the liquid product.

7.2 Simulation of the Case study: Part II.

The simulation of the hydrotreating unit is as follows: Each individual bed is treated as a single plug-flow reactor. Each bed is simulated until steady-state with 100 nodes in position. The outlet conditions are introduced into the ProII file. The quench is handled in the ProII file that performs the VLE calculation. If no quench is needed in the current bed segment, the quench stream in the ProII file is set to zero. The results from the ProII file are conveyed to the next bed. The procedure is repeated with the second and third bed. The data available from the unit are the design objectives (Figure 7.1) and a set of data obtained from a handful of sensors in the unit. The data from the test run are the averaged values of the sensors at each position (Figure 7.2). The simulation of the test run is performed using the quench data from the unit design. More specifically the flowrates and the temperature of the quench. The input parameters are given in table 5.7 which correspond to the test run. The number of pseudocomponents are the same used in Chapter 5 in Table 5.4 as well as the boiling point curves of the feed, naphtha and product are given in Tables 5.3, 5.5 respectively. In order to represent the real length of the unit, the space that is not occupied by the packed beds, is set to 5.5 m. This is only illustrative as the volume reserved for the quench zones does not play any role during the VLE calculation in ProII.
7.2. Simulation of the Case study: Part II.

Figure 7.2. Schematic representation of the data available from the sensors of the large-scale hydrotreating unit during a test run.

7.2.1 The plug-flow model phase change calculation at the quench zones.

A number of simulations are conducted to test the implementation of the simulation framework using industrial data. The results of the temperature profiles of the liquid for three cases are shown: 1) The outcome of the simulation framework using data for the test run, 2) The readings of the sensors of the hydrotreating unit during the test run and 3) The operation design specifications (Figure 7.3).

The simulations with VLE demonstrate the effect of considering phase change in the hydrotreating reactor model. In Figure 7.3, one can observe that the test run temperatures are lower than the operation design. The inlet is fed 2°C lower, consequently, the outlet temperature of the first bed is 10°C lower than the operation design. This trend continues throughout the reactor, resulting in a difference of 4°C compared to the operation design. In contrast, the results of the simulation framework are overall higher than both of the reference cases. The inlet of the simulation is the same as the test run, yet the outlet temperature of the first bed is 22°C higher.
However, the direction of the results of the simulation framework tend to converge with the real data towards the outlet of the reactor.

The results in Figure 7.3 show that the temperature after the first bed is 22°C higher in the simulation compared to the test run, and up to 15°C compared to the operation design. Higher temperature implies higher conversion of sulfur compounds. Therefore, by considering the vaporization effects in the simulation, the temperature rise and the overall simulation error can be reduced. The results show that higher conversion of reactant is predicted in the first bed. However, the concentration of reactive species is lower in the last segment of the first bed, where the simulated temperature rise is smaller. In order to obtain highly realistic results, adjustments in the reaction kinetics are necessary or accounting for the vaporization effects inside the beds.

It is worth pointing out that the arrangement of the simulation framework to perform VLE calculations in the quench zones, provides a good description of the temperature profiles. Therefore, the assumption that gas-liquid reach equilibrium in the quench zones seems reasonable.

7.2.2 Plug-flow model with phase change calculation inside the beds.

The simulation can be further developed with the inclusion VLE calculation within the beds. Allowing vaporization of species inside the bed will counteract the effects of the temperature rise. To this end, each bed is segmented in three equal-size parts and a VLE calculation is performed between each segment. Given a total of 9 seg-
7.2. Simulation of the Case study: Part II.

Figure 7.4. Temperature before and after the VLE calculations performed inside the reactor beds.

ments for which, the model solution is perfomed using the simulation framework. The simulation results for inlet and outlet temperatures of each bed segments are displayed in Figure 7.4 as well as the temperatures obtained after the VLE calculations.

In Figure 7.4 it can be clearly observed that in-bed VLE calculations have an effect on the overall temperature profile. The highest temperature rise occurs close to the inlet of the reactor as expected, reaching its maximum in the second bed segment. Also, the results in Figure 7.4 show that the implementation of the phase change calculation decreases the outlet temperature of the first segment in 11°C approximately. This temperature difference continues to grow towards the outlet of the reactor up to 22°C. This can be explained by the progressive vaporization of oil species caused by the exothermic reactions through the catalyst beds, which is more evident towards the outlet of the reactor (Figure 7.5). Moreover, Figure 7.5 suggests that quenching produces a step decrease in the vaporization of oil due to the partial condensation of the hydrocarbons in the vapor phase.

Accounting for VLE, in principle bridges the gap between the simulation and the real data. In order to compare the results of the simulation framework, only the inlet and outlet bed temperatures are plotted in Figure 7.6, alongside with the inlet and outlet temperatures of the operation design as well as the test run.

The outlet temperature of the first bed is 2°C higher in the simulation with vaporization effects than the operation design and 15°C higher than the test run. However, after the first quench, this difference is maintained at roughly the same 15°C when the simulation and the real data are compared. This is a result of the selection of the quench. Even though the outlet temperature of the first bed is
similar before the quench at 3.3m, the behaviour of the simulated blend seems to differ due to the selection of the properties. This phenomenon is evident in the last bed, in which, the simulation generate a temperature up to $9^\circ$C lower than the real counterpart. This means that a considerable part of the heat released by the reaction in the third bed is responsible for the vaporization of simulated oil species during the VLE calculation.

It is worth pointing out the subtle differences between the test run and the operation design, especially in the region of the first quench zone. The temperature achieved at the first quench are equivalent, which suggests that the amount of quench gas used during the test run differs slightly from the one in the operation
design as the inlet temperatures are 5°C apart. At the second quench, this difference in temperatures grows up to 10°C. However, the three profiles tend to converge to a similar value at the outlet.

Towards the outlet of the hydrotreating unit, specifically after the second quench, the results of the simulation come close to those of the test run due to the cooling effect. However, the temperature decrease due to quenching in the simulation is too small and the outlet temperature of overall reactor is also low compared to the plant data.

Regarding the qualitative aspect of the simulation framework, the Boiling Point curves of the process product and the simulated product are compared in Figure 7.7. The results show that the boiling point curves of the simulation and the real product follow a similar trend. The Boiling point curves correspond to the liquid phase only. Therefore, the difference between the simulated product and the real one can be consequence of the selection of pseudocomponents.

Finally, the Sulfur-concentration in the liquid phase obtained from the simulation framework is shown in Figure 7.8. The sulfur-compounds are present in the gas phase, additionally, these compounds are transported due to mass transfer considered in the plug-flow model. However, the VLE calculation performed in the quench zone, leads to an increase in the sulfur-concentration in the liquid, more evidently for BT, which is up to 63 wppm higher than the inlet concentration. This phenomenon can be explained by the contribution of two factors: 1) the partial vaporization of the liquid phase; and 2) the condensation of a portion of the sulfur-compounds present in the gas phase due to the decrease in temperature
caused by the quenching. This behaviour appears again at the region of the second quench, although with a less pronounced increase in the concentration of sulfur-compounds due to consumption while the reaction takes place. The results show that the simulated sulfur-concentration at the outlet for both compounds BT and DBT are consistent with the results of the plug-flow simulation presented in Figure 5.4F in Chapter 5.

The simulation of a trickle-bed reactor using the simulation framework proposed in this thesis builds upon the plug-flow tubular reactor model, which is recurrent in literature. By allowing species to vaporize due to the high temperatures, the simulation framework allows us to depict a more realistic outlook of the behaviour of a real large-scale hydrotreating unit, especially with the quench zones with reasonable locations.

In conclusion, considering phase change in the quench zones is justified. However, the VLE calculation to predict the vaporization effects inside the beds is an arguable drawback of the proposed simulation framework. Therefore, a reasonable approach could comprise accounting for a fraction of the liquid in the VLE calculation or to include a rate based evaporation expression inside the plug-flow model.
The modeling and simulation of hydrotreating reactors is a complex task that involves a hefty number of variables to take into account. Therefore, the development of a simulation methodology that increases in complexity progressively, ensures that the outcome of every stage is coherent. The main advantage of this simulation development is the possibility to investigate the uncertainty of values of the model parameters.

The plug-flow and CSTR in series modelling approach, allow us to study the model parameters by means of a sensitivity analysis of the numerical solution. The results benefit the operation knowledge on how the reactor responds to a variety of conditions, even in harsh scenarios. Unfortunately it is impractical to acquire the real concentration of each component in the hydrotreating unit in every position. Acquiring such experimental data from a reactor that is subject to an industrial agenda is hardly possible.

To alleviate this, the numerical solution presented in this thesis represents a huge advantage to predict the behaviour of the hydrotreating reaction system due to its easy implementation. One of the main outcomes of modelling hydrotreating reactors as plug-flow reactors offers a good trade-off between simulation time and consistency of the results. On the other hand, the simulation of the reactor as CSTR in series can be useful to obtain quick results due to the straightforward construction and low solution time. Moreover, the CSTR in series approach can be further developed as an optimization problem. Equal-sized reactor are not ideal to obtain an accurate solution, making the plug-flow model superior. However, the optimization can be performed by determining the number of reactor and their sizes for which, the results resemble the plug-flow simulation with less computational cost. The results can be implemented for similar systems allowing a much quicker prediction of the behaviour of the reactor.
There are important things to consider for the development of a simulation approach that produces realistic results, such as the selection of the pseudocomponents. The determination of the pseudocomponents is a burdensome task that is an entire field of study on its own. Therefore, using the pragmatic approach presented in this thesis, is a meaningful contribution to the field because reasonable and fruitful results can be obtained with rather commonly available tools. Any hydrotreating simulation approach can be undoubtedly benefited with a pseudocomponent generation algorithm, nonetheless.

In literature, only a few modelling and simulation works include the phase change calculation. Remarkably, many a Plug-flow reactor simulations are implemented as a single unit without considering the length of the beds, the quench zones or the industrial applicability at large scale. This is not ideal because the simulation is fundamentally performed as a single bed that takes the entire volume of the reactor. This only proofs that advancements can still be made and that the problem can be tackled from different perspectives.

The operational data used for the cases presented in this thesis are exclusive for one hydrotreating reactor operating under specific conditions. Hydrotreating systems with different operational characteristics will certainly have completely different results. However, the simulation procedure can be improved to increase its robustness to cover more diverse scenarios such as hydrocracking conditions and even account for different simulation resources. One of the main shortcomings of the simulation framework is the flawed use of ProII as an automated tool that can be accessed from an external platform.

Besides the resources for the implementation of the simulation framework, a crucial element of the success of the simulation of the hydrotreating unit is the selection of the kinetic parameters and their experimental validation. It is possible that the lack of availability of the best suitable kinetic data has affected the quality of the simulation results.

The simulation framework and studies proposed in this thesis represent a step forward in the simulation of such complex systems. Understanding the important aspects of hydrotreating reactors is fundamental for the development of more robust modelling and simulation tools.

**Recommendations for future work**

Experimental validation and far-reaching kinetic studies of hydrogenation reactions in large-scale conditions can be a substantial improvement in the development of the field.
License-clearing procedures proved to be an important obstacle for the simulation framework proposed in this thesis. Finding a suitable ecosystem in which the reactor model and the phase change calculation coexist and work connectively, while ingeniously maintaining easy-access to the operators and researches, would be particularly valuable.

The automation of the calculations is exceptionally encouraged. A fully automated simulation procedure can lead to optimization investigations that can potentially improve the operation of existing hydrotreating units and contribute to the enhanced design of new ones.
Chapter 9

Thesis Conclusions

The fundamental objective of this thesis is to extend the knowledge and understanding of large-scale hydrotreating units. This is carried out through stages attained in the different chapters. Starting with a thorough review of the state of the art of the simulation of hydrotreating processes in Chapter 2. The main outcome of this review is the development of a hydrotreating reactor model that expands on the models available in literature. Two different approaches were used in the development of the model and presented in Chapter 3: 1) a Plug-flow tubular reactor and 2) as a series of Continuous stirred-tank reactors. The approach of modelling a hydrotreating reactor using a series of CSTRs is overlooked in literature.

In Chapter 4, the plug-flow model approach is implemented for an example case study. The performance of the numerical implementation of the reactor model is evaluated. A convenient number of nodes were determined for a good balance between computational time and accuracy. The approach of simulating a hydrotreating reactor as a series of CSTRs was also implemented and compared to the solution of the plug-flow model. The result of this comparison, show that the CSTR approach gives acceptable results when using a series of 10 equal-sized reactors. The performance of the approach of CSTR in series can be benefited by an optimization of the number and size of the reactors. Especially in the region close to the inlet of the hydrotreating unit.

Based on the evaluation of the two different modelling approaches, the plug-flow approach is corroborated to be the most robust simulation approach for a hydrotreating reactor. Therefore, in Chapter 5, the plug-flow modelling approach was implemented using the Feed stream data of a real large-scale hydrotreating unit. A kinetic model, taken from literature, was used in the simulation. However the value for the different parameters was acquired from diverse sources. It was concluded the values for heats of reaction of polyaromatics found in literature are
arguable since real values tend to be higher. The value used in the model served its purpose and the results are admissible, nonetheless.

The sensitivity analysis of different parameters in the simulation was performed and the most influential model parameters were determined. This study leads to the conclusion that, in order to obtain a refined prediction of the behaviour of the hydrotreating unit, a review of the kinetic model and its parameters must be considered.

Further development in the plug-flow model was performed to include the effects of vaporization of species during the hydrotreating reactor. This thesis presented, in Chapter 6, a methodology to build a simulation framework that couples the reactor model coded in MatLab, with a commercial process simulator to handle the vaporization of species by means of a built-in flash calculation module and, at the same time, take advantage of pseudo-components to simulate oil streams.

The simulation framework was implemented for the example case. The information exchange between different software platforms verify that it is possible to couple a commercial process simulator with a plug-flow model developed in-house to simulate a hydrotreating unit.

The last study presented in the thesis is the implementation of the simulation framework previously developed. The simulation framework was executed to simulate a real large-scale hydrotreating unit. Specific real operational data was used to evaluate the performance of the simulation framework to forecast the behaviour of the reaction system with encouraging results. Despite the variety of the sources of the model parameters, the use of pseudocomponents and the information exchange between platforms, the simulation framework was able to resemble the steady-state behaviour of the industrial hydrotreating reactor.

In particular, the framework consisting of a rigorous plug-flow model in MatLab coupled with flash calculations in PROII is useful to describe a reactor with quench zones between the reactor beds.

Further work is needed to obtain more accurate predictions of distribution of vapor and liquid compounds through the reactor bed by including vaporization phenomena in the trickle-bed reactor model.

The topics presented in this thesis are considered to provide insight and extends the knowledge in the field of simulation of hydrotreating reactors. The insight can aid the reactor designer and expand the expertise in the predictive performance of existing simulation practices.


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