A simplified kinetic model for continuous hydrotreating of HTL biocrude

João Guilherme de Santos Brandão
Hetune Vipin Manmohandas
TEPE 4/1002
Master Thesis

Aalborg University
Energy Engineering

AALBORG UNIVERSITY
STUDENT REPORT

Energy Engineering
Aalborg University
http://www.aau.dk

Title:
A simplified kinetic model for continuous hydrotreating of HTL biocrude

Theme:
Bio-fuel

Project Period:
Spring Semester 2020

Project Group:
TEPE4/1002

Participant(s):
João Brandão
Hetune Manmohandas

Supervisor(s):
Daniele Castello

Copies: 1

Page Numbers: 107

Date of Completion:
May 28, 2020

Abstract:

In this study, two packed bed hydrotreating reactors are modelled with the purpose of estimating the kinetic parameters of deoxygenation and denitrogenation for a two-stage upgrading of biocrude produced from hydrothermal liquefaction (HTL). In order to simplify the many reactions happening during the process, the oxygen and nitrogen are lumped into a single compound each (O,N), whose concentration is equal to the concentration of O,N in the biocrude. Although the model showed good results up to 370°C, more severe conditions showed considerable errors for the N concentration. So, an optimization was performed, where the nitrogen was divided in two compounds, as "high" and "low" reactivity. Moreover, the study commenced with experimental work on hydrotreating of HTL miscanthus biocrude, under different temperatures, 250°C, 300°C and 350°C. This biocrude showed high instability, leading to the experiment at 350°C where coking reactions were predominant, encouraging the two-stage hydrotreating investigation.

Contents

Preface

This thesis is submitted as partial fulfillment of the requirements for the degree Master of Science Program for the Thermal Energy and Process Engineering studies at the Department of Energy Technology, Aalborg University.

The thesis started with experimental work, with the purpose of upgrading HTL biocrude through hydrotreating, in the AAU biofuel laboratory. However, due to the Covid-19 outbreak, the laboratory work was no longer an option, stimulating us to investigate the kinetic modelling for the hydrotreating process. This project was conducted under the supervision of the Assistant Professor Daniele Castello, whom we share our gratitude for all the expertise and support along the way. Moreover we would also like to thank PhD Salman Haider and PhD Antonio Azuara for all the advises and skills during all the experimental work in the laboratory.

Aalborg University, May 28, 2020

João Brandão
<jdesan18@student.aau.dk>

Hetune Manmohandas
<hvipin18@student.aau.dk>

Foreword

This thesis was conducted in the time period between 1st of February and 29th of May 2020 of the Thermal Energy and Process Engineering Master Program, part of the Department of Energy Technology of Aalborg University.

Reading guide

The layout of the report is designed for one sided print.

Figures, equations and tables are numbered according to the chapter of their appearance. For example, the third figure in Chapter 3, will be numbered 3.3, same applies for equations and tables. Every figure and table is provided with a caption, explaining its content.

References are made according to the IEEE standard. In the text sources are indicated by numbers in square brackets, sorted by alphabetic order. Citations for single sentences are placed before the dot. If a passage of multiple sentences refers to the same source, the citation is placed after the dot and followed by a line break. Information on the respective source is found in the Bibliography at the end of the report. The Appendices are located at the end of the report and are denoted A, B and so on.

All simulations are performed using MATLAB®.

In order to avoid excessive repetitions, synonyms are used for frequently used terms.

Nomenclature

Abbreviations

AAU	Aalborg University
C	Carbon
DTL	Direct Thermochemical Liquefaction
EU	European Union
F	Sulfur
$FTIR$	Fourier transform infrared spectroscopy
$GC - Gas$	Gas chromatography
$GC - MS$	Gas chromatography mass spectrometry
H	Hydrogen
H/C	Hydrogen to carbon atomic ratio
H_2/Oil	Hydrogen(L) to oil(L) Ratio
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDS	Hydrodesulfurization
HHV	Higher Heating Value [MJ/kg]
HTL	Hydrothermal Liquefaction
HYD	Hydrogenation
IEA	International Energy Agency
LPG	Liquefied Petrol Gas
N	Nitrogen
N/C	Nitrogen carbon atomic ratio
O	Oxygen
O/C	Oxygen to carbon atomic ratio
ODE	Ordinary Differential Equation

$RMSE$	Root mean square erro
$SimDis$	Simulated Distalation
$SRGO$	Straight-run Gas Oil
SRK	Straight-run Kerosene
SRN	Straight-run Naphta
SS	Sewage Sludge
TAN	Total Acid Number [mg KOH / g oil]
VGO	Vacuum Gas Oil
$WHSV$	Weight Hourly Space Velocity [h^{-1}]

Variables

ρ	Density [$\mathrm{kg/m^3}$]
C_x	Concentration of element x [$\mathrm{mol/m^3}$]
E_{act}	Energy of Activation [J/mol]
H^{cp}	Henry's Law Constant[$\mathrm{mol/(m^3}Pa)$]
k_0	Pre-exponential Factor [m3/kg $\cdot s$]
m	Mass [kg]
M_x	Molar Mass of element x [kg/mol]
P	Pressure [Pa]
Q	Volumetric Flow Rate [$\mathrm{m^3}/s$]
R	Gas Constant [J/mol $\cdot K$]
r	Rate of Reaction [mol/kg]
S	Surface Area [$\mathrm{m^2}$]
T	Temperature[K]
V	Volume [$\mathrm{m^3}$]
W	Molar Rate [mol/s]
$wt.\%$	Weight Percentage [%]

Chapter 1

Introduction

The global demand for primary energy is increasing due to global growth and emerging markets. Nowadays, the most commonly used energy source is fossil crude, which represents a significant contribution to global warming. Also, the quantity and quality of this resource is gradually decreasing. Therefore, to meet the energy demands and lower the greenhouse gas emissions, alternative sources of energy need to be investigated. [47]

According to recent statistics, over 100 million barrels of crude oil are consumed daily worldwide, primarily in the transport sector [56]. Although many steps have been taken towards more sustainable solutions in the transport sector, such as the use of electrical vehicles, the consumption of liquid fuel still represents a significant share of the world's energy. Long-distance transportation, such as aviation and marine traffic, depends highly on liquid fuel and is predicted that it will not change in the near future. An alternative renewable energy source that presents great potential to provide liquid, gaseous and solid fuels is biomass. [7] [10]

Biomass is continually being replenished, while, on the contrast, the fossil fuels requires millions of years to form. Biomass consists of organic matter that is originated from plants or animals, and can be directly burned to create energy, a stationary method, or biochemical/thermochemically converted into more valuable products, such as biocrude. Since the transportation sectors require liquid or gaseous fuel, the conversion of biomass to such fuels by chemical and/or physical methods is of high interest. Biocrude can be processed and refined into various transportation fuels that can be applied in existing vehicles without or with little modification to engines and fuel systems. [10] [36] [67]

The biomass is converted into biofuels through two main processes: biochemical and thermochemical. Figure 1.1 illustrates the biomass conversion methods and their products.

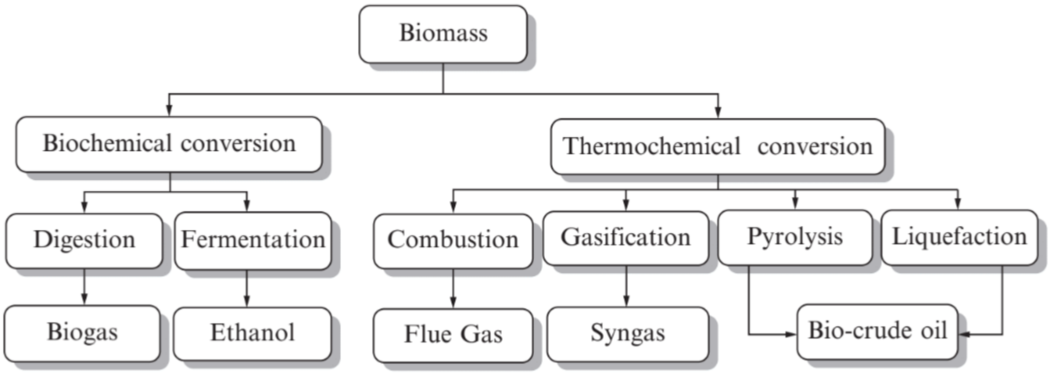

Figure 1.1: Biomass conversion methods and the respective products. [47]

Thermochemical conversion consists mainly of combustion, gasification and direct thermochemical liquefaction (DTL), that produces biocrude oil. DTL is divided in two technology groups: Hydrothermal Liquefaction (HTL) and Pyrolysis. Both of them proven to be viable solutions to produce relevant fuel types with environmental sustainability and economically feasible, as the production cost is only 20 - 50% higher than the average cost fossil equivalent. [53]

Biocrude, which refers to oil produced from HTL, consists of a dark viscous liquid which is immiscible with water, with a higher heating value (HHV) around 35-40 MJ/kg and high oxygen content when comparing to crude oil. Biocrude still requires significant upgrading to fulfill the requirements for drop-in transport fuel, due to the presence of heteroatoms and low hydrogen-to-carbon ratio. Therefore, an upgrading process is required for the biocrude to become compatible with the current transportation infrastructure. The most commonly used technology to upgrade the biocrude is hydrotreating, that is, reacting biocrude with hydrogen at high temperature and pressure in the presence of a catalyst. [10] [34]

1.1 Biomass feedstocks and conversion methods

Biomass is a renewable source of energy used to produce biofuels. The characteristics of biomass, such as moisture content, heteroatoms composition, bulk density, particle size/shape distributions, among others, will have a direct impact on the conversion technology and the composition of the biofuel [65]. Biomass includes a wide range of resources and is divided in three different generations.

The first-generation biomass is food-crop feedstock that is grown in arable lands, such as corn, sugar, starch, and grains. The use of first-generation biomass for the production of biofuel is controversial due to the possible competition between food and fuel. This competition can make the price of food to increase, with serious social consequences for the lowest social classes. The conversion processes in this generation are mainly biochemical processes, which result in production of biogas, biodiesel, syngas and others. Due to the mentioned controversy, the researchers started focusing on non-food crop feedstocks, second-generation biomass. [43]

The second generation biomass can be divided into two main groups, lignocellulosic biomass and organic waste, like sewage sludge and manure. The price for this feedstock is significantly lower compared to the first-generation biomass, however, due to its different composition, it may require more complex processing associated with higher capital costs. This generation focuses more in the use of thermochemical processes, although mostly still in pilot stages, being it HTL or pyrolysis. [43] [51]

The third-generation biomass applies to feedstocks that present a high energy dense per area of harvest than the first and second generation, such as algae and duckweed. The algae biomass presents lipid content around 80%, and this part can be extract and converted to fuel. Also, this feedstock is known by growing quickly, in reduced land and through photosynthesis, linked to the utilization of CO_2 as feed. [1] [43]

Among the various forms of biomass, each one with different advantages and disadvantages, a few of them are listed here according to the recent studies published in the biofuels field and also the process technology associated in each generation.

- **Sugar cane:** First-generation biomass that has proven to be promising for the future due to the production of biofuel, such as ethanol, that is commonly used for low level blends with transport fuel. This technology focuses mainly on biochemical conversion, where the sugar canes are crushed in water to separate the sugars from bagasse, that is burned after for the production of heat or electricity. The impurities from the sugar are removed and proceed to a fermentation process, where the sugars are converted to ethanol and CO_2. [55] [24]

- **Lignocellulosic:** This biomass is composed of plant matter and is widely used in the paper industry, presenting great potential for the production of biofuels. The biomass quality depends highly on the plant structure and is mainly composed of: cellulose, hemicellulose, lignin and small amounts of pectins, proteins and others. Both the cellulose and hemicellulose are composed of carbohydrates polymers. Hemicellulose is a polymer constituted of multiple sugars and with much shorter chains than cellulose, which is made of long chains of glucose. Lignin is commonly found in the cell wall, which fills the space between cellulose and hemicellulose, holding the plant together, and is composed of complex branched polymers. The use of the DTL technology with this biomass is highly viable for the production of liquid biofuel and maximize the feedstock utility. [9] [44] [58]

- **Sewage Sludge:** Organic waste includes biomass such as sewage sludge, manure, food and municipal waste. They present great economic advantage due to their low price, high availability and some can help alleviate the problem of waste management. The sewage sludge resource is composed of organic and inorganic matter, containing around 60-80% of organic matter and is mainly composed of proteins, lipids, and carbohydrates. Also other undesired elements can be found such as sulfur, nitrogen, and chlorine [42] [57]. These substantial amounts of lipids and carbohydrates show the potential for sewage sludge to be used as a resource for the production of biofuels, however, the presence of impurities will highly influence the fuel quality. [45] [41] [70]
- **Algae:** Algae is a third-generation feedstock and consists of a diverse group that varies from unicellular to multicellular. Algae are an aquatic photosynthetic organism that utilizes sunlight and CO_2 to produce energy. This biomass presents a high lipid content, that can be extracted to produce biofuel. The main advantage of this resource is that it presents a fast growing rate, requires a small area and has high photosynthetic efficiency [19]. The biggest problem is the cost of harvesting and the large amount of water required for its production. It is estimated that the harvesting and dewatering account for 90% of the equipment cost for the production of open pound algae. Due to its high water content, thermochemical processes that require wet environment for the reaction, such as HTL, are favoured. [10] [64] [16]

Among the different generations explained, the ones that stand out the most are the second and third-generation feedstocks due to their abundance and non-competitiveness with food crops, to be used as feedstock for DTL. [59] [62]

1.2 Drop-in Biofuels

Through out this report the term drop-in biofuel is going to be widely utilized. According to the IEA (International Energy Agency), drop-in biofuels can be described as: [39]

> "Drop-in biofuels are liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure."

This means that drop-in biofuels are renewable fuels which can be blended with crude oil products and also can be used in the current infrastructure of pipelines, pumps and other equipment of petroleum refineries. This is not the case for traditional biofuels, like bioethanol and fatty acid methyl esthers (biodiesel). Compared to drop-in biofuels, traditional biofuels have various limitations: [39]

- Are inappropriate for use in sectors such as aviation, as they do not meet some fuel specifications, like density requirements for example.
- Are mainly derived from first generation biomass, which are "food-based" as mentioned. This creates issues around competition with food, while other types of feedstocks like wastes and lignocellulosic biomass are much more abundant.

In order to produce drop-in biofuels, biomass must go through different processes, as Figure 1.2 shows for lignocellulosic biomass.

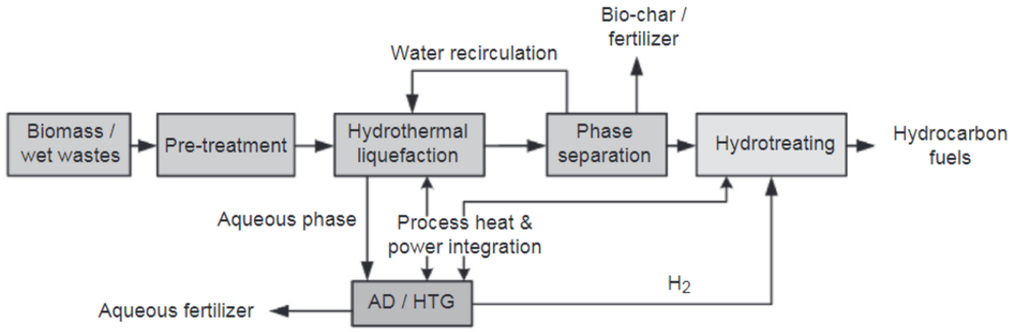

Figure 1.2: Process flow diagram of the path from lignocellulosic biomass feedstock to drop-in biofuels. [4]

Out of the presented processes, this study will focus on the hydrotreating stage, while out of the two processes in the DTL, this project will use biocrude produced by HTL technology, as the figure suggests, that is better explained in the next section.

1.3 Hydrothermal Liquefaction

HTL consists on a reaction of biomass in the presence of water at hydrothermal conditions, that is, temperature ranging from 200 to 500ºC and pressure 5 to 30 MPa [66]. At theses conditions the organic materials undergo a series of physical and chemical treatments resulting in four products: gas phase; biocrude, aqueous phase and solid phase [61]. Figure 1.3 shows a simple HTL process scheme and the obtained products:

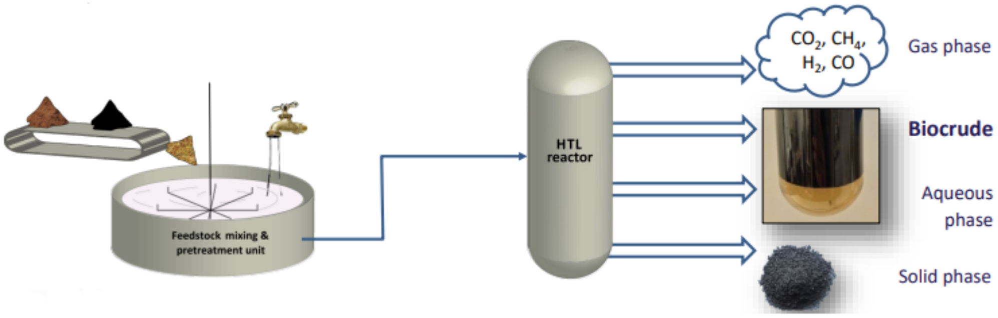

Figure 1.3: HTL process scheme and its products. [61]

The main advantage of HTL process is that it occurs in a wet environment. This enables the use of wet feedstocks in which additional pretreatment such as drying process becomes unnecessary [66]. HTL biocrude presents a lower oxygen content, around 10%, compared to 40-50% in the pyrolysis process, also lower water content and other beneficial characteristics making it a more promising technology to produce drop-in bio-fuels.[34].

At hydrothermal conditions, water experiences a nonlinear change in thermophysical properties, that can be seen in Figure 1.4. For water, the critical point is at P_{cr} = 22.064 MPa and T_{cr} = 373.95°C, represented by the red dot in the image. At this stage, the saturated liquid and saturated vapor are identical and cannot be distinguished. If those parameters are exceeded, the medium will be in supercritical conditions, otherwise it remains subcritical. [50]

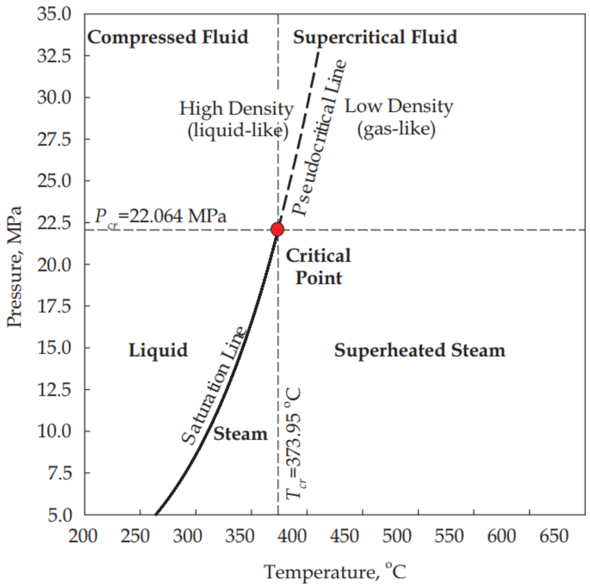

Figure 1.4: Water critical point [50]

One of the parameters to evaluate the water solubility is the dielectric constant. The water dielectric constant drops with the increase of temperature, specifically from 78 at atmospheric conditions to 6 at the critical point and to around 2 at supercritical. In other words, from a polar, highly hydrogen-bonded solvent in ambient conditions, water changes to behavior more typical of a non-polar solvent like hydrocarbons when at critical conditions. Thus, the solubility of organic compounds in water will increase as the temperature and pressure increase. Therefore, in supercritical state and in near critical conditions, it is possible to dissolve organic matter that does not dissolve in water under atmospheric conditions, which results in a homogeneous reaction environment, where mass-transfer limitations are minimized and much higher reactivity is achieved. [11] [50]

HTL biocrude shows yields between 20-50%, depending on the chemical composition of the biomass and the process conditions. The biocrude still requires to be upgraded through hydroprocessing, due to its high viscosity, low HHV and poor thermal stability making it impossible for it to be directly used.[11] [34]

1.3.1 Biocrude composition depending on the feedstock

The HTL biomass will undergo three basic steps: [25]

- **Depolymerization** of the long structure chains of polymers into shorter chains.
- **Decomposition** step involving dehydration, decarboxylation and deammination, forming water soluble content and gases.
- **Repolymerization** of the reactive substances.

Different compounds will have different reaction patterns, with these paths strongly determining the characteristics and behavior of the produced biocrudes, according to the initial composition of their feedstocks.

Cellulose

The cellulose is a long chain of Polysaccharides, denoted by $(C_6H_{10}O_5)_n$, which have high molecular weight and high polymerization order. Figure 1.5 shows two long cellulose chains and hydrogen bonds within them. Cellulose presents strong intramolecular hydrogen bonds, resulting in a stiff structure. This means that it will require high energy amounts to break these bonds and also the strong intermolecular bonds between adjacent cellulose molecules. These intermolecular bonds act as non-polar compounds at ambient temperature, however, with the increase of the temperature tend to be more soluble. [25] [6]

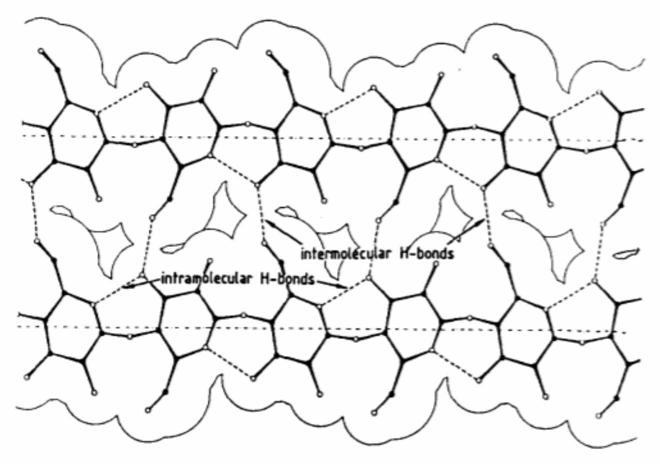

Figure 1.5: Intermolecular and intramolecular hydrogen bonds in two cellulose chains [6]

The ether bonds of cellulose start to decompose around 200-250°C, and around 280°C all the cellulose is completely decomposed. The main products obtained are products of glucose, C3-C6 sugars, aldehydes and furans. [60] [54]

Hemicellulose

Hemicellulose is a branched polymer composed of many pentoses and hexoses. The hemicellulose, compared to cellulose, is less stabilized by hydrogen bonds allowing easier disintegration of the polymers [54]. The main chains of hemicelluloses are frequently composed of pentoses, mannose, glucose and galactose. The side chains are made of functional groups responsible for the solubility of the hemicellulose in the aqueous phase, such as acetic acid, pentose, hexoses, heruronic acids and deoxyhexoses [6]. Figure 1.6 represents a simple chain of hemicellulose and its side chain:

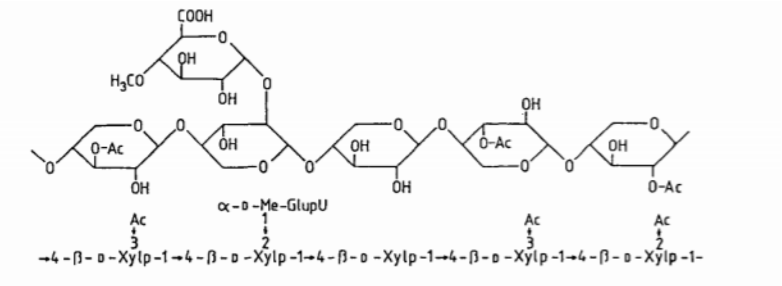

Figure 1.6: Hemicellulose compostion in hardwood.[6]

Hemicellulose starts to decompose in water at temperatures below 200°C, and around 230°C close to all the hemicellulose is converted. The main degradation products obtained are gycolaldehyde, gyceraldehyde and dihydroxyacetone. [60] [54]

Lignin

The other main fraction of lignocellulosic biomass is lignin, commonly referred as an aromatic compound, where ethoxy groups and phenyl-propane with hydroxyl groups are linked with ether bonds. Three basic building blocks sum up all of lignins, trans-p-coumarlyl alcohol, coniferyl alcohol and sinapyl alcohol. Due to its complex and cross-linked structure, lignin is very resistant to degradation. Lignin presents higher energy content than the other two components, leading to a higher heating value in the products [25]. Figure 1.7 represents a lignin structure, composed by many phenolic compounds, which possess several oxygen-containing molecules.

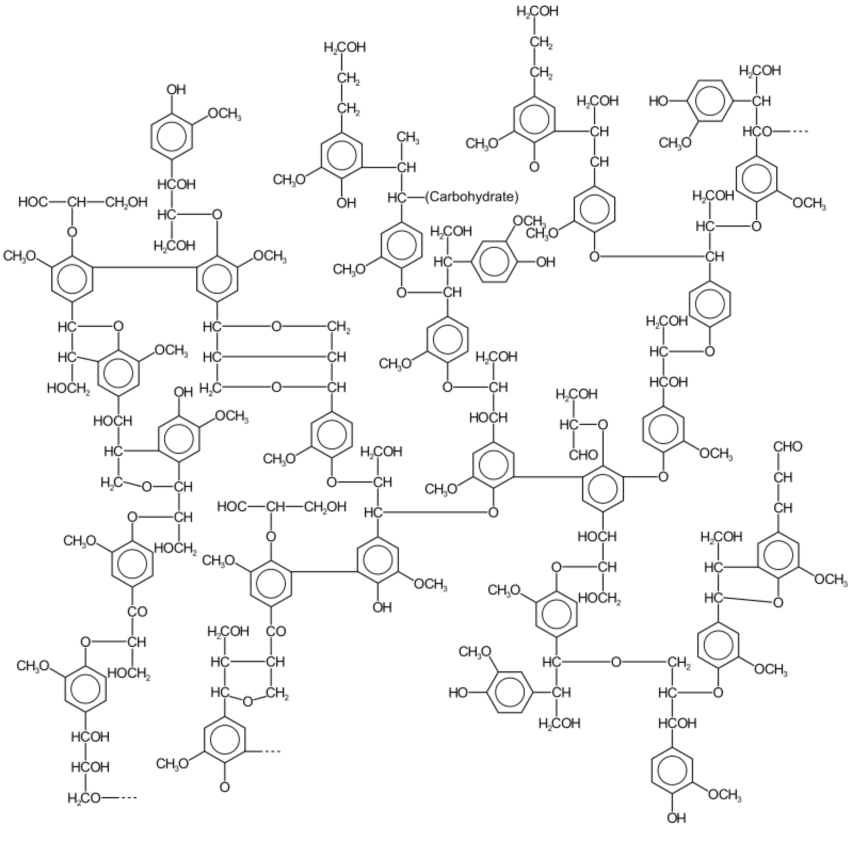

Figure 1.7: Example of a lignin structure. [23]

A significant part of the lignin starts to decompose below 200ºC and forming various phenols and methoxy groups, by hydrolysis of ether-bonds. The lignin is responsible for the formation of solid residues at hydrothermal conditions. In studies at hydrothermal conditions that lignin was converted, between 58-79% of organics are dissolved in the water phase and around 12-37% become solid residues[6]. Most of the products obtained resulted of phenol deviates and methoxy groups, such as, 3,4-dimethoxy-phenol, 2-methoxy-phenol and 1,2-benzenediol [60]. In the study done by Zhang et al. [68] in hydrothermal treatment of kraft pine lignin, the solid formation was due to the condensation of phenolic products of the lignin degradation.

Lipids

Biomass such as algae is mainly composed of lipids. These components are non-polar compounds at atmospheric temperature, however with increase of temperature tend to become more polar.[25]

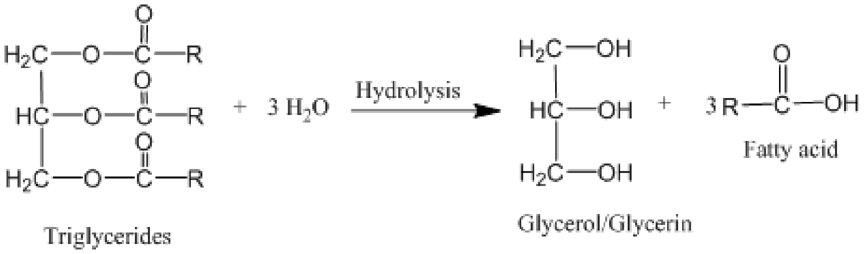

Figure 1.8: Hydrolysis of triglycerides. [28]

At hydrothermal conditions, the triglycerides are decomposed into triesters of fatty acids and glycerol, a major co-product in biodiesel production, as represented in Figure 1.8. Further degradation of the glycerol leads to the conversion to acrolein, allyl alcohol, ethanol, acetaldehydes, formaldehyde and other gaseous products, such as, carbon monoxide, carbon dioxide and hydrogen. Fatty acids are thermally stable, however are still partly degraded at hydrothermal condition to produce long-chains of hydrocarbons.[60] [25]

Proteins

Proteins are a major constituent of different kinds of biomass, found mainly in organic waste, algae, food crops and in small portions in lignocellulosic biomass. Proteins consist of polymers of amino acids and present peptide bonds that link amino acids together, through an amide bond between carboxyl and amine groups. The degradation of the amino acids, due to their high complexity and strong bonds, is challenging. Figure 1.9 shows the different paths that an amino acid can be decomposed:

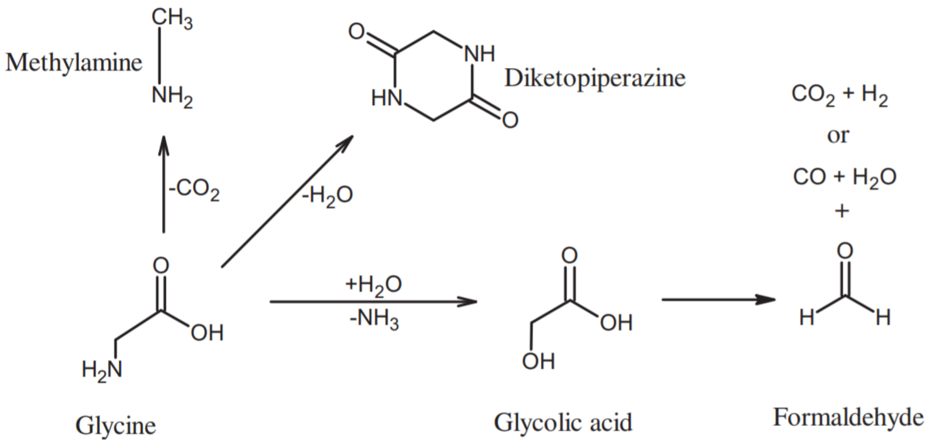

Figure 1.9: Decomposition of an amino acid glycine. [60]

The proteins are also associated with the production of large amounts of nitrogen heterocycles, pyrroles and indoles [3]. Upon the HTL reaction, the protein undergoes decarboxylation and deamination reaction, as can be seen in Figure 1.9. These reactions contribute for the removal of oxygen and nitrogen, improving the quality of the oil products. These reactions lead to the formation of hydrocarbons, amines, aldahydes and acids. [25] [60]

Biocrude produced from second and third generation biomass, as expected, are significantly different between each other. Lignocellulosic materials are mainly composed by cellulose, hemicellulose and lignin, therefore the biocrude composition is characterized by a high level of oxygen, due to the presence of sugars and many phenolic compounds, that derive from lignin, also a very low or non-existent values of nitrogen and sulfur [10]. This resource presents high potential, due to its large abundance and by being an alternative for disposal of paper/agriculture/forest residues [33].

Other biomass composed of lipids and proteins, such as sewage sludge, manure and algae, present a large content of nitrogenated species due to the association with proteins. The presence of lipids and proteins is also associated with a high conversion rate in the formation of bio-oil compared with carbohydrates [3]. This biomass results in a more stable bio-oil, with lower oxygen content, however it contains parts of nitrogen and sulfur compounds, that are undesirable contaminates for fuel production. The use of waste resources can also alleviate their disposal expenses. [10] [33]

HTL shows various benefits comparing to pyrolysis, including superior conversion efficiency, better product quality in terms of co-processing potential in existing refineries and, most importantly, the high costs of evaporating water (in order to dry the feedstock) are completely avoided [31]. This study will focus on the upgrading of HTL biocrude. This upgrading process is done through hydroprocessing, basically processing the biocrude obtained from HTL with hydrogen, which the next section will go deep into.

1.4 Hydroprocessing

Hydroprocessing involves a large group of processes in which pressurized hydrogen is used to manipulate oil properties, in the presence of a catalyst. Within these various processes, the main reactions that occur can be divided as hydrogenation (HYD), hydrodeoxygenation (HDO), hydrodenitrogenation (HDN), hydrodesulfurization (HDS) and hydrocracking. The first four reactions can be agglomerated into hydrotreating, which can be defined as removal of heteroatoms and saturation of carbon-carbon bonds, while hydrocracking breaks down complex hydrocarbon molecules.

1.4.1 Hydrogenation

HYD can be described as saturation of carbon-carbon bonds. This means the addition of pairs of hydrogen atoms to a molecule, often an alkene as presented in Figure1.10:

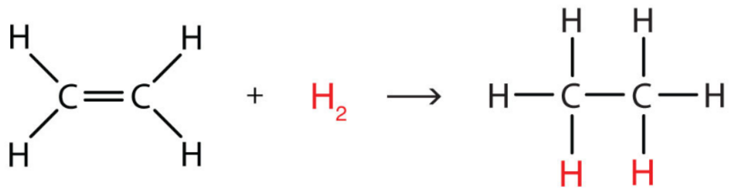

Figure 1.10: Example of hydrogenation reaction. [48]

Basically, HYD reduces double and triple bonds in hydrocarbons. These are redox reactions, often highly exothermic, which can be thermodynamically favorable. The presence of a catalyst is essential for the feasibility of this reaction.

1.4.2 Hydrodeoxygenation

Deoxygenation is the main objective of the hydrotreating process that biocrude has to go through. HDO can be defined as removal of oxygen atoms, replacing it with hydrogen bonds.

Both operation conditions and hydrogen consumption needed to achieve high HDO conversions depend, not only on the oxygen content of the biocrude, but also on the type of existing oxygen-containing compounds in the oil [21]. Different oxygenates possess different HDO reactivity, which also means different hydrogen consumptions. Figure 1.11 orders different oxygenates according to their HDO reactivity and the associated hydrogen consumption for complete deoxygenation: [34]

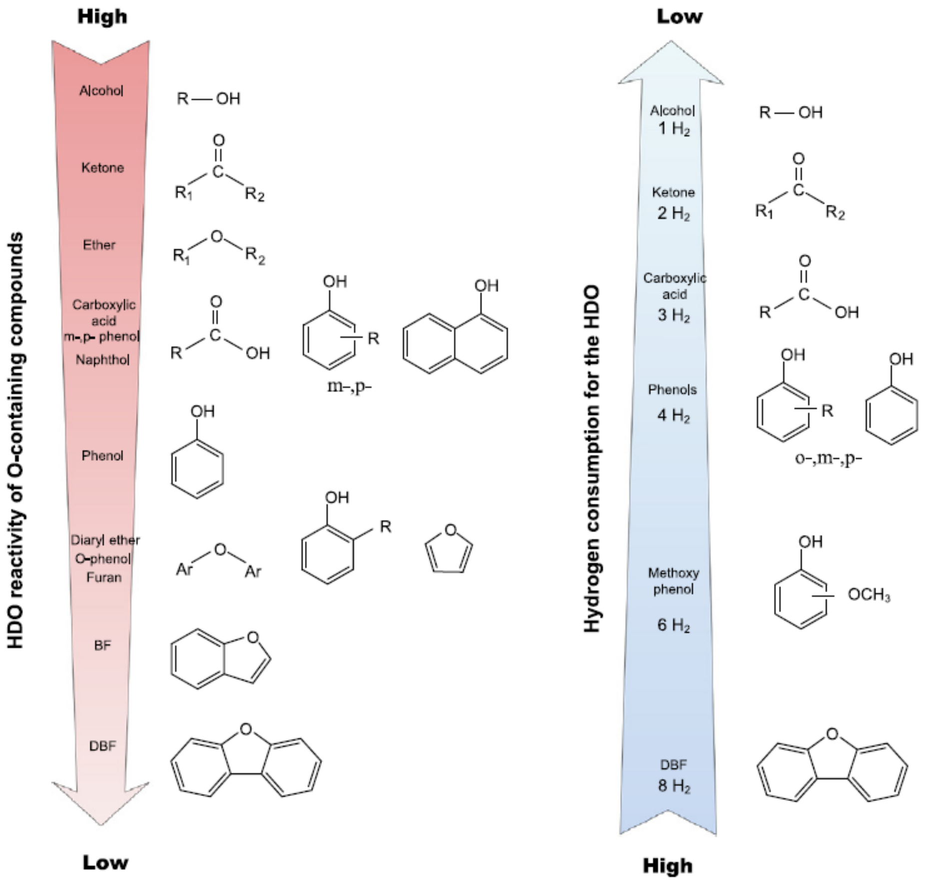

Figure 1.11: HDO reactivity and hydrogen consumption required for deoxygenation of some different oxygen-containing compounds by HDO. [34]

Oxygen causes coke and soot formation and promotes polymerization, which leads to failure in engines and combustors. Moreover, oxygen increases oil polarity, making biocrude, which contains considerable content of oxygen, poorly miscible with fossil streams.

1.4.3 Hydrodenitrogenation

HDN is characterized as the process of removing nitrogen atoms from oils, most commonly petroleum. Nitrogen-containing compounds can cause contamination of catalysts during refinery and later, upon combustion, generate a pollutant, NOx, and that is why its removal is required. In order for denitrogenation to be feasible, various hydrogenation reactios of different structures have to occur, as Figure 1.12 presents:

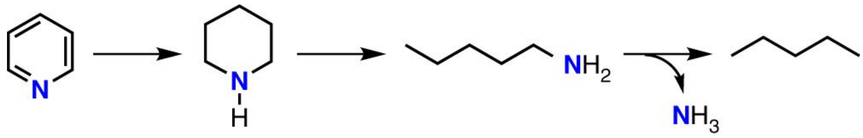

Figure 1.12: Example of a hydrodenitrogenation process. [48]

Nitrogen-containing compounds are classified as non-heterocyclic and heterocyclic, with the non-heterocyclic compounds showing a higher HDN reactivity. Just like it was explained for the HDO, higher reactivity will result in lower hydrogen consumption, as Figure 1.13 shows.

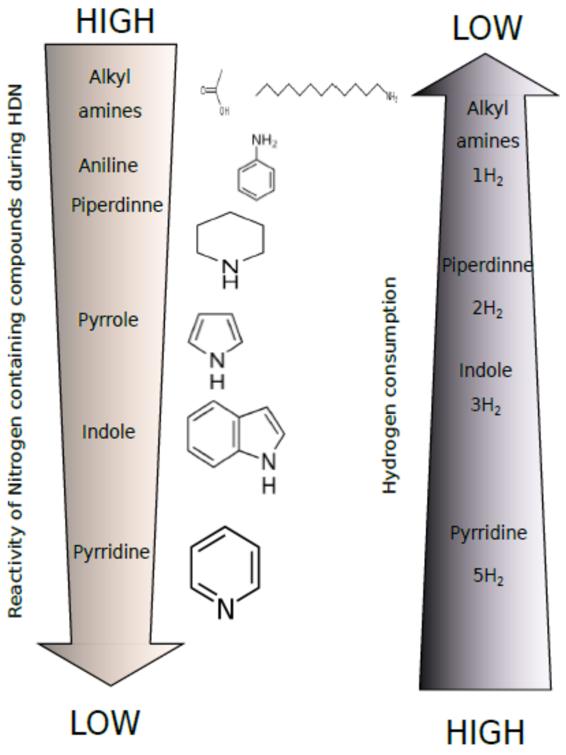

Figure 1.13: Reactivity of some nitrogen containing compounds and though HDN [22]

1.4.4 Hydrodesulfurization

HDS is a catalytic process extensively utilized for removal of sulfur atoms from petroleum and natural gas. The main reason for this process is minimizing the emissions of SOx gases upon combustion of the fuel, which are extremely pollutant. Moreover, even small sulfur content can poison the noble metal catalysts exisiting in catalytic reformers within a crude oil refinery.

Sulfur removal is the main objective of the hydrotreating process of petroleum, while the contrary is true for the upgrading of biocrudes, where the hydrotreatment is focused on deoxygenation and denitrogenation, with the HDS reaction being of lesser importance for this study, although some biocrudes, like algae, may contain none negligible S content.

1.4.5 Hydrocracking

Hydrocracking can be outlined as a severe form of hydroprocessing that breaks carbon-carbon bonds and reduces molecules weight. Average molecular weight decreases and yields of fuel products increase. It can be seen as the sum of catalytic breaking and hydrogenation, as Figure 1.14 suggests:

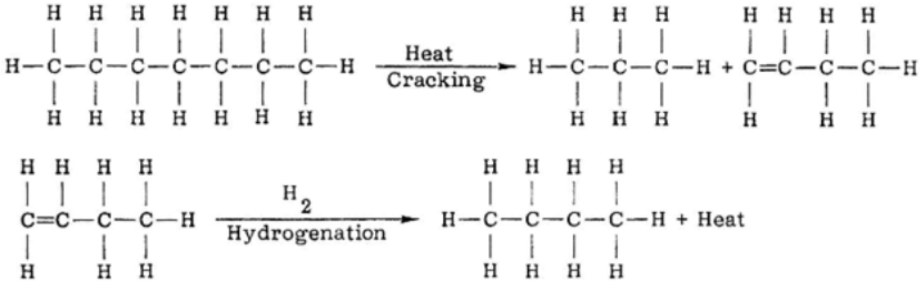

Figure 1.14: Example of a hydrocracking process. [13]

Cracking and hydrogenation are complementary, with the cracking reactions providing alkenes for hydrogenation, while hydrogenation supplies heat for cracking. Cracking reaction is endothermic, while hydrogenation is exothermic.

1.5 Hydrotreating

Catalytic hydrotreating is a process which consists of removal of impurities, such as sulfur, oxygen, nitrogen and metals, from liquid petroleum fractions. These contaminants have prejudicial effects on the quality of the final product, as the oxygen content represents instability in fuel combustion, nitrogen and sulfur being connected to environmental concerns, having harmful emissions of NOx and

SOx in the fuel combustion respectively, but also on the refinery equipment and on the used catalysts. For this reason, hydrotreating is usually performed before additional processes such as catalytic reforming so the catalyst will not be contaminated by untreated feedstock. Even though being mostly connected to petroleum refinery, in the recent decades the hydrotreating process has been studied as an upgrading strategy for biocrudes, in order to produce drop-in biofuels. [21] [63]

The hydrotreating process in petroleum refineries is typically carried out at temperature and pressure ranging around 300-600ºC and 3.5-17 MPa respectively [17], and in the presence of a catalyst. For petroleum, this process is specially employed in order to remove sulfur, being normally called as HDS. However, for biocrude the main objective is the removal of oxygen, and for some feedstocks also nitrogen, which means that the process in this case will focus on HDO and HDN instead. As mentioned above, the heteroatoms content strongly depends on the biomass feedstock of the biocrude. This means that these conditions are not appropriate for bio-oils, as biocrude is extremely unstable at high temperatures, becoming highly viscous and possibly occuring phase separation, while the probability of coke formation at high temperatures and pressures is also very elevated. Coke formation can be really troublesome, as it may plug reactor and refinery components while also deactivating catalysts by depositing on their active sites. [17]

For algae and sewage sludge biomass the nitrogen content is considerably high and the denitrogenation process is of extreme importance, while for lignocellulosic biomass it is quite low and the focus is mostly placed on oxygen removal. As this study will use HTL biocrude from miscanthus, a type of lignocellulosic biomass, HDO will be the main focus of the hydrotreating process. [18]

The oxygenates present in lignocellulosic HTL biocrude have, for the most part, medium to high HDO reactivity, such as alcohols, carbonyls, phenols and carboxylic acids [31]. This is very suitable, as the deoxygenation process becomes less expensive by requiring eased operation conditions and having a lower hydrogen consumption. However, some oxygenates are also expected in the higher boiling fractions, presumably as part of the residue fraction. HDO for these compounds has a higher hydrogen consumption along with more severe operations conditions, because of the need for HYD to take place for the aromatics. [34]

1.5.1 Biocrude deoxygenation and its implications

The deoxygenation of biocrude is obtained through three different reduction reactions, which are the previously mentioned HDO plus decarbonylation and decarboxylation. During HDO, hydrogen is oxidized, resulting in the oxygen being removed as water. In decarbonylation, oxygen is removed as carbon monoxide along with a water molecule. For decarboxylation, the carboxyl group is oxidized, with the oxygen removal happening as carbon dioxide production. Figure 1.15

presents examples of these three reactions:

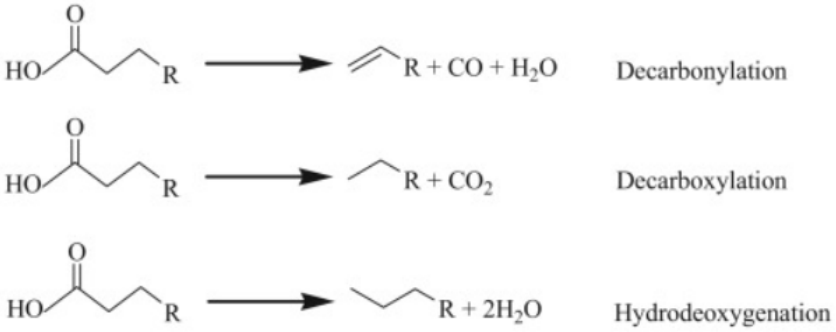

Figure 1.15: Deoxygenation reactions. [49]

When decarbonylation and decarboxylation occur, carbon content is lost, resulting in a reduced hydrocarbon yields. While the input of hydrogen in order to remove oxygen usually results into a higher yield of hydrocarbons, however the hydrogen consumption has to be controlled for cost reduction and enhanced sustainability. In sum, the objective of the hydrotreating process is, not only heteroatoms removal, but also to enrich carbon chains with hydrogen, with the purpose of raising the hydrogen to carbon ratio (H/C ratio). This parameter will be further developed in the next subsection, nevertheless, this ratio should be close to the values for the refined petroleum products.

It is important to mention that the produced gases during the deoxygenation process (CO and CO_2) must be removed, otherwise some issues may come up, like modifying the hydrogen partial pressure, corrosion and inhibition of catalyst activity. Moreover, at very high temperatures, carbon monoxide can react with hydrogen and produce methane, increasing hydrogen consumption. [17]

1.5.2 Effective H/C ratio

The hydrogen to carbon ratio is a useful parameter used in the petroleum sector to evaluate the energy density of fossil feedstocks along with how hydrogen rich they are. This metric reflects the oxidation state of the molecule, so it describes the energy that will be discharged by its combustion. However, biocrudes are highly oxygenated, and during the combustion the oxygen will consume hydrogen, producing water and reducing the H/C ratio. One atom of oxygen consumes two atoms of hydrogen, to form H_2O molecule, which does not contribute any energy to the combustion system. For this reason, the effective hydrogen to carbon (H_{eff}/C) ratio is introduced, taking into account the oxygen content. It is calculated using the equation 1.1: [40]

$$H_{eff}/C = \frac{n(H) - 2n(O)}{n(C)} \tag{1.1}$$

During the hydrotreating process, the H/C ratio of the biocrude has to be elevated up to the values of gasoline, diesel and jet fuels, which are around 2, as Figure 1.16 shows. It presents a "staircase" where each step represents hydrogen inputs required to obtain the final fuel, along with the H_{eff}/C for different biomass feedstocks:

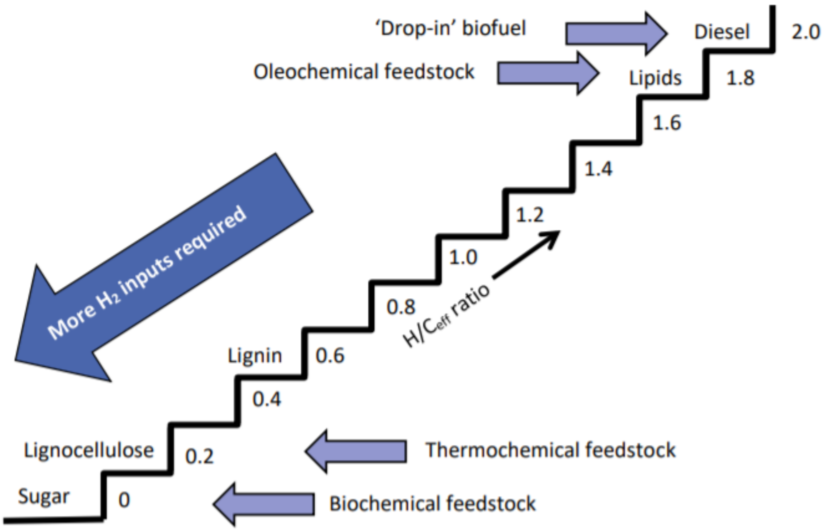

Figure 1.16: Hydrogen to carbon ratio "staircase" for different feedstocks. [17]

This "staircase" can serve as a rough indicator of the extent of upgrading that normally will be needed to produce a deoxygenated drop-in biofuel. However it is a simplified analysis parameter, as for example ethanol and butanol both have a H_{eff}/C of 2 but still need considerable deoxygenation to obtain drop-in biofuels. [40]

1.5.3 Multi-stage process

As previously mentioned, biocrudes are thermally unstable and possible polymerization and coking may occur at the temperature conditions of the hydrotreating process. In order to prevent this, a two-stage biocrude upgrading method can be used to stabilize and fully deoxygenate the biocrude.

The first stage happens at lower operation conditions and has the objective of stabilizing the biocrude by, following Figure 1.11, reacting with the oxygenates with high HDO reactivity. This stage usually removes most of the water of the oil, with the resulting hydrophobic liquid being more stable and able to deal with further catalytic upgrading. The second stage occurs at more severe conditions with the purpose of fully deoxygenating the biocrude, reacting with the remaining medium and low HDO reactivity oxygenates.

The parameters that boost the possibility of coking are high temperatures and pressures along with low H/C ratio compounds and highly oxygenated molecules. Double bond molecules like alkenes, ketones and aldehydes are also extremely susceptible to polymerization and coking. The objective of the first stage is also to hydrogenate these molecules in order to enhance the biocrude stability before the second stage. [39]

The hydrotreating process has various positive outcomes, as increasing the bio-oil HHV and decreasing its water content, bulk density and viscosity. These benefits result in a higher H/C ratio of the produced oil along with higher HHV [18]. With the hydrotreating process explained, it remains to investigate on how to utilize the upgraded bio-oil. It is widely accepted that the biofuel should be delivered as finished, a drop-in biofuel, however this option is still overly expensive. Other strategy is to upgrade the biocrude to a point where it is compatible for co-processing with petroleum at existing refineries, without necessarily being completely hydrotreated (drop-in biofuel). This possibility is presented in the next section.

1.6 Co-processing of biocrude in existing refineries

A method to ensure competitive prices for drop-in biofuels is to co-process the biocrude with crude oil at existing refineries. The heterogeneous nature of biomass leads to various biocrude compositions, which creates issues for products with high specifications such as fuels in refineries. At this point in time, in order to reach market penetration, it is favorable to cooperate with the crude oil industry instead of competing against it. [34]

As refineries are optimized to the specific crude feed and also to the targeted market, hydrotreatment of the biocrude prior to the co-processing is essential in order to meet conventional petroleum requirements before introducing it in the refinery streams. As already mentioned, in this process the focus is placed on oxygen removal (deoxygenation), as conventional petroleum refineries are not developed to deal with oils with high oxygen content, that would create corrosion issues during refining. [31]

An ideal outcome to enhance co-processing compatibility of biocrude is to utilize milder operations conditions of hydrotreating, reducing the cost of the process, and remove all medium to high HDO reactivity oxygenates so that the co-process at an existing refinery is possible. The only remaining oxygenates would be the low HDO reactivity ones, most likely present in the residue fraction, that consume large ammounts of hydrogen and require severe process conditions. These oxygenates could be then converted at refineries, where robust process units would remove the remaining heteroatoms and lower the boiling point by cracking reactions. [34]

The main idea is that the operating conditions of the hydrotreating process can be tuned in order to adjust the final product characterisitics, in order to achieve either drop-in biofuels or co-processing compatible upgraded bio-oils.

1.6.1 Refinery's point of view on co-processing

For the petroleum refinery, biocrude is seen as a possible alternative feedstock, if the decrease in petroleum quality results in high expenses for the crude oil processing, but also a feedstock that goes into accordance with the world's demand of renewable fuel production. Biocrudes can be included in the class of opportunity crudes, which have both TAN (total acid number) and overall density higher than crude oil, not being necessarily renewable, but HTL biocrude usually matches their characteristics. Due to their worsen fuel properties, opportunity crudes are usually sold at lower prices compared to petroleum. However, this will not be the case for biocrudes, due to their sustainability element, but also to the fact that when mixing biocrude with crude oil, CO_2 production is reduced and so are the costs of the process. [34]

The remaining question is where exactly in the refinery should the biocrude be inserted in order to co-process it with the crude oil. Each refinery is designed in its own way, depending on the characteristics of the used petroleum, which means that the requirements for the upgrading of the biocrude depend on the specific refinery it is going to be introduced into. Also, the heteroatoms content in crude oils rises along with the boiling point, significating that the heteroatoms removal in petroleum refineries is mostly placed in the heavy boiling fractions. [34]

Heteroatoms in HTL bio-oil are evenly distributed through all the boiling fractions [31], which is an issue for a possible early co-processing. The biocrude in order to blend with petroleum needs to have a similar distribution of heteroatoms [34]. To address this problem, hydrotreating is introduced as an intermediate stage for the biocrude to be upgraded and become more compatible for co-processing. Before possible insertion points are addressed, a small introduction on the different stages of a petroleum refinery is going to be performed.

1.6.2 Conventional Petroleum Refinery

Building refineries solely focused on biofuels is an impossible approach in the present days, due to logistical issues, requiring quite some time, and economical reasons, with a very high investment being at hand. A much more convenient way for a short-term perspective is to use already existing petroleum refineries to execute part of the process of biofuels production. Co-processing fossil crude and biocrude at existing refineries is considered to be a very promising method to achieve implementation of drop-in biofuels in the market, by lowering the production costs. [53]

A deeper look into the conventional petroleum refinery has to be performed to understand the process in more detail, with the objective to study possible biocrude insertion points among other parameters and characteristics. Figure 1.17 presents a simplified scheme of the different processes that occur in a refinery. These processes can be divided into separation and conversion processes, being described as: [53] [59] [63]

- Separation Processes
  - **Atmospheric Distillation:** Desalted crude oil goes through an atmospheric distillation unit and is divided into many fractions according to their boiling points, resulting in liquefied petroleum gas (LPG), straight-run naphtha (SRN), straight-run kerosene (SRK), straight-run gas oil (SRGO) and residue. These are denominated as the straight-run products.
  - **Vacuum Distillation:** The atmospheric residue is fractionated in vacuum conditions (lower pressure leads to lower boiling points), resulting in vacuum gas oil (VGO) and vacuum residue.
- Conversion Processes
  - **Hydrotreating:** Uses hydrogen to extract impurities such as nitrogen, sulfur and oxygen. For crude oil it is mostly focused HDS.
  - **Reforming:** Converts desulfurized naphtha molecules into higher-octane molecule to produce reformate, which is a component of the end-product gasoline. Hydrogen, a significant by-product, is separated from the reformate for recycling and use in other processes. (Mostly used for heavy naphtha)
  - **Isomerization:** Converts linear molecules into higher-octane molecules for blending into gasoline. (Mostly used for light naphtha)
  - **Merox process:** Desulfurization process for kerosene and jet fuel.
  - **Hydrocracking:** Cracking of heavy oil fractions to produce, in the presence of catalyst and hydrogen, lighter and more valuable reduced viscosity products with lower boiling products.
  - **Fluid Catalytic Cracking:** Heavy oil fractions go through catalytic cracking to produce lighter and lower boiling point products. Main incentive for catalytic cracking is the need to increase gasoline production.
  - **Coking:** Severe thermal cracking of very heavy residual oils resulting in gasoline and diesel fuel, leaving solid coke as residual product.

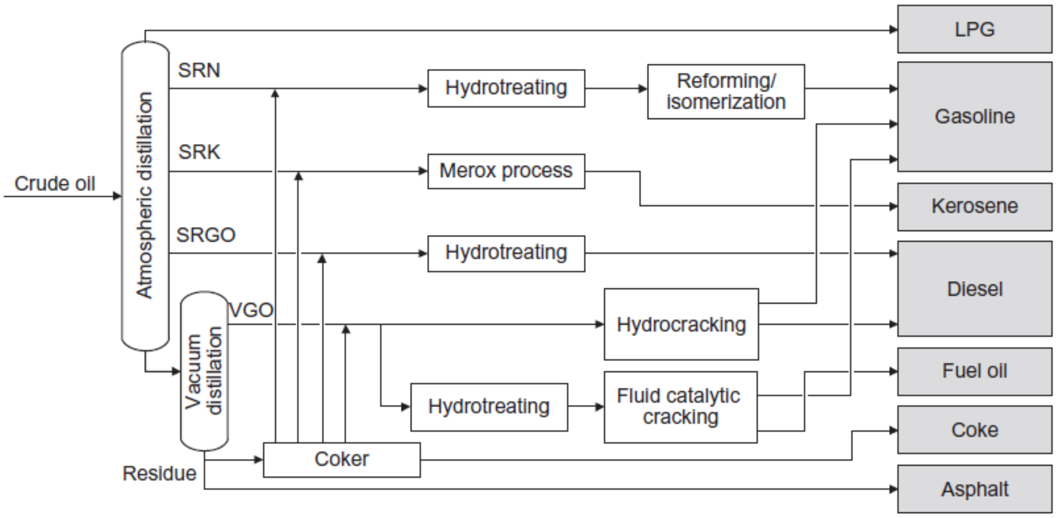

Figure 1.17: Simplified process scheme of a conventional petroleum refinery. [53]

1.6.3 Assessment on possible insertion points

There are various possible insertions points in a refinery, as seen in the last subsection, however each location represents certain risks to the refinery. In Figure 1.18 a simple case with three different insertion points is presented, along with a scale of potential risk to the refinery infrastructure:

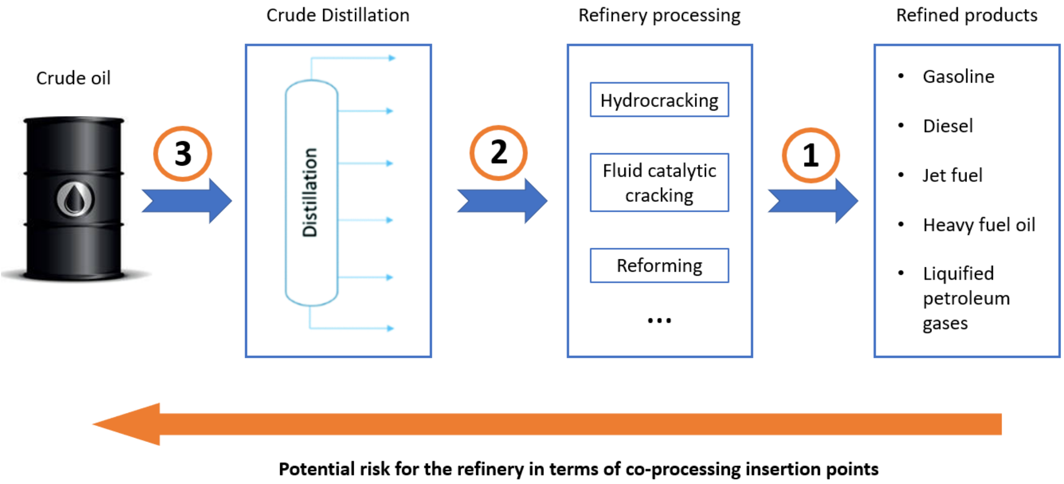

Figure 1.18: Possible insertion points for co-processing and correspondent risks for the refinery.

This is a simple scenario for just three different insertion points, with the risk for the refinery increasing with how early in the process the upgraded biocrude is introduced. These insertion points can be characterized as, according to Figure 1.18 numeration:

1. The first insertion point is only for finished drop-in biofuels. As mentioned, this means that the biocrude has been completely hydrotreated and is totally compatible with petroleum engines. These entirely upgraded biocrudes are usually used for blendstocks with other products from the petroleum refinery, as the image suggests. As previously mentioned, this is the most studied and used method in the majority of the literature, as biofuels are mostly delivered as finished transport grade fuels.

2. The second point relates to the possibility of inserting the bio-oil in intermediate processes of the refinery. Usually, for this case, the most used methods are to introduce the bio-product either before the FCC or before the hydrocracking stage. However this scenario is not ideal, as upgraded HTL biocrude is too valuable to be blended with residue from the atmospheric distillation. The risks with this insertion point also increase, as for example the hydrocracking reactors are very sensitive to oxygen content, with possible contamination to the catalysts among other issues for the refinery.

3. The third insertion point represents the best case scenario relating to co-processing but also the one with the most risk for the refinery. For example, if the introduced bio-oil contains some sort of contaminant, the possible contamination can spread throughout the all refinery. At this stage of the refinery, the biocrude has to be basically free of any oxygen, contaminants and reactive species (like alkenes and high HDO reactivity oxygenates for example). Other factor, as mentioned above, is the fact that the heteroatoms distribution in crude oil increases with the boiling point, while for HTL biocrude it is virtually evenly distributed through all the boiling fractions. For the blending of petroleum and the upgraded biocrude to be possible, making this insertion point a feasible option for co-processing, the heteroatoms distribution of the biocrude must be similar to the one of crude oil.

Outside of trying to establish a more efficient upgrading process for mischantus HTL biocrude, the objective of this study is also to assess the best way to proceed with the obtained products from the different operation conditions tested during the experiments. In fact, different severity of hydrotreating lead to different characteristics of the upgraded oil, being possible for it to be compatible with co-processing before the distillation or, if totally hydrotreated, turnout to be a totally finished drop-in biofuel.

1.7 Fuel Boiling Points

Crude oil is a complex mixture of several hydrocarbons that throughout the years are contaminated with other undesired compounds such as sulfur, nitrogen, oxygen and metal [52]. Being mainly composed of carbon and hydrogen, the hydrogen to carbon ration affects the crude oil physical properties. If the ratio of H/C is low, higher the boiling point of the hydrocarbon will be. Therefore the hydrocarbons are separated in different groups, defined by their boiling point ranges. These groups of hydrocarbons, after being divided in different fractions, undergo specific treatment to obtain the desired end product. Figure 1.19 represents the different fractions of fuel according to boiling point and their final products: [38]

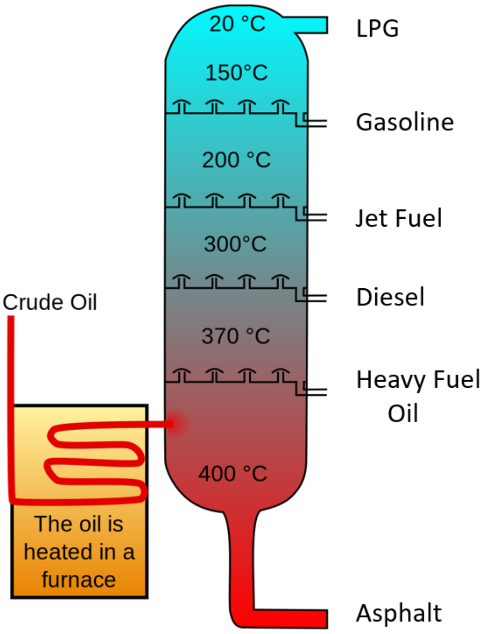

Figure 1.19: The different boiling point for each hydrocarbon fraction. All of the fractions are processed further in other refining units resulting in the respective final product.

In order to use the fuel, it is necessary to evaluate various parameters, such as octane number, viscosity, sulfur content, cetane number and other factors. The different fuels, represented in the Figure 1.19, can be evaluated as: [20]

- **Liquefied petroleum gas:** This group presents the lowest carbon number and has the lowest boiling point. It is mainly composed of ethane, propane and butane. Typically containg hydrocarbons with 1 to 4 carbons.
- **Gasoline:** The gasoline is classified based on the octane levels. The octane measure is the resistance of petrol to autoignition in spark-ignition engine.

Higher the octane level, higher the gasoline rating. Contain hydrocarbons with 4 to 12 carbon atoms per molecule.

- **Jet fuel:** Jet fuel are produced to a standardized international specification. Consists in a mixture of a variety of hydrocarbons and its main restriction is the freezing point. The carbon number can vary between 5 to 16 depending if it is naphtha-type jet fuel or kerosene-type jet fuel.
- **Diesel:** The diesel quality is expressed by the cetane number. Opposite to the gasoline, it uses compression-ignition engine. The cetane number represents the volume percentage of cetane in the mixture. Higher the cetane levels, smoother and easier the start of the engine. Usually varies between 30-60%.
- **Heavy fuel oil:** Fuel oil is composed of long hydrocarbons chains and aromatics, and is typically used for the generation of heat. This fuel contain 9 to 70 carbon atoms per molecule.
- **Asphalt:** Asphalt is a important tool for the construction industry. Not only asphalt is obtained from the distillation residues, as other products like lubricants and waxes are also obtained.

1.8 Problem Formulation

The global consumption of oil is gradually increasing. As a response, the European Union (EU) as set ambitious goals for 2030, by reducing the greenhouse emissions and committed to reach 14% of renewable energies in the transport sector. Currently, biofuels account for 4% of the world road transport fuels, and in order to strive for the goals set by the EU, the production of biofuels needs to accelerated. [12]

However, the thermochemical conversion of biomass to biocrude is considered as an intermediate process that still requires upgrading in order to meet the demands of the fuel specifications or to be compatible with petroleum co-processing. The main strategy used to upgrade biocrude is hydrotreating and finding the optimal conditions is quite challenging due to several process variables, such as temperature, pressure, residence time, composition of the biocrude and other factors. Moreover, to obtain this optimal point of procedure, the biocrude properties must be taken into account along with the desired final product characteristics, being both information crucial to determine the operating conditions of the upgrading process, as illustrated in Figure 1.20:

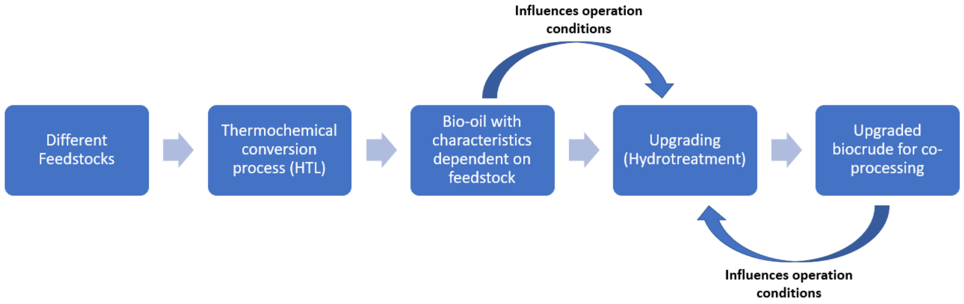

Figure 1.20: Schematic of the influential data for the hydrotreating conditions.

This means that both the biocrude composition prior to upgrading and the purpose of the final upgraded products have a strong impact on how the operation conditions of the hydrotreating process are established. The first because, naturally, the quantity of heteroatoms that need to be removed will define how much the biocrude needs to be hydrotreated, and the second factor, if the objective is co-processing for example, will also weight on the hydrotreating process, as the heteroatoms distribution for every boiling fraction of the biocrude need to be similiar to the ones of the crude oil used in the specific refinery where the co-processing is going to occur.

With all these issues at hand, the main objective of this thesis project is to answer the following questions:

- *How does a multi-stage upgrading process enhances the hydrotreating of HTL biocrude*?
- *Depending on the upgraded biocrude charactheristics, is it favourable to co-process or further hydroprocess to directly produce drop-in biofuels*?

With the semester development and the laboratories shut-down, a new approach for the study had to be performed, as experimental work became an impossibility. Therefore, this study changed its course and the new objective set was to model the two-stage hydrotreating process and try to estimate the kinetic coefficients for the deoxygenation and denitrogenation reactions taking place during the biocrude upgrading.

1.8.1 Structure of the report

This project focuses solely on upgrading the biocrude through the hydrotreating process. The biocrude used in this experiment was obtained by Aarhus University, Denmark, through the HTL process. Following Figure 1.2, the first three processes, pre-treatment, HTL, and phase separation, were performed at Aarhus University. Additional preparation was performed at Aalborg University, to improve quality and favor the hydrotreating process. After all these procedures, the initial biocrude characteristics were evaluated along with the respective upgraded samples.

The structure of this report is carried out in the following order:

- Review of literature regarding biocrude hydrotreating, focusing on lignocellulosic biomass, along with possible co-processing strategies for upgraded biocrude at existing petroleum refineries. This is presented in the first two chapters of the report.
- Setting up an experimental methodology and performing the experimental procedure at different operation conditions, which will be in the third chapter. Along with this, the characterization and analysis of the biocrude and the few upgraded samples will also be presented.
- After this, the report will focus exclusively on the modelling of a two-stage hydrotreating process for HTL biocrude using MATLAB. This will be divided in model description, calibration, validation, optimization and application throughout the remaining chapters of the thesis.

Chapter 2

State of the Art

2.1 HTL Biocrude characterization

Multiple studies have been performed in the upgrading of HTL biocrude to produce relevant fuel types. As previously mentioned in Section **??**, the biocrude composition highly depends on the type of biomass and the process conditions [65]. In these studies, different biomass feedstocks and conversion conditions are used and, therefore, each biocrude presents an unique elemental composition and biochemical composition. Table 2.1 compares the characteristics of the different biocrudes, with one crude oil for reference, and their different production conditions, being subcritical for references [10],[27], [32] and [5] and supercritical for references [26], [35] and [34].

The crude oil presents the lowest heteroatoms content and the highest H/C ratio, therefore the largest higher heating value (HHV).

Lignocellulosic biomass exhibits the highest value of oxygen content and the lowest for nitrogen and sulfur comparing with the other biocrudes. Among the lignocellulosic biomass, despite the process conditions, the biocrude composition depends highly if is grass-type or wood-type [54]. In the case of Miscanthus [10], the oxygen content is the highest in all the feedstocks, around 19.6%, and also the highest amount of nitrogen in the group of lignocellulosic. The oxygen content is mainly due to phenolic (derived from lignin), aromatic, sugars and aldehydes compounds. Lignocellulosic biomass, presents the lowest H/C ratio values, varying from 1.28 to 1.48. The lower H/C ratio, as explained in Section 1.5.2, higher is the hydroprocessing required in order to obtain the desired values for fuels. The low H/C ratio represents the high aromatic nature of theses biocrudes, derived mainly from the lignin components [10].

For sewage sludge, a feedstock with a high content of proteins, compounds such as glycine, aldehydes and acids represent the high oxygen and nitrogen levels [25]. Compared to lignocellulosic biomass, SS and algae presents a significantly

Table 2.1: Biocrude composition

Biocrude & Reference	**Feedstock**	**HTL condition**	**Elemental Balance (wt.%)**					**HHV (MJ/kg)**	**H/C**	ρ **(kg/m^3)**	μ **(cP)**
			C	**O**	**H**	**S**	**N**				
- [34]	Northern sea crude	-	86.6	0.3	13.1	-	-	44.4	1.8	846 (15.6°C)	-
A [26]	Forest residue	390 to 420 ° C 300 to 350 bar	79.4	10.9	9.1	-	-	37.6	1.37	1055.1 (20°C)	3975 (40°C)
B1 [35]	Pine/spruce	390 to 420 ° C 300 to 350 bar	80.6	10.1	9.1	309 ppm	1500 ppm	37.2	1.34	-	17360 (40°C)
B2 [35]	Pine/spruce	390 to 420 ° C 300 to 350 bar	81.4	9.8	8.7	100 ppm	1224 ppm	38.6	1.26	1103 (15°C)	80432 (20°C)
C1 [10]	Miscanthus	350 ° C 220 bar	70.5	19.6	8.2	-	1.7	32.2	1.4	-	-
D [34]	Hardwood	400 ° C 320 bar	83.9	5.3	10.4	-	0.4	40.43	1.48	970 (15.6°C)	-
F1 [32]	Pine wood	347 ° C 201 bar	83	10	6.7	0.03	0.18	-	0.97	1100 (40°C)	11000 (40°C)
C2 [10]	Sewage sludge	350 ° C 220 bar	74.5	11.0	10.6	-	3.9	37.4	1.71	-	-
F2 [32]	Sewage sludge	347 ° C 201 bar	77	8.4	10	0.63	4.3	-	1.6	1000 (40°C)	628.1 (40°C)
C3 [10]	Algae	350 ° C 220 bar	75	6..9	10.4	-	7.7	37.7	1.66	-	-
E [27]	Algae	350 ° C 220 bar	75	6.9	10.4	-	7.7	37.6	1.66	-	-
G [5]	Algae	345 to 355 ° C 175 to 195 bar	72.8	11.1	9.4	0.8	6.0	36.1	-	-	-
F3 [32]	Algae	347 ° C 201 bar	79	3.1	11	0.6	5.5	-	1.6	960 (40°C)	295 (40°C)

higher H/C ratio, mainly due to the high concentration of lipid derivatives [32]. In algae, the presence of oxygenates compounds and nitrogen is due to their association with fatty acids and nitrogen heterocyclic compounds [25]. Algae [10] and [27] stand out with a relatively low oxygen content, around 6.9%, for a subcritical HTL process. As previously mentioned, algae bio-oils also possess, in principal, a high H/C ratio, which makes it a promising biocrude.

Due to the still relatively high content of heteroatoms in all the presented biocrudes, a significant upgrading is still required in order to produce drop-in biofuels. These biocrudes will undergo hydrotreating process, resulting in an upgraded biocrude with higher HHV, higher H/C ratio and lower heteroatoms content. The results for the upgrading stage for each of the presented studies is going to be presented an analyzed in the next section.

2.2 Biocrude Upgrading by Hydrotreating

Hydrotreating is a process that can be used for upgrading biocrude into petroleum-like transport fuels, with the main focus being on deoxygenating the bio-oil. This is especially true for cases using lignocellulosic biomass as feedstock.

Lignocellulosic HTL biocrudes have low content of both nitrogen and sulfur, accounting for less than 0.5 wt.% each, which indicates the lower impact that HDN and HDS will have in this process [34]. Other study done at AAU specifically with miscanthus biocrude, showed no content of sulfur and less than 2 wt% of nitrogen content [10]. Due to a quite high presence of carbonyl and hydroxy groups in lignocellulosic HTL biocrude, deoxygenation is expected to follow HYD and then HDO [34].

The HDO process can be described by the following conceptual reaction:

$$C_1H_{1.33}O_{0.43} + 0.77H_2 \quad \longrightarrow \quad \mathrm{CH_2} + 0.43H_2O \; [8]$$

As the reaction equation represents, for each carbon atom produced in the final fuel, 1.5 (0.77*2) atoms of hydrogen are consumed. Also, assuming full carbon conversion, the resulting hydrocarbons should have a H/C ratio of 2, which is the desired value that indicates high paraffinic nature of the fuel. However, in practice, the HDO reactions do not take place alone during the hydrotreating process, as multiple reactions happen at the same time, redirecting the hydrogen and/or the carbon atoms from the liquid fuel product. These include gasification reactions to form methane or CO_x, reactions forming hydrocarbons with low H/C ratio, like olefins and aromatics, and, also, condensation and polymerization that produce coke and tar. [39]

By removing heteroatoms from the biocrude, the hydrotreating process results in lower yields of upgraded oils, with, for example, oxygen being converted into various gaseous products and also water. Also coking highly affects the yields, being it due to lower hydrogen availability, which generally happens at lower pressures, or too high temperatures. Usually coking also means more gas formation. [10]

In terms of carbon loss, for most lignocellulosic feedstocks, only minor effects come from decarboxylation and decarbonylation. The compounds that mostly indicate that these reactions will occur are aldehydes and carboxylic acids, which appear in low concentrations in this type of biocrude. The formation of gases like CO and CO_2 also show some carbon loss, however these gases can be converted into water and hydrocarbons by way of another reactions, which would result in a higher hydrogen consumption. [11] [34]

The injection of hydrogen is not only for heteroatoms removal but also for hydrogenation of the oil. This means that hydrocarbons are saturated, which results into a higher H/C ratio [10].

In the following sections, the results of the upgraded oils from various HTL biocrudes presented in Table 2.1 are reported. Moreover, subsections related to the impact of the operating conditions, the boiling range of the upgraded products and the two-stage hydrotreating process will also be presented to complement the characteristics shown in the next tables.

The results presented are divided according with the chemical reactors, batch or continuous, along with an analysis for each hydrotreating upgrading process performed in the different studies. Batch and continuous reactors present many difference between them, with the hydrotreating process, this differences are between the coupling of pressure with hydrogen availability and weight hourly space velocity (WHSV) for each case. For continuous hydrotreating, the hydrogen is continuously supplied in the system, making the hydrogen concentration practically constant and the pressure is independent from the hydrogen availability, while for batch experiments the hydrogen is inserted at a specific pressure, which is the initial pressure of the system. As the hydrogen is consumed in the batch reactor, the pressure of the system reduces. The WHSV is defined as the weight of the feed flowing per unit of catalyst per hour, which is only applied for continuous, as Equation 2.1 shows.

$$WHSV = \frac{totalmassfeedflowratetothereactor}{totalcatalystvolume} = h^{-1} \tag{2.1}$$

For batch reactor, a similar parameter is defined, in order to compared with the continuous experiment. This parameter is characterize as WHSV*, being calculated by the following equation:

$$WHSV* = m_{biocrude}/(m_{catalyst} * t_{reaction}) \tag{2.2}$$

Other parameter that is going to be presented and analyzed is the TAN, which is a measure of the quantity of acidic compounds existent in a petrochemical sample. It represents the how much milligrams of potassium hydroxide is necessary to neutralize the acids in one gram of oil. The TAN number signals the potential of corrosion issues that an oil may bring to the refining plant. [37]

2.2.1 Hydrotreatment in continuous reactor

The study presented in Table 2.2 was a continuous hydrotreating process that had the objective of investigate the effects of four different parameters: temperature (A1), WHSV (A2), pressure (A3) and hydrogen availability (A4). On top of these parameters effects, also a possible two-stage hydrotreating (A5) was examined, with the objective being to achieve a deeper conversion with the second stage. [26]

A deeper look into the impact of the operating conditions on the hydrotreating process will be performed in Subsection 2.2.3, however, the high impact of the temperature will be easily visualized with the presented tables. For this case, it can be seen that, for the single-stage hydrotreating, the lowest deoxygenation was obtained at 320°C, while the highest is achieved at 370°C. This can also be concluded by looking at the viscosity levels, dropping just 16% at 320°C, while at 370°C the value decreases in more than 98%. Moreover, the TAN is reduced in more than 90% and the H/C ratio increases with the temperature of the process. On the other hand, increasing the WHSV results in both higher viscosity and TAN number, and also in a lower H/C ratio and decreased deoxygenation. Over the

Table 2.2: Upgraded oils characteristics for different hydrotreating conditions in continuous reactor, obtained by Haghighat et al. [26]

	T (°C)	P (bar)	WHSV (h^-1)	H2/oil ((Nm/m)^3)	Catalyst	Elemental balance (wt.%)			HHV (MJ/kg)	H/C	ρ at 20°C (kg/m^3)	μ at 40°C (cP)	TAN (mg KOH/g oil)
						C	O	H					
Biocrude	-	-	-	-	-	79.4	10.9	9.1	37.6	1.37	1055.1	3975	63.2
A1.1	320	95	0.3	900	CoMo/Al_2O_3	84.2	4.7	10.4	39.4	1.48	1022.8	3321	13.3
A1.2	350					85.3	3.2	10.8	40.6	1.52	991.0	339	8.2
A1.3	370					86.1	2.2	11.0	41.4	1.53	965.9	78	6.1
A2.1	350	95	0.2	900	CoMo/Al_2O_3	85.9	2.4	11.0	41.1	1.54	980.2	173	3.7
A2.2			0.3			85.4	3.1	10.9	40.4	1.53	989.5	268	7.0
A2.3			0.5			84.8	3.8	10.7	40.0	1.51	1001.5	480	8.5
A3.1	350	80	0.3	900	CoMo/Al_2O_3	84.9	3.8	10.5	40.5	1.49	1004.8	375	9.2
A3.2		95	0.3			85.3	3.2	10.8	40.6	1.52	991.0	339	8.2
A3.3	370	80	0.3	900	CoMo/Al_2O_3	85.9	2.5	11.0	41.3	1.53	968.8	90	7.8
A3.4		95	0.3			86.1	2.2	11.0	41.4	1.53	965.9	78	6.1
A4.1	350	95	0.3	900	CoMo/Al_2O_3	85.3	3.2	10.8	40.6	1.52	991.0	339	-
A4.2				1300		85.4	3.1	10.9	40.4	1.53	989.5	268	-
A4.3	370	95	0.3	900	CoMo/Al_2O_3	86.1	2.2	11.0	41.4	1.53	965.9	78	-
A4.4				1300		86.3	1.9	11.2	41.5	1.56	964.5	67	-
A5.1	350 + 320	95	0.3	900	CoMo/Al_2O_3 + NiMo/Al_2O_3	-	2.3	-	42.4	1.6	964.5	23	3.0
A5.2	350 + 350					-	1.8	-	42.7	1.62	937.6	9	1.4

range covered by the study, pressure showed to have less impact on the upgrading process comparing to WHSV and temperature, with just the TAN, density and viscosity presenting slight improvements. The effects of varying the hydrogen availability in the system, under the studied range, proved to be even smaller than the total system pressure, with basically all parameters showing minimal changes. The two-stage hydrotreating process will also be further developed later in this section, in Subsection 2.2.4. For this study, significant improvements of the viscosity, TAN and H/C ratio can be observed. [26]

Table 2.3 presents the results of a hydrotreating study done by Jensen et al. [35], where one HTL biocrude from pine feedstock (B1) was tested in a continuous hydrotreating process in two different operating conditions (B1.1 and B1.2) and with a presulfided catalyst.

Table 2.3: Upgraded oils characteristics for different hydrotreating conditions in continuous reactor, obtained by Jensen et al. [35]

	T (°C)	P (bar)	WHSV (h^-1)	Catalyst	Elemental Balance (wt.%)					HHV (MJ/kg)	H/C	ρ at 15°C (kg/m^3)	μ at 20°C (cP)	TAN (mg KOH/g oil)
					C	O	H	N (ppm)	S (ppm)					
Biocrude (B1)	-	-	-	-	80.6	10.1	9.1	1500	309	37.2	1.34	1103	80432	55.7
B1.1	350	62	0.5	NiMo/Al2CO3	88.1	0	11.9	1175	389	42.1	1.61	989	297	<0
B1.2	370	62	0.5	NiMo/Al2CO3	88.4	0	11.6	986	212	42.2	1.57	989	166	<0

It can be seen that, for the continuous upgrading products (B1.1 and B1.2), complete deoxygenation and TAN elimination were obtained for both cases. Moreover, the viscosity is reduced in almost three orders of magnitude (more than 99,7% reduction). This study also investigated the possibility of spiking the B1 biocrude with butanethiol to increase the sulfur content to 1 wt%. This was done based on observations on the first continuous campaign (B1.X) that showed potential desulfurization of the catalyst, and it indicated that the HYD is considerably improved during the spiked hydrotreating, which may be relevant data for diesel and marine fuels production that require high degree of HYD. However, this method may increase the H_2S concentration in the gaseous phase, which may lead to high expenses on gas cleaning equipment. [35]

In the Table 2.4 the study performed by Jarvis et al. [32] is presented, where the hydrotreatment was conducted at 400°C and 100 bar. In this experiment, HTL biocrude from different feedstocks were upgraded, comparing the results of lignocellusic with sewage sludge and algae.

Table 2.4: Upgraded oils characteristics for different hydrotreating conditions of different feedstocks in continuous reactor, obtained by Jarvis et al. [32]

	T (°C)	**P (bar)**	**Catalyst**	**Elemental Balance (wt.%)**					**H/C**
				C	**O**	**H**	**N**	**S**	
Pine Biocrude (F1)	-	-	-	83	10	6.7	0.18	0.03	0.97
F1.1	400	100	$CoMo/Al_2O_3$	87	2	11	0.05	46 ppm	1.6
SS Biocrude (F2)	-	-		77	8.4	10	4.3	0.63	1.6
F2.1	400	100	$CoMo/Al_2O_3$	84	1.2	15	0.05	23 ppm	2.0
Algae Biocrude (F3)	-	-	-	79	3.1	11	5.5	0.6	1.6
F3.1	400	100	$CoMo/Al_2O_3$	86	1.2	15	0.05	17 ppm	2.1

It can be seen in Table 2.4, that the pine feedstock biocrude present the highest oxygen content, followed by sewage sludge (SS) and finally algae. Compared to the pine biocrude, the SS and algae present a relatively higher H/C ratio and higher nitrogen and sulfur content, this is mainly due to the presence of proteins and lipids [32]. In all the experiments, the heteroatom removal is evident, the oxygen content reduces in the order of 80%, 85% and 61% for pine, SS and algae. While the HDN present around 99% of nitrogen removal in the algae and SS, while pine biocrude around 72%. All the three upgraded biocrude show a significant change in their composition, both the hydrogen and carbon content is enriched while the heteroatoms are reduced. Also, the H/C ratio is higher for all the hydrotreated biocrude compared to the raw biocrude.

2.2.2 Hydrotreating in batch reactors

The study by Jensen et al. [35], also presented in Section 2.2.1, examined the possibility of a two-stage hydrotreating process, where batch reactors were used. Important to mention different biocrudes and catalysts are used in the batch and continuous reactor, that will impact the hydroprocessing reaction. This investigation was done using non-sulfided catalyst, with the biocrude B2, from pine feedstock, being the feed for the first stage B2.1, while the partially upgraded obtained from this stage is the feed for the second stage B2.2. For batch reactor processes the parameter WHSV* is used as a comparison to the continuous process, as previously explained. These experiments results are presented in Table 2.5.

Table 2.5: Upgraded oils characteristics for different hydrotreating conditions in batch reactors, obtained by Jensen et al. [35]

	T (ºC)	P (bar)	WHSV*	Catalyst	Elemental Balance (wt.%)					HHV (MJ/kg)	H/C	ρ at 15ºC kg/m^3
					C	O	H	N	S			
Biocrude (B2)	-	-	-	-	81.4	9.8	8.6	1124 ppm	100 ppm	38.6	1.26	1051
B2.1	350	100	0.5	$NiW/SiO_2/AL_2O_3$	89	0.7	10.3	66 ppm	61 ppm	42.4	1.38	914
B2.2	350 + 300	100	0.5 + 1	$NiW/SiO_2/AL_2O_3$ + Pd/AL_2O_3	88.3	0	11.7	0	0	43.5	1.58	892

The biocrude single-stage (B2.1) presents significant heteroatom removal, the oxygen varies from 9.8% to 0.7% and the nitrogen and sulfur are also relatively low, 66ppm and 61ppm respectively. The upgraded biocrude presents a significant improvement in the HHV and density compared to raw biocrude while the H/C ratio where only mildly improved. The two-stage biocrude presents further upgrading in the biocrude and complete heteroatom removal. The second-stage upgrading enhanced the HDY reactions and the H/C ratio increased from 1.38, end of the first-stage to 1.58.

The study presented in Table 2.6, by Castello et al. [10], investigated the hydrotreatment of HTL oil from three different feedstocks. This experiment was conducted under with two different temperatures (350 and 400ºC) and two different pressures (40 and 80 bar). The upgraded bio-oils are presented based on their feedstocks, mischantus (C1.x), sewage sludge (C2.x) and algae (C3.x).

As explained in Subsection 1.3.1, the SS and algae raw biocrude present a higher H/C ratio, due to the high presence of lipids [32]. In contrast, the miscanthus biocrude has the lowest H/C ratio, 1.4 and also the highest oxygen content. With the hydrotreatment process, all the three biocrudes show significant improvement in their bulk properties. In none of the cases complete heteroatoms removal was obtained, however, a complete deoxygenation was achieved in the upgrading of

Table 2.6: Upgraded oils characteristics for different hydrotreating conditions of three different types of biocrudes in batch reactors, obtained by Castello et al. [10]

	T (ºC)	P (bar)	WHSV* (h^-1)	Catalyst	Elemental Balance (wt.%)					HHV (MJ/kg)	H/C	Yields (wt.%)
					C	O	H	N	S			
Miscanthus Biocrude (C1)	-	-	-	-	70.5	19.6	8.2	1.7	-	32.2	1.4	-
C1.1	350	40	0.5	NiMo/AL_2O_3	81.1	9.0	8.8	1.1	-	37.8	1.3	60 ±4
C1.2	350	80			84.7	4.3	10.2	0.8	-	41.1	1.45	65 ±1
C1.3	400	80			87.4	0.8	10.3	1.5	-	42.2	1.37	61 ±3
SS Biocrude (C2)	-	-	-	-	74.5	11.0	10.6	3.9	-	37.4	1.71	-
C2.1	350	40	0.5	NiMo/AL_2O_3	83.1	1.2	12.1	3.6	-	43.1	1.75	74 ±3
C2.2	350	80			84.1	0	13.4	2.5	-	45.1	1.91	77 ±2
C2.3	400	80			85.3	0	13.8	0.9	-	46.1	1.95	72 ±3
Algae Biocrude (C3)	-	-	-	-	75	6.9	10.4	7.7	-	37.7	1.66	-
C3.1	350	40	0.5	NiMo/AL_2O_3	82.2	1.3	11.1	5.4	-	41.6	1.62	75 ±3
C3.2	350	80			84.0	0	12.1	4.0	-	43.5	1.72	73 ±2
C3.3	400	80			83.7	0	12.1	4.1	-	43.7	1.76	63 ±4

sewage sludge and algae biocrude. At 350ºC and high pressure, 80 bar, a better HDN and HDO are obtained in all cases, compared with mild pressure, 40 bar. Particularly for SS and algae, complete deoxygenation is obtained at these high conditions. Miscanthus biocrude also presents significant improvements in the biocrude characteristics from 40 bar to 80 bar, and a higher degree of deoxygenation is obtained by raising the temperature. However, due to the high heteroatom content, the H/C ratio of the miscanthus does not show much improvement, since the hydrogen is being mainly used in the heteroatoms removal and not hydrogenation. SS presents high degree of deoxygenation at mild conditions, around 89%, and at severe condition complete deoxygenation. A constant increase in the H/C ratio is observed, particularly at hydrotreating at 400ºC, with H/C ratio of 1.9 being obtained, translating in a highly paraffinic nature [10]. Algae, similar to to SS, present relatively high HDO at mild condition, 40bar, around 81%, and complete deoxygenation at 80 bar. This parameter will be further analyzed in Subsection 2.2.3. Operating conditions have a significant role in this experiment, with an operation at high pressure and high temperature being crucial for the heteroatom removal, however excessively high temperature can result in coking. In this study the yields parameter is presented, which tends to present better results at high pressures, however, at high temperatures the yields decrease, due to the instability of the oil.[10]

Table 2.7 presents a study done by Jensen et al. [34], where the effects of temperature (D1), pressure (D2) and hydrogen availability (D3) are explored. The hydrotreating process was done in batch reactors with the catalyst $NiMo/Al_2O_3$, with a weight hourly space hourly velocity of 2.5h^-1. The pressure values presented are the maximum obtained during the experiment and not the input pressure in the reactor.

Table 2.7: Upgraded oils characteristics for different hydrotreating conditions in batch reactors, using $NiMo/Al_2O_3$ as catalyst and WHSV* = 2.5 h^-1, obtained by Jensen et al. [34]

	Temperature (ºC)	**Pressure Max (bar)**	**H2/oil (NL / L)**	**Elemental Balance (wt.%)**					**HHV (MJ/kg)**	**H/C**	**ρ (kg/m^3)**
				C	**O**	**H**	**N**	**S**			
Biocrude (D)	-	-	-	83.9	5.3	10.4	0.4	-	40.43	1.48	970
D1.1	150	75	374	83.8	5.0	10.8	0.5	-	40.58	1.54	966
D1.2	250	84-86	356	83.8	4.6	11.0	0.5	-	40.90	1.56	943
D1.3	300	93-96	355	86.2	1.8	11.5	0.5	-	42.51	1.59	927
D1.4	350	95-98	355	87.5	0.2	12.0	0.2	-	43.73	1.63	904
D2.1	300	93-96	355	86.2	1.8	11.5	0.5	-	42.51	1.59	927
D2.2		134	318	86.5	1.6	11.7	0.2	-	42.67	1.56	925
D2.3	350	62-63	338	86.5	1.3	11.6	0.6	-	43.5	1.6	902
D2.4		95-98	355	87.5	0.2	12.0	0.2	-	43.75	1.63	904
D2.5		146-148	337	87.2	0.3	12.2	0.4	-	43.9	1.67	894
D3.1	350	94-100	152	87.7	0.4	11.6	0.3	-	43.49	1.58	911
D3.2		95-98	355	87.5	0.2	12.0	0.2	-	43.73	1.63	904
D3.3		97	550	87.4	0.1	12.1	0.4	-	43.88	1.65	890

This study consists of a parametric study on hydrotreating of hardwood biocrude. For all the procedures, around 90 wt.% ± 5 liquid recovery was obtained including water. Starting by evaluating the effects of the temperature (D1), there is a strong influence in the HDO of the biocrude. At low temperatures, 150 and 250ºC, only 6% and 13% of oxygen reduction is obtain, respectively. However, at high temperatures, around 66% oxygen reduction is observed at 300ºC, going up to 96% for 350ºC. At 350ºC, the higher HHV and H/C ratio are observed and also a decrease in the oil density. The effects of the pressure (D2), are evaluated under two temperatures, 300°C and 350°C. At 300°C, the hydrotreated biocrude at higher conditions (D2.2), presents a slightly better heteroatoms removal, lower density and small increase in the HHV and H/C ratio. The pressure effect is more evident at 350°C, with a constant increase in the HHV, H/C ratio and enhancement of the bulk properties being observed. Although the heteroatoms removal is not evident at high pressures, pressure plays an essential role in the saturation o C-C double bonds, leading to higher HHV and lower density. The hydrogen availability (D3), is another important parameter due to the catalyst deactivation, further explained in Subsection 2.2.3. According to the experiment, higher HDO is observed when there is higher hydrogen liter per liter of oil, and also a slightly better HHV, density and H/C ratio. Due to high hydrogen availability, an improvement in the hydrogen content is evident, resulting from higher degree hydrogenation. This process condition has a crucial role in effectively deoxygenate HTL biocrude and improve its characteristics, as the hydrogen availability ensures maximum conversion and avoids catalyst deactivation.[34]

Table 2.8 presents a study by Haider et al. [27] on hydrotreating of algae biocrude . Three parameters are examined in this study, that is, temperature, pressure and residence time. Furthermore, three additional experiments (E9) are performed, with the objective of obtaining a higher degree of denitrogenation. The hydrotreating process was conducted in batch reactors with $NiMo/Al_2O_3$ as a catalyst.

All the experiments were carried out in batch reactor and around 90 wt.% ± 5 of liquid was recovered, similar to the study in Table 2.7. For the first eight experiments (E1-E8), the parameters were varied in two levels. For the temperature, the low level at 250°C and the high level at 350°C. Similarly, the initial pressure, varying from 40 to 80 bar and the residence time from 2 to 4h, for low and high level, respectively. Complete deoxygenation is only achieved at more severe conditions (E8), at 350°C, 80 bar, and 4h of resident time. Also, the higher hydrogen consumed is observed at those conditions, resulting in the heteroatoms removal, higher degree of HDY. At these experiments, high temperatures are shown vital for HDO and HDN, comparing with 250°C. While mild conditions, still affect the oxygen content, whereas the nitrogen remains almost the same. At high pressure and larger resident time, results, in good effect in the heteroatom removal, particularly in the nitrogen. The three additional experiments (E9.X), were conducted at different temperatures, pressure and resident time. At these three additional experiments, the results present complete deoxygenation to study the effects of the HDN.The higher degree of denitrogenation is found at 375°C (E9.1), around 60%. High temperatures are needed for further heteroatoms removal, however at very high temperature, due to the high polarity of the oil, can cause to form coke and possibly the catalyst deactivation. The two experiments at 400°C presented lower

Table 2.8: Upgraded oils characteristics for different hydrotreating conditions of algae biocrude in batch reactors, using $NiMo/Al_2O_3$ as catalyst, obtained by Haider et al. [27].

	Temperature (°C)	**Pressure (bar)**	**WHSV* (h^-1)**	**Elemental Balance (wt.%)**				**HHV (MJ/kg)**	**H/C**	**n H2 consumed**
				C	**O**	**H**	**N**			
Biocrude (E)	-	-	-	75.01	6.94	10.4	7.65	37.59	1.66	-
E1	250	40	1	76.94	5.11	10.79	7.19	38.93	1.68	0.0025
E2	350	40	1	81.24	1.95	11.18	5.55	41.24	1.65	0.006
E3	250	40	0.5	77.72	5.00	10.76	6.53	39.18	1.66	0.0033
E4	350	40	0.5	82.24	1.28	11.05	5.44	41.51	1.61	0.0058
E5	250	80	1	77.16	5.53	10.66	6.66	37.59	1.66	0.0033
E6	350	80	1	82.62	1.17	11.87	4.35	42.64	1.72	0.0108
E7	250	80	0.5	76.82	6.13	10.98	6.36	38.68	1.67	0.0045
E8	350	80	0.5	84.31	0	12.13	4.03	43.7	1.73	0.0125
E9.1	375	70	0.667	84.55	0	12.66	3.09	44.38	1.8	0.0103
E9.2	400	65	0.8	84.17	0	11.99	3.84	43.45	1.71	0.008
E9.3	400	70	1	84.37	0	12.44	3.19	44.05	1.77	0.0093

H/C ratio, HHV and lower heteroatoms removal, this is mainly due to coking reactions.

The study presented in Table 2.9, is conducted by Biller et al. [5], in which the effects of the catalyst were verified under two temperatures, 350°C and 400°C. The hydrotreatment of the biocrude was performed with either, no catalyst (G1.X), or $NiMo/Al_2O_3$ (G2.X) or with $CoMo/Al_2O_3$ catalyst (G3.X).

Table 2.9: Upgraded oils characteristics for different hydrotreating conditions of algae biocrude in batch reactors at WHSV* = 2.5 h-1, obtained by Biller et al. [5]

	T (°C)	**P (bar)**	**Catalyst**	**Elemental Balance (wt.%)**					**HHV (MJ/kg)**	**H/C**	**Yields (wt.%)**
				C	**O**	**H**	**N**	**S**			
Biocrude Algae (G)	-	-	-	72.8	11.1	9.4	6.0	0.8	36.1	-	-
G1.1	350	60-66	-	79.6	5.00	10.8	4.7	0.117	41.5	-	94.8
G1.2	405	60-66		83.5	1.5	11.3	3.6	0.072	44.7	–	68.9
G2.1	350	60-66	$NiMo/Al_2O_3$	80.4	4.2	10.5	4.7	0.206	41.5	-	93.1
G2.2	405	60-66		84.5	1.5	11.6	2.4	0.002	44.9	-	41.0
G3.1	350	60-66	$CoMo/Al_2O_3$	79.4	4.7	10.9	4.6	0.420	41.6	-	89.0
G3.2	405	60-66		84.4	1	11.9	2.7	0.000	45.4	-	69.4

In general, the yields are higher at lower conditions, however, a lower degree of hydrotreatment. The use of non-catalyst presented a higher yields at mild conditions compared to the use of catalyst, also at high temperature presents a good results in terms of yields and HHV, however the nitrogen content remains high. At mild conditions, the bio-oil obtained is very similar for the three cases, with higher deoxygenation being obtained in the presence of catalyst. For the case of NiMo catalyst, at the high temperature, the highest degree of nitrogen removal is obtained, around 84% and low sulfur content, around 20ppm. Both, NiMo catalyst and no-catalyst are equally effective in the deoxygenation at 405°C. The CoMo catalyst, at high temperatures, achieves complete desulfurization and the lowest oxygen content, around 1.0%. Also, at this conditions, the highest HHV and yields are obtained using CoMo catalyst. [5]

In the tables presented, it is clear that the hydrotreating operating conditions have a significant role in the upgrading of the biocrude. Therefore, in the next section, four main parameters are examined in more detail.

2.2.3 Effects of operating conditions

The extent of deoxygenation is not only influenced by the oxygenates types existent in the biocrude, as explained in the subsection 1.4.2, but also on the operation conditions of the hydrotreating process. Moreover, these are important additions for economical evaluations, on top of hydrogen and catalyst expenses. For this reason, the effects of the operating conditions of the hydrotreating process are going to be analyzed, with more focus on the lignocellulosic biocrudes results.

- **Effect of operating temperature:**

  By the tables presented, is easy to conclude that the temperature is most influential parameter in the hydrotreating process. It can be seen for all cases that the heteroatoms removal and the oil characteristics are improved with higher temperature, with few exceptions for very high temperature (for example camparing E9.1 at 375ºC with E9.2 and E9.3 at 400ºC) or when working with low pressures. However, temperatures excessively high can create coking and other issues. The effects of this operating condition are evaluated for each presented study.

  Other parameter that the study done by Haghighat et al. [26] evaluated was water yields, not presented in Table 2.2. The data shows the oxygen wt% of the biocrude and the upgraded oils, which gives information on how the much deoxygenation took place during the process, but does not specify how much of it is by HDO or by decarboxylation/decarbonylation. As previously explained, a HDO reaction creates water, so the water yields translate how much HDO takes place during the hydrotreating. The results, for the temperature study (A1.x), showed yields of 5.3% at 320ºC, 7.3% at 350ºC and 8.9% at 370ºC, meaning higher rate of HDO at higher temperatures. The hydrogen consumption increased with higher temperature, with the quantity of light hydrocarbons in the gaseous phase also rising. At the lowest temperature (320ºC), 75% of the oxygenates were removed by HDO and the remaining 25% being extracted by decarboxylation/decarbonylation. This ratio changed to 90% and 10% respectively at the highest temperature (370ºC), with the final concentration of CO_2 for both cases being similiar due to the higher hydrogen consumption of the 370ºC case. This shows that the production of CO_2 did not increase with higher temperature. With the increase of temperature, the boiling point distribution decreased. The boiling range of the upgdraded products will be further developed in the Subsection 2.2.5, but this means that by increasing temperature the products distribution altered towards lighter materials with lower boiling points. This is result of higher rate of cracking reactions at higher temperatures. The aromaticity of the upgraded oils was reduced with higher temperature, shown by lower intensity of absorption of all peaks related to aromatic functional groups. Moreover, the O-H and C=O bonds also showed lower intensity of absorption with the increase of temperature. [26]

  In the investigation performed by Jensen et al. [35], higher temperature resulted in reduced rate of HYD, shown by the lower hydrogen wt% in the 370ºC case compared to the 350ºC one. This is justified by the fact that HYD is an exothermic reaction, being favoured by lower temperature until kinetics become rate limiting. Also higher degree of cracking is observed at higher temperature, as expected, but coming at the expense of reduced HYD rate. [35]

The study done by Castello et al. [10] shows an important parameter, which are the yields of the upgraded oils, strongly related to the temperature of the system. Heteroatoms removal, with the conversion of O and N into gases or other liquid products, reduces the yields of upgraded oil, but operating at higher temperatures results in reduced yields not only from higher heteroatoms removal but also due to a higher extent of coking and cracking reactions. For the mischantus biocrude, it can be seen that from 350ºC (C1.2) to 400ºC (C1.3) both the yields and the oxygen wt% are reduced. However the nitrogen wt% increased. This is explained by the onset competition between HDN and HDO for the hydrogen utilization. Therefore, it can be concluded that the reaction rate of HDO is way more accelerated compared to HDN. This fact is especially seen for mischantus due to its very high initial oxygen content. As it is seen for the sewage sludge and algae cases, the H/C ratio of the upgraded oils generally is enhanced. However this is not the case for mischantus, where the variations are basically negligible. These lower values of H/C ratio for the mischantus biocrude shows its highly aromatic nature, where the phenolics compounds coming from lignin have strong influence. [10]

In Table 2.7, where the different upgraded oils investigated in the study by Jensen et al. [34], the very strong effect of temperature in the deoxygenation of the biocrude can be easily seen through the four different studied temperatures. On top of that, the reduction in absorbance of both unsaturated carbons and oxygen bonds is also evident with higher temperature. Both the elemental analysis and the presence of carbonyl functional group absorption with 300ºC or less display that the deoxygenation process is incomplete for temperatures lower than 350ºC. [34]

The study done by Haider et al. [27], focused on the hydrotreating of algae biocrude, also showed that high temperatures are vital for the removal of nitrogen, which is of major importance for this feedstock. While higher temperatures are needed for higher denitrogenation, both HHV and H/C ratio decreased from 375ºC to 400ºC, meaning that the higher degree of denitrogenation was obtained with loss of fuel quality. This may be caused by coking reactions at 400ºC, with possible catalyst deactivation and polymerization happening at such high temperature. [27]

- **Effect of operating space velocity:**

As described above for the study by Haghighat et al. [26] in Table 2.2, decreasing the WHSV results in lower density, viscosity and TAN plus higher degree of deoxygenation and H/C ratio. This study also got results showing that the selectivity (which is the concentration of a specific gas on all the gaseous phase excluding H_2) of CO_2 decreased with lower WHSV, which suggests that decarboxylation reactions progress at a slower rate when compared to other gases forming reactions. This effect is also seen with increased selectivity of light hydrocarbons with lower WHSV. The hydrogen consumption increased more than 2.5 times from a WHSV of 0.5 h-1 to 0.2 h-1. [26]

The study performed by Haider et al. [27] also tested the effect of space velocity by doubling the reaction time in each experiment, which is equivalent to reduce the WHSV by half. All the studied oil characteristics showed to be improved by the reduction of WHSV, as seen in Table 2.8, where the elemental balance, HHV and H/C are enhanced, with the hydrogen consumption also increasing. [27]

- **Effect of operating pressure and hydrogen availability (**H_2**:oil)**:

The hydrogen partial pressure in the gas phase influences the solubility of hydrogen in the liquid phase. Moreover, the partial pressure of the hydrogen depends on the pressure of the system and on the concentration of hydrogen in the gas phase. For batch reactors, this can be adjusted by manipulating the H_2/oil ratio, which leads to the effects of both these parameters being studied together for the batch approach. This is not the case for continuous reactors, where hydrogen is continuously supplied and its concentration is practically constant.

Over the ranges studied, the pressure showed to have a lower impact compared to that of temperature and WHSV. Density, viscosity and TAN presented slight improvements with the increase of pressure, while the oxygen wt%, HHV and H/C ratio did not considerably vary. The impact of varying the hydrogen availability showed even less effects than pressure, with minimal changes in basically all the parameters. Results on hydrogen solubility showed that the increase from 80 to 95 bar in pressure resulted into an increase of 15% on the solubility of hydrogen in the biocrude. This means that increasing the total system pressure may improve the hydrogen availability over catalysts particles, facilitating HYD and HDO reactions of biocrude. [26]

The findings mentioned above also go into accordance with the study done by Castello et al. [10], where a lower operating pressure (40 bar) was experimented. It showed that operating at low pressure leads to lower hydrogen availability, which results in coking and more extensive gas formation. [10]

For the study performed by Jensen et al. [34], when operating with temperatures lower than 350°C, it was concluded that the effect of pressure is less detectable. This is assumed to be due to the high impact that the operating temperature has on the conversion levels, extremely reducing the pressure influence. However, at high temperatures (>300°C), it has been found that the operating pressure has influence on the deoxygenation of the lower HDO reactivity oxygenates. The effect of pressure is also clear from the saturation of carbon-carbon double bonds, with higher pressures increasing the mentioned saturation, leading to a higher HHV and lower density. This study also investigated the hydrogen availability impact on the hydrotreating process, where the improvement of density, HHV, oxygen wt% and H/C ratio happens with the increase of H_2/oil ratio. Moreover, the carbonyl functional group and the carbon-oxygen bonds have their absorbance reduced with the increase of hydrogen availability. The higher rate of HYD is also presented, with the carbon-carbon double bond absorption also being decreased. [34]

The effects of pressure are also examined in the study carried out by Haider et al. [27], where the findings go into accordance with the previous statements. The upgraded oils that showed the best results were hydrotreated in the highest pressure tested (80 bar), the highest temperature (350°C) and lowest WHSV (0.5 h-1), while all the experiments enhanced from 40 to 80 bar.

2.2.4 Two-stage Hydrotreating

Although still being an unusually used method, two of the presented studies tested the possibility of upgrading the biocrude with a two-stage hydrotreating. Unlike it was explained in subsection 1.5.3, both these experiments used more severe operating conditions in the first-stage, followed by lighter conditions or the same for one case. In both of the studies, this approach was tested with the objective of ensuring a high rate of HYD on the second stage.

One of the studies that investigated the two-stage hydrotreating strategy was Haghighat et al. [26], presented in Table 2.2 by the upgraded oils A5.1 and A5.2, with A4.1 being the feedstock for the second stage. This one-stage hydrotreating product can be assumed as partially upgraded, as additional upgrading is required in order to produce drop-in biofuels. The bio-oil A4.1 was firstly removed, with the produced water and gases being separated, in order to prevent catalyst deactivation in the second stage. A parameter not presented in Table 2.2 is the hydrogen consumption, that was determined as 0.015g for the first stage and 0.003g for the second stage at 320°C and 0.008g for the one at 350°C. This lower consumption of hydrogen in the second stage can be explained by the fact that the feedstock for this stage is an already partially upgraded biocrude, which will present lower reactivity. However, the results showed to go into accordance with the objective of enhancing the HYD during the second stage, as Figure 2.1 shows:

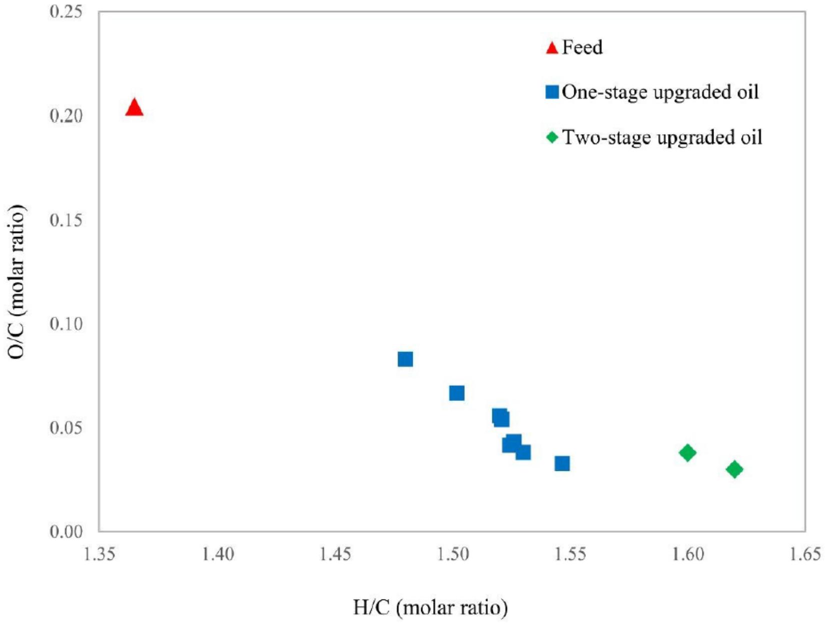

Figure 2.1: Effects of one-stage and two-stage upgrading strategies on the O/C and H/C ratios of the biocrude, obtained from the study by Haghigat et al. [26] and the values presented in Table 2.2.

Jensen et al. [35] also examined the two-stage upgrading process, based on the desire to enhance the H/C ratio of the biocrude. The first stage had the objective of achieving high deoxygenation of the biocrude and a reduction of the boiling point distribution, with the second focusing on deep HYD to increase the H/C ratio. The oxygenated functional groups are basically erased during the first stage of the process, while the aromatic and olefinic absorptions are decreased during the second one, which indicates the desired HYD reactions. Moreover, the products of the second stage showed the biggest reduction in the boiling point distribution, stating a notable improvement in the amount of distillates produced. [35]

2.2.5 Boiling point distribution

Conducting reactions at high temperatures and pressures enhances cracking reactions, which lead to the upgraded oils having lighter materials and lower boiling point compounds.

As mentioned above related to the study performed by Haghighat et al. [26], the increase of temperature in the hydrotreating process resulted in a reduced boiling point distribution. That effect can be visualized in Figure 2.2, where the simulated distillation (SimDis) of the upgraded biocrudes from this study are presented:

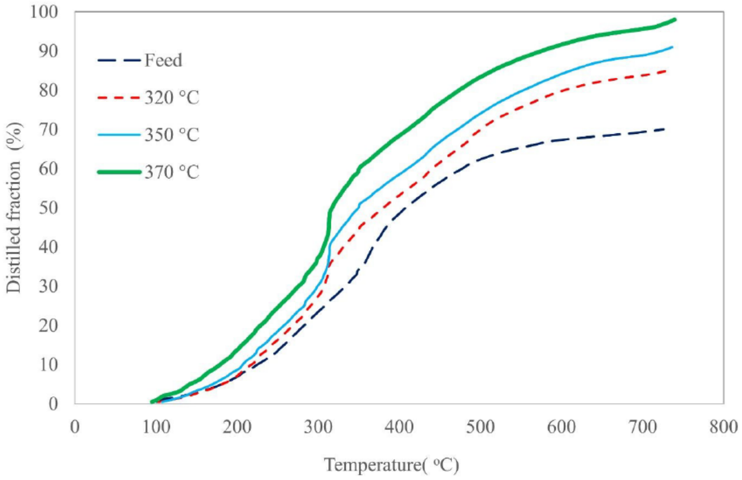

Figure 2.2: SimDis from upgraded biocrudes for different T°C at P=95bar, H2/oil=900 and WHSV= 0.3 h-1 presented in Table 2.2, obtained from the study performed by Haghighat et al. [26]

The presented 350°C case is the partially upgraded biocrude that serves as feedstock for the two-stage process, with this approach showing an even further enhancement on the boiling point distribution, as Table 2.10 presents:

Table 2.10: Boiling point distribution in percentage for the two-stage hydrotreating study by Haghighat et al. [26], where A4.1 is partially upgraded biocrude of the first stage and A5.1 and A5.2 are the second stage at 320°C and 350°C respectively. The characteristics of these oils are presented in Table 2.2.

	Gasoline 0-180°C	**Diesel 180-343°C**	**LVGO 343-454°C**	**HVGO 454-550°C**	**Residue >550°C**
Biocrude	5	27	25	8	35
A4.1	6	42	20	12	20
A5.1	8	50	22	11	9
A5.2	12	52	20	11	5

It is clear the reduction of the boiling point distribution from raw biocrude to the one-stage hydrotreating and also from the one-stage to the two-stage upgrading strategy. This can be seen from the significant decrease in the residue fraction. Consequently, the lower boiling fractions increase, with diesel (in this study assumed as 180-343°C) being the main product of the upgrading process.

Jensen et al. [35] also studied the boiling point distribution of the upgraded oils from different conditions. Just as the previous study, the two-stage upgrading process showed to have the most enhanced boiling point distribution, as seen in Figure 2.3. Another observed result was the better boiling point distribution of the spiked biocrude compared to the nonspiked.

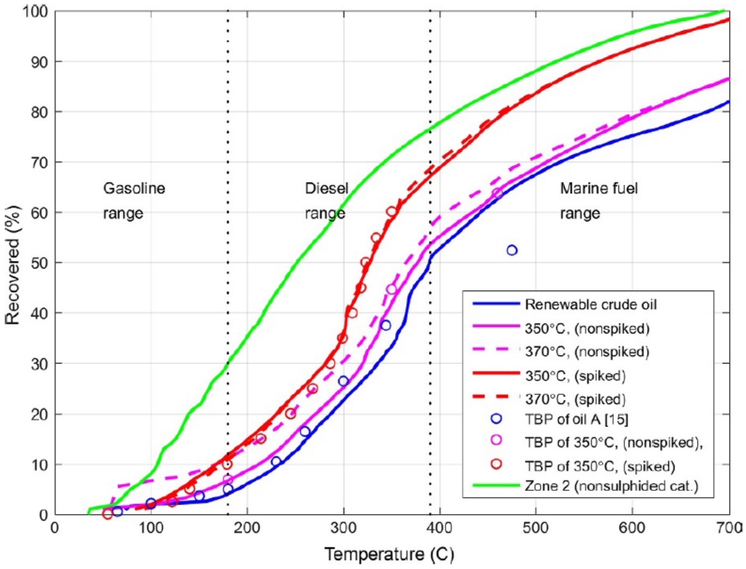

Figure 2.3: SimDis from the different upgraded biocrudes, obtained from the study performed by Jensen et al. [35]

Castello et al. [10] investigated the boiling point distribution for the three different biocrudes at the different conditions tested, with the results being presented in Table 2.11:

Table 2.11: Boiling point distribution in percentage for the biocrudes presented in Table 2.6, obtained by the study by Castello et al. [10]

	Gasoline 0-193°C	**Jet fuel 193-271°C**	**Light Diesel 272-321°C**	**Heavy Diesel 321-425°C**	**VGO 425-564°C**	**Residue >564°C**
Mischantus Biocrude (C1)	11.3	8.1	14.5	13.1	11.7	41.3
C1.1	13.1	13.7	8.3	12.8	12.8	39.3
C1.2	13.4	16.1	11.9	17.2	15.0	26.4
C1.3	26.9	20.7	11.8	14.0	9.3	17.3
SS Biocrude (C2)	5.5	12.8	14.1	37.6	14.5	15.5
C2.1	6.9	11.9	20.1	17.2	16.8	27.1
C2.2	11.3	17.1	31.2	15.9	12.3	12.2
C2.3	14.1	20.6	31.4	14.2	8.3	11.4
Algae Biocrude (C3)	16.2	11.7	8.5	25.2	15.9	22.5
C3.1	7.1	16.3	13.7	20.4	19.2	23.3
C3.2	17.8	23.0	20.9	16.2	10.4	11.7
C3.3	17.8	26.5	22.2	14.1	7.1	12.3

Experiments at low pressure, 40 bar, present very low changes compared to the raw biocrudes. For higher pressures, an increase in the low boiling point fractions recovery can be seen, with the increase of temperature showing more relevant changes than pressure. Moreover, it can clearly be visualized that the fractional cuts with higher recoveries strongly depend on the used feedstock.

The boiling point distribution was also investigated by Haider et al. [27], where the differences between performing a hydrotreating process in mild conditions (E1), that basically showed no changes comparing to the raw biocrude, and severe conditions (E8), where the boiling point distribution significantly improves. This results are presented in Table 2.12:

Table 2.12: Boiling point distribution in percentage for the biocrudes presented in Table 2.8, obtained by the study by Haider et al. [27]

	Gasoline 0-190°C	**Jet fuel 190-290°C**	**Diesel 290-340°C**	**VGO 340-538°C**	**Residue >538°C**
Biocrude (E)	3.9	14.5	8.9	38.9	33.8
E1	3.0	15.5	8.5	34.7	38.3
E8	13.1	32.2	18.4	23.8	12.5
E9.1	4.8	33.4	15.3	29.0	17.5
E9.2	5.6	34.0	13.6	26.3	20.5
E9.3	7.9	34.5	14.5	27.5	15.6

The experiments E9.X were performed with the desire of enhancing the denitrogenation, being done at higher temperatures. This resulted in a higher residue content comparing to the upgraded oil E8, showing that the decrease in boiling point distribution is probably not directly proportional to the increase of temperature, possibly due to coking and other issues.

2.3 Analysis of the presented literature

In this section the oxygen and nitrogen removal from the different reviewed studies are going to be analyzed, along with the Van Krevelen plot for each upgraded biocrude. The figures presented will only take in consideration single stage experiments at pressure equal or higher than 80 bar.

2.3.1 Deoxygenation vs Denitrogenation

From the previously presented tables, it is possible to check that a high degree of deoxygenation is easier to obtain comparing to denitrogenation. This subsection has the objective of demonstrating the difference between these two reactions in a clearer way. Figure 2.4 maps the percentage of deoxygenation and denitrogenation (blue and orange points respectively) for each presented study at their respective temperatures. Along with the mapped points, an exponential fit for each reaction is plotted for a better visualization of their rates.

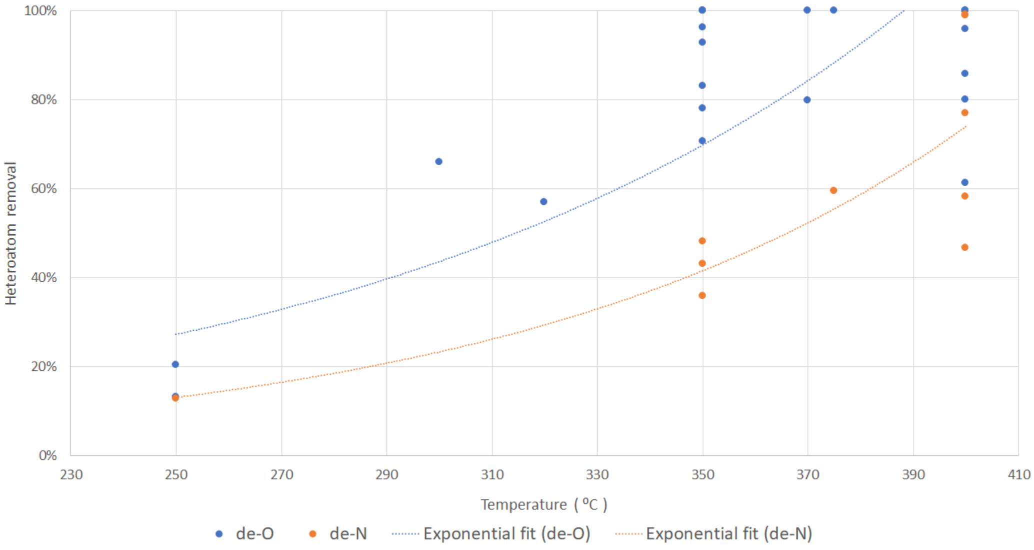

Figure 2.4: Comparison between deoxygenation and denitrogenation rates, based on presented literature.

It is important to mention that the fits presented in Figure 2.4 are not an accurate representation of the deoxygenation and denitrogenation conversions, as different feedstocks and different operating conditions were used for each presented point, however it is suitable for a qualitative comparison between the two reactions.

Starting at low temperature, at 250°C, the deoxygenation and denitrogenation basically at same levels, where only around 10-20% of oxygen and nitrogen were removed. With the increase of the temperature, both the HDO and HDN obtain higher rates. At 350°C, for most of the cases, significant deoxygenation is obtained, above 70% and, for exceptional cases, close to complete deoxygenation, while the denitrogenation improved a bit however remains bellow 50%. With temperatures above 350°C up to 400°C, the oxygen removal raises to above 80% and the denitrogenation increases to around 60%. It can be seen that high temperatures have a good effect on heteroatom removal. Moreover, Figure 2.4 clearly shows the higher dependency on temperature that the denitrogenation reactions present comparing to the deoxygenation.

2.3.2 Van Krevelen diagrams

In this subsection the Van Krevelen diagrams for the studied literature are presented. These diagrams cross-plot the O/C in function of H/C to help assess the raw biocrude and the upgraded biocrude. The literature data is divided in two sections, lignocellulosic and non-lignocellulosic biocrude, this comes from the fact that lignocellulosic biocrude usually presents larger content of oxygen, leading to high O/C ratio and also presenting low H/C ratio, while the non-lignocellulosic biocrude presents a relatively low oxygen content and high H/C ratio. For non-lignocellulosic biocrude, an additional Van Krevelen diagram is present cross-plot the nitrogen:carbon atomic ratio (N/C) and H/C ratio, due to the high nitrogen content in the raw biocrude.

Lignocellulosic biocrude

Figure 2.5 presents the cross-plot of O/C and H/C ratios for raw biocrude and upgraded biocrude for both batch and continuous reactors of the lignocellulosic biocrudes.

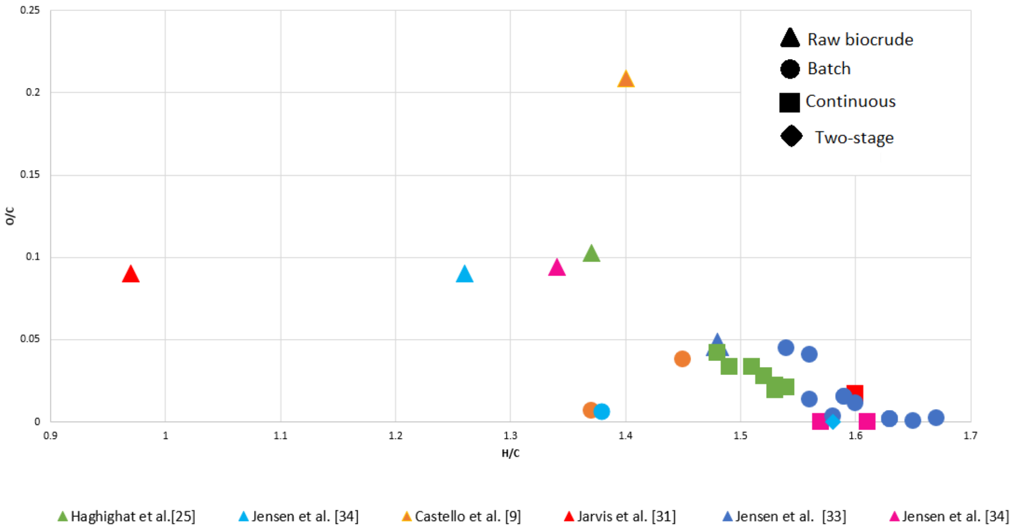

Figure 2.5: Van Krevelen diagram for lignocellulosic biocrude, based on presented literature.

It can be seen that even being all lignocellulosic biocrudes, the specific feedstock still has weight on the composition of the oil. For example, the hardwood biomass feedstock used by Jensen et al. [34] presents a high H/C ratio and a low oxygen content (which translates in a low O/C ratio) for lignocellulosic biomass, while the miscanthus biocrude used by Castello et al. [10] stands out with the highest oxygen content, therefore, the highest O/C ratio.

The only study that achieve complete deoxygenation was conducted by Jensen et al. [35]. Both the continuous experiments, at 350°C and 370°C, obtained complete deoxygenation, with higher HYD being obtained at 350°C. The batch experiments, for the single-stage investigation, the oxygen content reduce around 93% and complete deoxygenation was obtained at the two-stage hydrotreating. The second-stage also enhanced the HYD reactions, obtaining an higher H/C ratio.

The parametric study by Jensen et al. [34], higher deoxygenation was achieved under high temperatures, at 350°C, with around 95% of oxygen removal. Also with high the pressure and high hydrogen to oil ratio, resulted in higher HYD. Another parametric study was done by Haghighat et al. [26], the upgraded biocrude also presents a higher degree of HDO at severe conditions, 350°C and 95 bar. Moreover, the WHSV shown to have an impact on the HYD reaction, with the highest H/C ratio being obtained by lowering the WHSV.

As previously mentioned the miscanthus biocrude in the study conducted by Castello et al. [10], presents a high concentration of oxygen in the biocrude. The hydrotreating process has shown significant deoxygenation in the upgraded biocrude, therefore, a lower O/C ratio. The hydrotreatment at 400°C shows a higher degree of HDO, contain around 0.8% oxygen content while at 350°C the upgraded biocrude still presented around 4.3%. However, the HYD performed more effectively in at 350°C than 400°C, for this study. In the Jarvis et al. [32] study, the hydrotreatment was performed severe conditions, at 400°C and 100 bar, where significant deoxygenation was obtained, around 80% and also an increase in the H/C ratio 0.95 to 1.6 .

In all the experiments, hydrotreating resulted in an upgraded biocrude with lower oxygen content, therefore a lower O/C ratio, and also an increase of the H/C ratio, for most cases. For temperatures of 350°C or above, the upgraded biocrude obtained a high degree of HDO resulting in low oxygen content, around 1-2% weight percentage. Also the two-stage hydrotreating present a high heteroatom removal, obtaining complete deoxygentaion and further intensify the HYD reactions.

Non-lignocellulosic biocrude

The sewage sludge and algae raw biocrude, in general, present a lower concentration oxygen and higher of nitrogen compared to lignocellulosic raw biocrude, also a higher H/C ratio, as we can see in Figure 2.6.

The continuous experiments done by Jarvis et al. [32], both the algae and SS, show considerable improvement in the H/C ratio, although this can also be justified by the severe operating conditions (400°C and 100bar).

The parametric study performed by Haider et al. [27], complete deoxygenation was only obtained at high temperatures, above 350°C, while at mild conditions, 250°C, the O/C ratio remained close to the raw biocrude. Additionally, the upgraded biocrude show significant HYD, when lowering the WHSV.

For the algae study by Castello et al. [10], complete deoxygenation was also obtained for 350°C and 400°C, with a higher degree of HYD for 400°C. The upgraded SS biocrude also presents similar results to the algae, with high degree of HDO and HYD at both temperatures, still being more effective at 400°C.

In the study performed by Biller et al. [5] also presents higher degree of HDO at high temperatures,around 405°C, with the highest degree of deoxygenation being

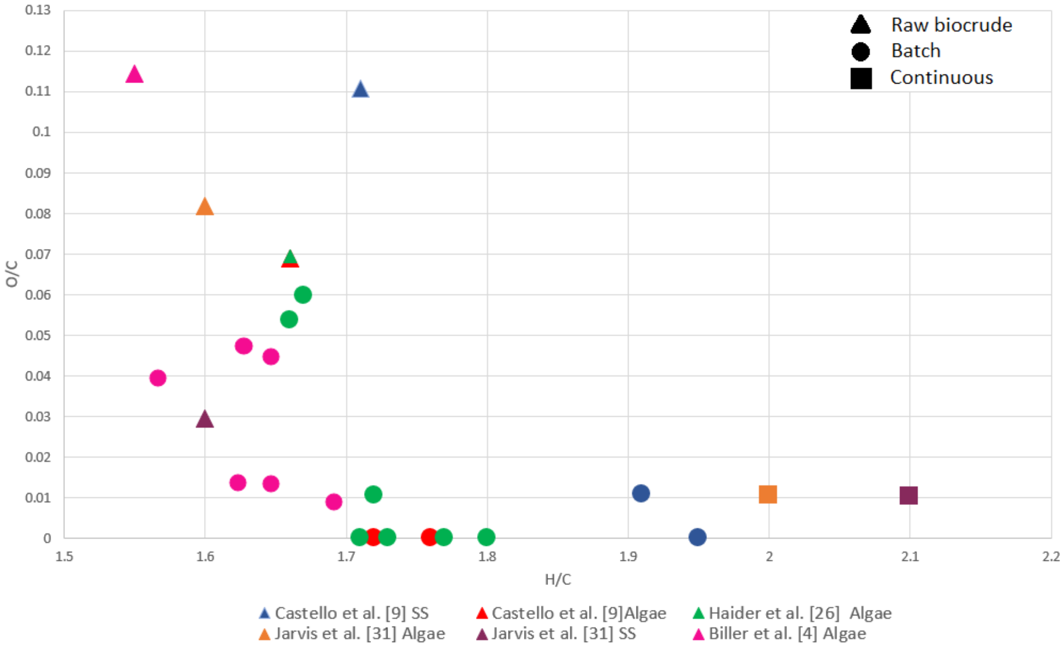

Figure 2.6: Van Krevelen diagram for sewage sludge and algae biocrude, based on presented literature for O/C.

obtained with $CoMo/Al_2O_3$ catalyst. The use of catalyst for hydrotreating presents higher degree of HYD compare to no-catalyst experiment, at high temperatures.

In upgrading non-lignocellulosic biocrude, for temperature of 350ºC and above, resulted in low oxygen content, around 1% or complete deoxygenation. This is mainly due to the low concentration of oxygen content is the raw biocrude compared to lignocellulosic biocrude, on the other hand the concentration of nitrogen is much higher, therefore the importance of studying the effects of the HDN in the hydrotreating process.

Figure 2.7, presents the N/C and H/C values for both the raw and upgraded biocrude.

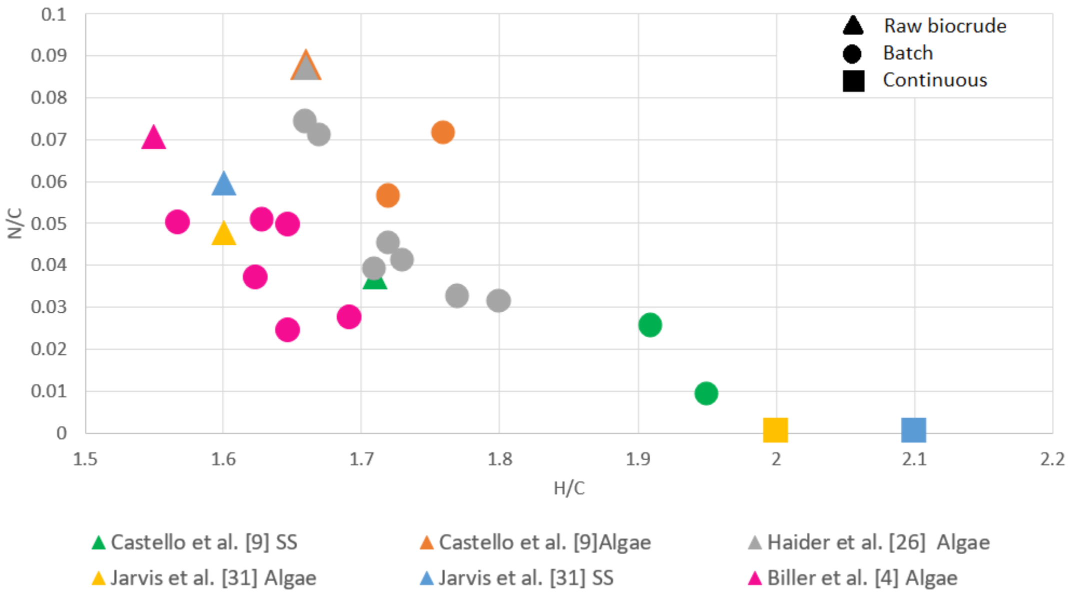

Figure 2.7: Van Krevelen diagram for sewage sludge and algae biocrude, based on presented literature for N/C.

The experiment conducted by Jarvis [32], both the experiment SS and algae present present complete denitrogenation at high conditions, 400ºC and 100 bar. This results, supports the idea, in Figure 2.4, where the HDN require high conditions in order to be more effective. Moreover the study performed by Castello et al. [10], in the SS achieves around 36% of denitrogenation at 350ºC and around 77% at 400ºC.

In the Biller et al. [5] study, higher degree of HDN is obtained at high temperatures (405ºC), also the use of catalyst obtained higher denitrogenation compared with no-catalyst experiment, with the use of $Nimo/Al_2O_3$ achieving the lowest values, around 2.4%.

The same effect is observed with the Haider et al. [27] study, the increase of temperature from 250ºC to 350ºC and to 375ºC show a positive effect in the HDN, removing around 17%, 47% and 60% of the nitrogen, respectively. In this study increasing the temperature to 400ºC did not show much better improvement in the denitrogenation compared to 375ºC, this is mainly due to the high polarity of the oil, possibly causing the deactivation of the catalyst.

It can been seen for all cases, hydrotreating at high temperature improved the oil characteristics and lower the heteroatom content. Also decreasing the WHSV presented better H/C ratio, that is, higher degree of HYD. As expected the operating conditions have significant influence in the reaction, therefore the need for studying in more detailed the influence in the HYD, HDO and HDN.

Chapter 3

Experimental Work

As explained in the first chapter, and with the state of the art strongly based on that fact, the initial target of this study was to perform experimental work on upgrading mischantus biocrude through hydrotreating. Being a biocrude with a large content of oxygen, mischantus biocrude presents higher instability and, consequently, higher potential for coking during the hydrotreating process. For this reason, the intent was to investigate a two-stage hydrotreating and evaluate how the upgrading process is enhanced.

Due to the outbreak of Covid-19, the university and its laboratories were shutdown, making a new approach for this study necessary. However, the experimental work had already been initiated and 3 experiments were performed.

3.1 Materials and Methods

The hydrotreating experiments were performed in the Biofuel Production Lab of AAU. The experimental set-up includes two 25 mL micro-batch reactors, a fluidised sand-bath, a shaking device to improve the mixing of the reactants, pressure transducer for each reactor plus a temperature and air flow controller. The schematic of the setup is presented in Figure 3.1. The mischantus biocrude utilized was produced in Aarhus University as a part of the Hyflexfuel project funded by the EU programme Horizon 2020.

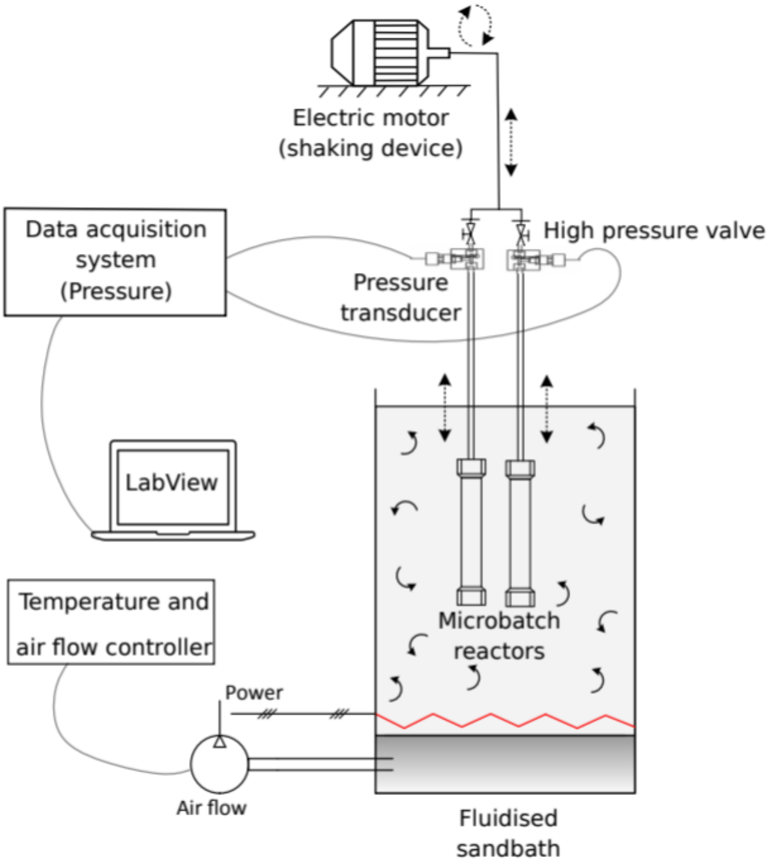

Figure 3.1: Schematic diagram of experimental setup. [46]

- **Micro-batch reactors:** Two 25mL Swagelok micro-batch reactors are used during the procedure to secure reproducibility and comparability of results. Micro-batch reactors were selected due to being more suitable for parametric studies, such as this one, where the impact of various parameters is investigated. The top part of the reactors has a valve to extract the gases, a pressure transducer to evaluate the pressure profile inside the reactors and a clamp, which is required to attach the reactors to the agitation device.

- **Sand-Bath:** To heat up the reactors to the desired temperature, a SBL-2D fluidized sand-bath (Techne, Stone, UK) was utilized. Having the sand behaving as a fluid (fluidization) improves the heat transfer, resulting in a quick heating of the reactors.

- **Shaking Device:** In order to obtain an efficient mixing, an electric motor is used in order to make a vertical tube, to which the reactors are connected, move up and down, creating agitation in the mixture.

- **Temperature and air flow controller:** Only the temperature in the sand-bath is controlled. Due to the large residence time of the reactors, the time that it takes for the reactors to achieve the stipulated temperature is assumed negligible. The air flow is controlled manually to ensure efficient fluidization of the sand.

- **Pressure Transducers:** The pressure within the reactors was continuously measured with an A-10 pressure transducer (Wika, Klingenberg, Germany). The pressure profiles were recorded and evaluated using a LabVIEW programme.

3.1.1 Experimental Procedure

The experimental procedure was conducted following the following steps:

1. Two micro-batch reactors were filled with 4 g of mischantus biocrude, 2 g of presulphided catalyst and 3 metallic spheres (diameter of 4 mm) to improve the mixing.
2. Reactors are closed and, in order to investigate possible leaks, are pressurized with nitrogen and are immersed in water to check for possible bubbles.
3. If no leaks are detected, the reactors are then purged with a small quantity of hydrogen in order to clean the reactor from possible residual gases.
4. Hydrogen is introduced to the reactor at the desired pressure.
5. The prepared reactors are linked with the pressure transducer in order to obtain the pressure temperature. Afterwards the reactors are attached to the shaking device and immersed in the sand-bath at the desired temperature.
6. As the desired residence time (2 hours) is reached, the reactors are taken out of the sand-bath and immersed in a water in order to cool down.
7. After cooling down, the gaseous products are collected before opening the reactor and extract the liquid products.

Figures 3.2 and 3.3 illustrate the miscanthus biocrude, and the $NiMo/Al_2O_3$ catalyst used in the experiments.

Figure 3.2: Miscanthus biocrude

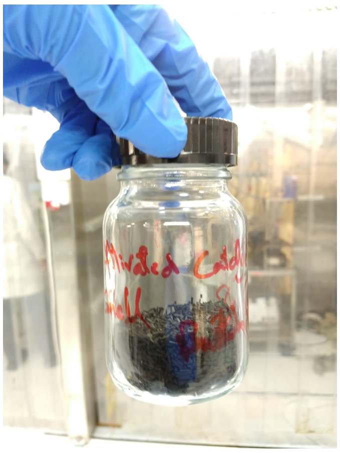

Figure 3.3: $NiMo/Al_2O_3$ catalyst

3.2 Experimental Results

The studied parameter in these experiments was the temperature, which was tested at 250°C, 300°C and 350°C in each test, with initial system pressure of 80 bar and a residence time of approximately 2 hours, obtaining a WHSV*=$0.5h^{-1}$ following Equation 2.2. Figures 3.4, 3.5 and 3.6 present the pressure profiles for each of these experiments, respectively. In the profiles it can be seen initial and final straight lines, which represent the time from the connection of the profile transducer until the introduction of the reactors in the sand-bath and the time of cooling down, respectively.

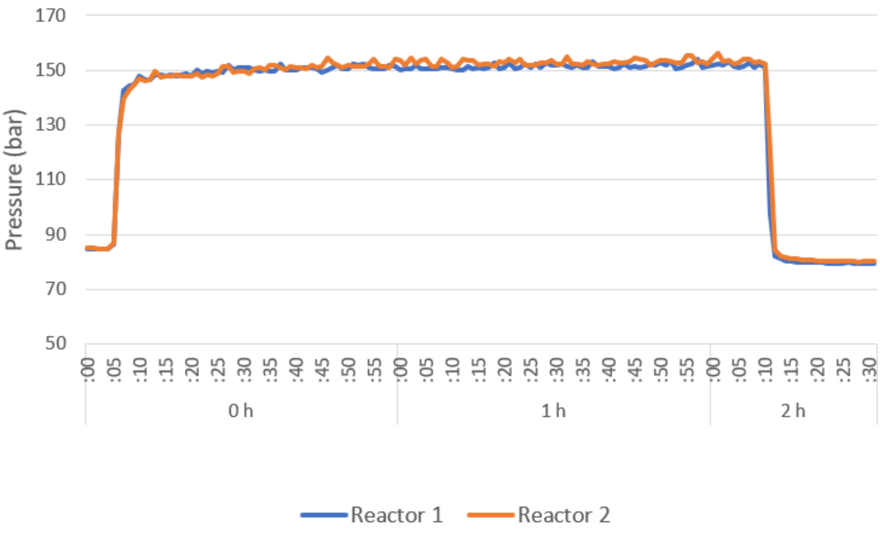

Figure 3.4: Pressure profile for both micro-batch reactors for the experiment at 250°C.

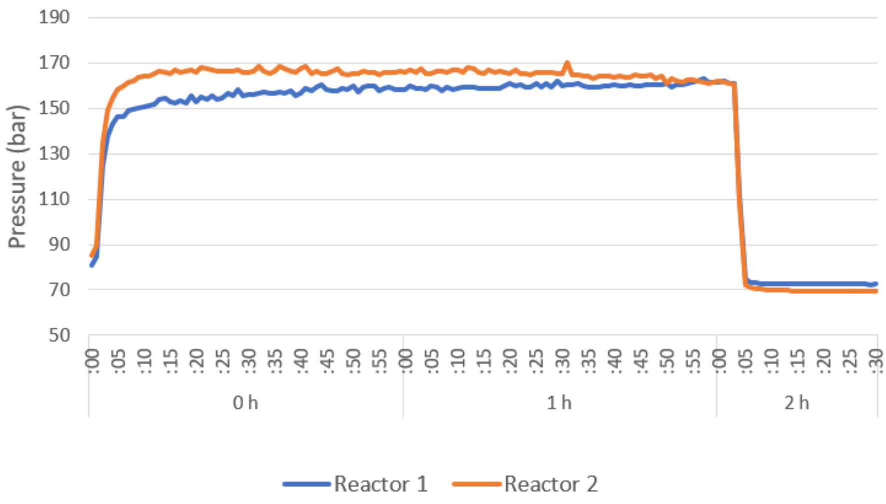

Figure 3.5: Pressure profile for both micro-batch reactors for the experiment at 300ºC.

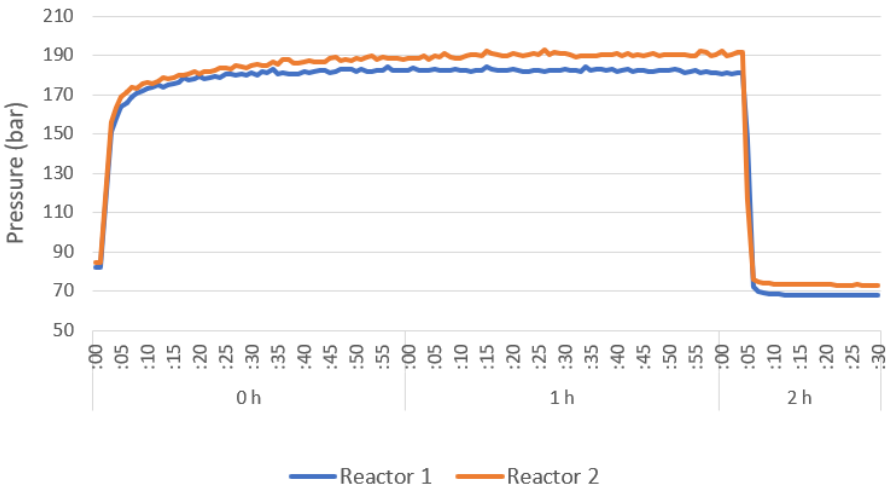

Figure 3.6: Pressure profile for both micro-batch reactors for the experiment at 350ºC.

It can be seen that, as the temperature of the system increases, the same happens for the pressure levels inside the reactor. For 250ºC a maximum pressure of around 150 bar is obtained, with 300ºC this value raises to 160-170 bar and with the highest tested temperature, 350ºC, it increased to close to 190 bar. It is important to mention that the differences between the two reactors in Figures 3.5 and 3.6 are related to their different initial pressure, as for both cases the reactors 1 and 2 started with 80 and 85 bar respectively.

A important parameter to evaluate in the pressure profiles is the final pressure of the system after being cooled down. The difference between the initial and final pressures is related to the quantity of hydrogen that was consumed, therefore how much the biocrude and the hydrogen reacted, presented in Equation 3.1.

$$n_{H_2} consumed = \frac{P_{initial} \cdot V}{R \cdot T} - \frac{P_{final} \cdot V}{R \cdot T} \tag{3.1}$$

As Figure 3.4 presents, for 250°C both reactors started close to 85 bar and finished around 80 bar, showing a low pressure drop for both. Resulting in the lowest hydrogen consumption around 0.00079 and 0.00063(kgH_2/kg_{feed}) for the first and second reactor respectively. For the 300°C the pressure drop increased, with the final pressures being around 70 bar, Figure 3.5, showing an enhanced reaction. The hydrogen consumption increased mainly in the second reactor, obtain the highest consumption around 0.00194(kgH_2/kg_{feed}) while the first reactor obtained 0.00111 (kgH_2/kg_{feed}). At 350°C, comparing to the previous case, the hydrogen consumption did not much improve, resulting in 0.00162 and 0.00121(kgH_2/kg_{feed}) for the first and second reactor. As expected with the increase of temperature, influence the hydrogen consumption, being more effective at high temperature. However, once the reactors were open for the products extraction, it was observed that the biocrude completely coked for the experiment at 350°C. As Figure 3.7 shows, coking reactions were predominant during the hydrotreating process, creating a "wall" of a solid mixture of biocrude and the catalyst at the bottom of the reactor. Comparing to another study performed in upgrading miscanthus biocrude by Castello et al. [10], opposite to the result obtain in this experiment, the study presented yields around 60-65% and around 50-75% of deoxygenation, for low and high pressures. While for this case the characterization was not even possible, since it was not possible to collect the products.

Figure 3.7: Coked mixture of mischantus biocrude and catalyst at the bottom of the reactor, after hydrotreating at 350°C.

This indicated the high instability of the bio-oil and pointed for a large content of high reactivity oxygenates. This fact gave strength to the idea of investigating a two-stage hydrotreating process for mischantus biocrude, where the first stage would be performed at milder conditions, in order to remove the high reactivity oxygenates from the biocrude and enhance its stability, followed by a second with more severe operating conditions, with the objective of completely deoxygenate the biocrude. As the oxygenates that would possibly cause coking reactions are removed during the first stage, this approach would lead to an improved hydrotreating with higher yields of upgraded biocrude.

Due to the coking in the 350°C case, the characterization was only performed for the experiments at 250°C and 300°C, along with the raw biocrude. Four different tests were performed: Gas chromatography (GC-Gas) CHNS analysis, Gas chromatography-mass spectrometry (GC-MS) and Fourier transform infrared spectroscopy (FTIR).

3.2.1 CHNS analysis

The elemental analysis is obtained via a 2400 Series II CHN/O analyzer (ASTM D-5291) from Perkin Elmer (Waltham, MA, USA). The carbon, hydrogen and nitrogen weight percentages were determined by the element analyzer, with the oxygen being calculated by difference, as can been seen in Table 3.1.

The estimation of the HHV for the biocrude and upgraded samples was estimated based in the propose by Beckman et al. [2], given in Equation 3.2

$$HHV = 0.352C + 0.944H + 0.105(S - O) \tag{3.2}$$

Table 3.1: Elemental analysis of the raw miscanthus biocrude and upgraded biocrude.

	Carbon (wt.%)	Hydrogen (wt.%)	Nitrogen (wt.%)	Oxygen (wt.%)	HHV (MJ/kg)	H/C
Raw Biocrude	74.6	7.6	1	16.8	31.7	1.22
Upg. Biocrude (250°C)	73.2	8.3	1.0	17.6	31.7	1.35
Upg. Biocrude (300°C)	77.2	8.9	1.5	12.4	34.3	1.38

The miscanthus biocrude presents a high oxygen content for HTL biocrude, with a value of 16.78 wt%, supporting the idea of the high instability of the oil. When hydrotreating at 250°C, an increase in the hydrogen content is seen, which also results in an increase in the H/C ratio, but, overall, no heteroatoms removal is obtained. Actually, the weight percentage of oxygen increased, contrarily to the literature presented by Jensen et al. [35] in pine wood at the same operating conditions, which shows the higher instability of the tested mischantus HTL biocrude.

At temperature of 300°C, a clear improvement can be visualized in the upgraded biocrude, obtaining around 26% of deoxygenation and also an increase in the hydrogen content. This results in the rise of the HHV from 31.67 to 34.25 MJ/kg and in an increase in the H/C ratio from 1.22 to 1.35.

3.2.2 GC-MS

The raw biocrude and the samples of upgraded biocrude were analyzed by GC-MS in order to evaluate their chemical composition, using a Trace 1300 ISQ QD-Single Quadrupole instrument (Thermo Scientific, Waltham, MA, USA), with a temperature range of 40 to 300°C. The chromatograph of the raw biocrude is presented in Figure 3.8. The raw biocrude presents a complex mixture of various hydrocarbons and heteroatoms, mostly oxygen, as expected from the elemental analysis. The most abundant compounds were labelled, as identifying them all would be impossible, where it can be seen that the biocrude is dominated by the presence of phenols, where the most intense phenol is $C_{15}H_{16}O_2$, showing a high carbon number (C_{15}).

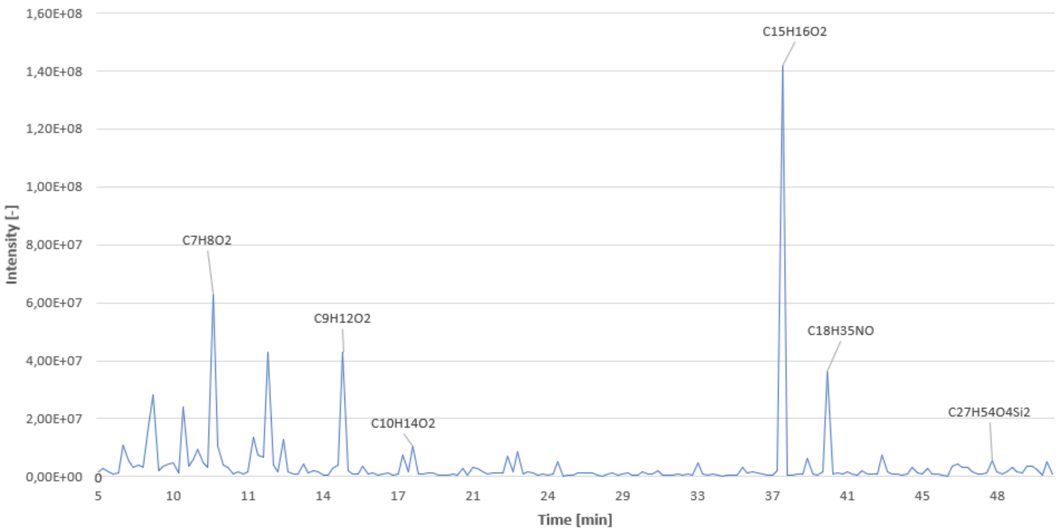

Figure 3.8: GC-MS chromatograph of raw biocrude.

Figure 3.9 shows the chromatograph of the upgraded biocrude at temperature of 250°C. As it was expected from the elemental analysis, it is still predominant by oxygenates, in particular phenols, but for this case the dominance or high carbon number drastically goes down, with the most intense phenol being $C_8H_{10}O$.

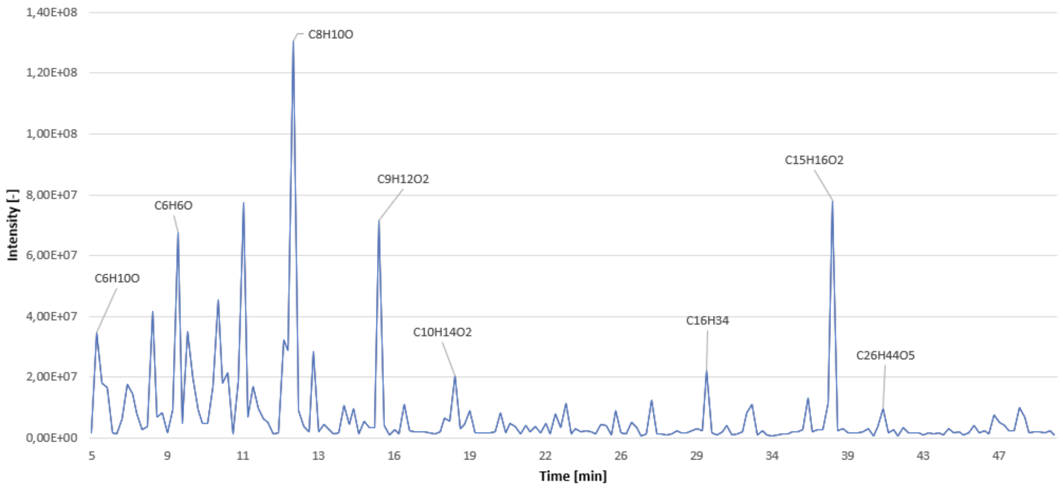

Figure 3.9: GC-MS chromatograph of upgraded biocrude at 250ºC.

The chromatograph of the upgraded biocrude at temperature of 300ºC is presented in Figure 3.10. It can be visualized that most of the peaks lowered down, as the decreased oxygen content seen in the elemental balance lead to believe, with phenols continuing to be the predominant compounds, but now for lower carbon number (C_6 and C_8). Overall, the upgrading experiments did not show major impact on the heteroatoms removal, however, hydrogenation and possibly cracking reactions took place, seen by the decrease in the carbon number by the predominant phenols in the biocrude.

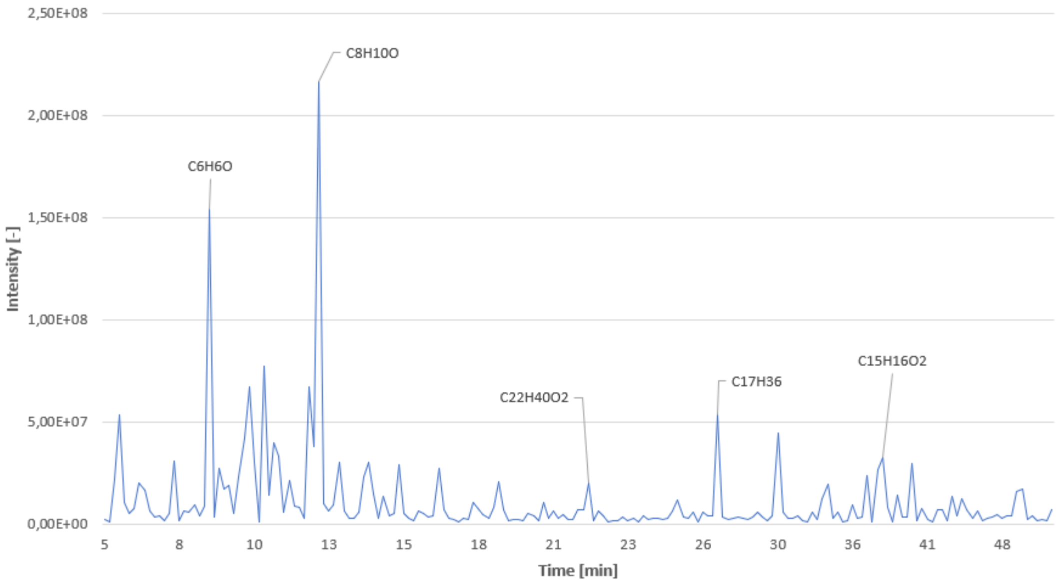

Figure 3.10: GC-MS chromatograph of upgraded biocrude at 300°C.

3.3 New Approach for the Study

As laboratory work became an impossibility, a new target for the study was determined, with the objective now being kinetic modelling of the deoxygenation and denitrogenation reactions for hydrotreating of biocrude. Using data from a continuous hydrotreating campaign of algae biocrude performed at AAU, a model will be constructed to estimate the kinetic constants for both reactions depending on the geometry of the reactor, the operating conditions of the process as well as on the initial and final concentrations of both oxygen and nitrogen on the biocrude.

The biocrude is characterized with several different oxygen and nitrogen compounds with different HDO and HDN reactivities, therefore the kinetic parameters are hard to determine and vary for different oils, plus there is not much literature on this field. Thus, in order to simplify the many HDO and HDN reactions occurring in the hydrotreating process, this model assumes that all the oxygenated and nitrogenated compounds in the oil are represented as "O" and "N", respectively, and assumed to follow the following reaction paths:

$$\begin{array}{lccc} \textbf{Reaction 1} & O + H_2 & \longrightarrow & \mathrm{H_2}O \\ \textbf{Reaction 2} & N + \frac{3}{2}H_2 & \longrightarrow & \mathrm{NH_3} \end{array}$$

As mentioned in the previous chapter, the operating conditions play a significant role in the heteroatom removal and HYD, therefore having serious impact on the quality of the upgraded oil. This model has the objective to evaluate the influence of the different parameters of the hydrotreating process. With a validated model, it is possible to use this model to optimize the different operating conditions and reactors set-up, in order to ensure effectiveness of both HDO and HDN during the hydrotreating of the biocrude. Also, in subsection 2.3.1 it can be seen that the deoxygenation reaction presents a much higher rate compared to the denitrogenation reaction, which will be seen in the difference between the kinetic constants for each reaction. Also, following the initial purpose of the experimental work and the data from the algae campaign, a second stage model will also be integrated, which creates two-stage hydrotreating model.

The kinetic model is performed in a fixed bed reactor that consists in a cylinder tube filled with catalyst pellets, with the reactants being converted into products as they flow through the catalyst surface in the reactor [30]. A packed reactor is illustrated in the Figure 3.11, where the red points presented in the center of the reactor represent temperature measurement points, used to characterize the temperature profile of the process, given the exothermicity of the hydrotreating reactions.

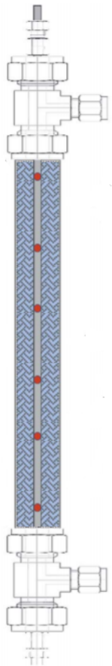

Figure 3.11: Schematic of a packed reactor used for hydrotreating.[26]

The following chapter will further develop the kinetic model in question, explaining how the model was constructed and how the data from the AAU campaign was integrated in the code to estimate the kinetic parameters for each reaction.

Chapter 4

Modelling

A model for a two-stage hydrotreating, based on the AAU set-up, was created in MATLAB, where two pseudo-components O and N were assumed as the all oxygenates and all the nitrogenen-containing compounds, respectively, in the biocrude. Two simplified reactions representing deoxygenation and denitrogenation with the objective of estimating the kinetic coefficients for each reaction. As the reactions are taking place in the surface of the catalyst, two sets of values for the kinetic parameters will be obtained, one for the catalyst A and the other for the catalyst B.

After obtaining and validating the modelled kinetic parameters, the values can be used to optimize the system, as they present the deoxygenation and denitrogenation behavior. Different targets could be defined, as to gather the optimal reactor dimensions for a specific objective, predict different operating conditions effects or define more effective mass and height of the catalyst, among other possible utilities.

4.1 System Description

For the purpose of studying the kinetic reactions of the oxygen and nitrogen in a hydrotreating process of biocrude, experimental data provided by Aalborg University was used. The AAU pilot plant consists of a dual-reactor setup using fixed-bed heterogeneous catalyst, this allows for the reactors to run in series, parallel or even turn one of the reactors off, that means running in single reactor. A simple schematic of the reactors can be seen in Figure 4.1.

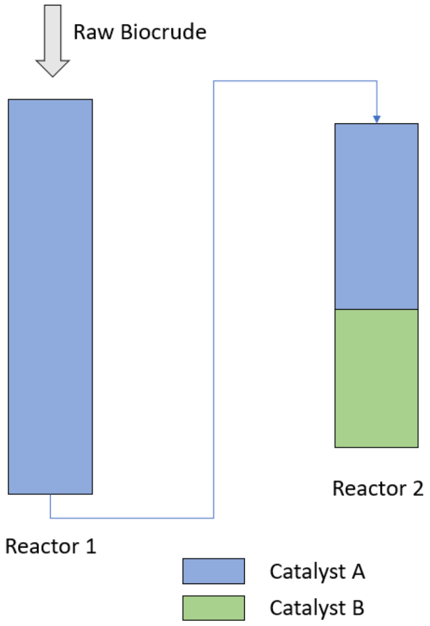

Figure 4.1: Schematic of AAU reactors setup.

As mentioned above, it is possible to run the presented system with a single reactor, as the second reactor can be turned off and a single stage hydrotreating process is performed in the first reactor. The second stage starts by using as feed the upgraded biocrude from reactor 1 and perfomers a further upgrading the biocrude. Data from a AAU campaign for continuous hydrotreating of algae biocrude that used the setup presented in Figure 4.1 was provided to investigate the kinetics of deoxygenation and denitrogenation reactions. Values for single-stage and two-stage experiments are utilized to estimate the rates of reaction for both catalysts A and B.

4.1.1 Experimental Data

Following the scheme presented on Figure 4.1, the information regarding the catalysts used during the AAU campaign and the reactors in which they are used is presented in Table 4.1:

Table 4.1: Catalyst data for each stage of the hydrotreating AAU campaign.

Reactor	Diameter (m)	Catalyst	Height of catalyst (m)	Mass of catalyst (g)
1	0.148	A	0.70	48.6
2	0.148	A	0.39	28.1
		B	0.20	20.5

Algae biocrude, which was also produced in Aarhus University as a part of the Hyflexfuel project funded by the EU programme Horizon 2020, was used for the remaining data presented in this subsection, which presented a density of 979.1 kg/m^3 and elemental composition shown in Table 4.2. As explained in Subsection 1.3.1, algae is mainly composed of lipids and proteins, therefore the high level of nitrogen in biocrude.

Table 4.2: Elemental balance of the algae biocrude used in the AAU hydrotreating campaign.

	Elemental Balance (wt%)			
	C	**H**	**N**	**O**
Algae Biocrude	75.1	10.8	7.6	6.5

The single-stage hydrotreating experiment, performed only in the first reactor, was conducted under 5 different temperatures, at 100 bar and a WHSV of 0.5h^(-1). The elemental balance of the upgraded biocrude can be seen in Table 4.3, where complete deoxygenation is obtained at 300°C.

Table 4.3: Elemental balance of the single-stage hydrotreating products at different temperatures. Fixed conditions: P=100 bar, and WHSV=0.5h^(-1).

Temperature (°C)	**Elemental Balance (wt%)**			
	C	**H**	**N**	**O**
200	75.1	11.1	7.6	5.9
250	77	11.6	7.6	3.8
300	80.7	12.8	6.5	0
320	81.3	13.1	5.6	0
340	82.3	13.5	4.5	0

In the second-stage hydrotreating 3 different temperatures were conducted, with the feed being the upgraded biocrude from the first reactor at 340°C. The results can be seen in Table 4.4, with fixed pressure of 100 bar and WHSV of 0.5 h^(-1).

Table 4.4: Elemental balance of the two-stage hydrotreating products at different temperatures. Fixed conditions: P=100 bar, and WHSV=0.5h^(-1).

Temperature	**Elemental Balance (wt%)**			
	C	**H**	**N**	**O**
340	84.1	15	0.9	0
370	84.2	15.1	0.8	0
400	83.5	14.3	2.1	0

All the presented data is going to be used to estimate the kinetic coefficients of the deoxygenation and denitrogenation reactions during the hydrotreating process of biocrude.

4.2 System Modelling

As hundreds of reactions take place during the hydrotreating process, creating an exact kinetic model of the system is an impossible task. To make it viable, various assumptions are taken to create the studied hypothesis:

- The process is performed in an isothermal reactor, therefore the temperature profile inside of the reactor remains constant.
- The hydrotreating is assumed to occur at steady-state.
- Plug flow, where the velocity of the fluid is assumed to be constant across any cross-section of the pipe perpendicular to the axis of the pipe.
- All oxygen-containing compounds are lumped into a single pseudo-compound (O), whose concentration is equal to the concentration of oxygen in the biocrude.
- All nitrogen-containing compounds are lumped into a single pseudo-compound (N), whose concentration is equal to the concentration of nitrogen in the biocrude.
- The reactions are assumed irreversible.
- The rates of reaction follow the Arrhenius equation.
- Density of the biocrude is assumed constant throughout the process.
- Dissolved H2 concentration is considered constant.

Figure 4.2 presents the flow chart that describes the methodology followed in this study to model the hydrotreating process.

The kinetics constants for each reaction, in both catalysts, are unknown, so they will be estimated based on experimental data. Guessing the initial values of the kinetic constants for the first reactor and calibrating the model using experimental data from one-stage hydrotreating experiments, the model will estimate the kinetic parameters that better fit the experimental values. Same process is performed in the second reactor using experimental data from two-stage hydrotreating, using the product from first reactor as feed.

Following the presented approach to model the studied system, the model can be divided in two parts:

- **First Stage Model:** Following the schematic presented in Figure 4.1, this model is used for Reactor 1. In this case, the biocrude with characteristics presented in Table 4.2 is the feedstock and the kinetic parameters for the reactions using catalyst A is calculated.
- **Second Stage Model:** This model is utilized for reactor 2 (Figure 4.1) and uses the final product of the first stage model as its feed. With the kinetic parameters for catalyst A already estimated, the conversions can be calculated on the second reactor for the height of catalyst A. Using the calculated concentrations after the catalyst A and having experimental data for a two-stage hydrotreating, the same methodology as in the first stage can be done and the kinetic constants for the catalyst B can be estimated.

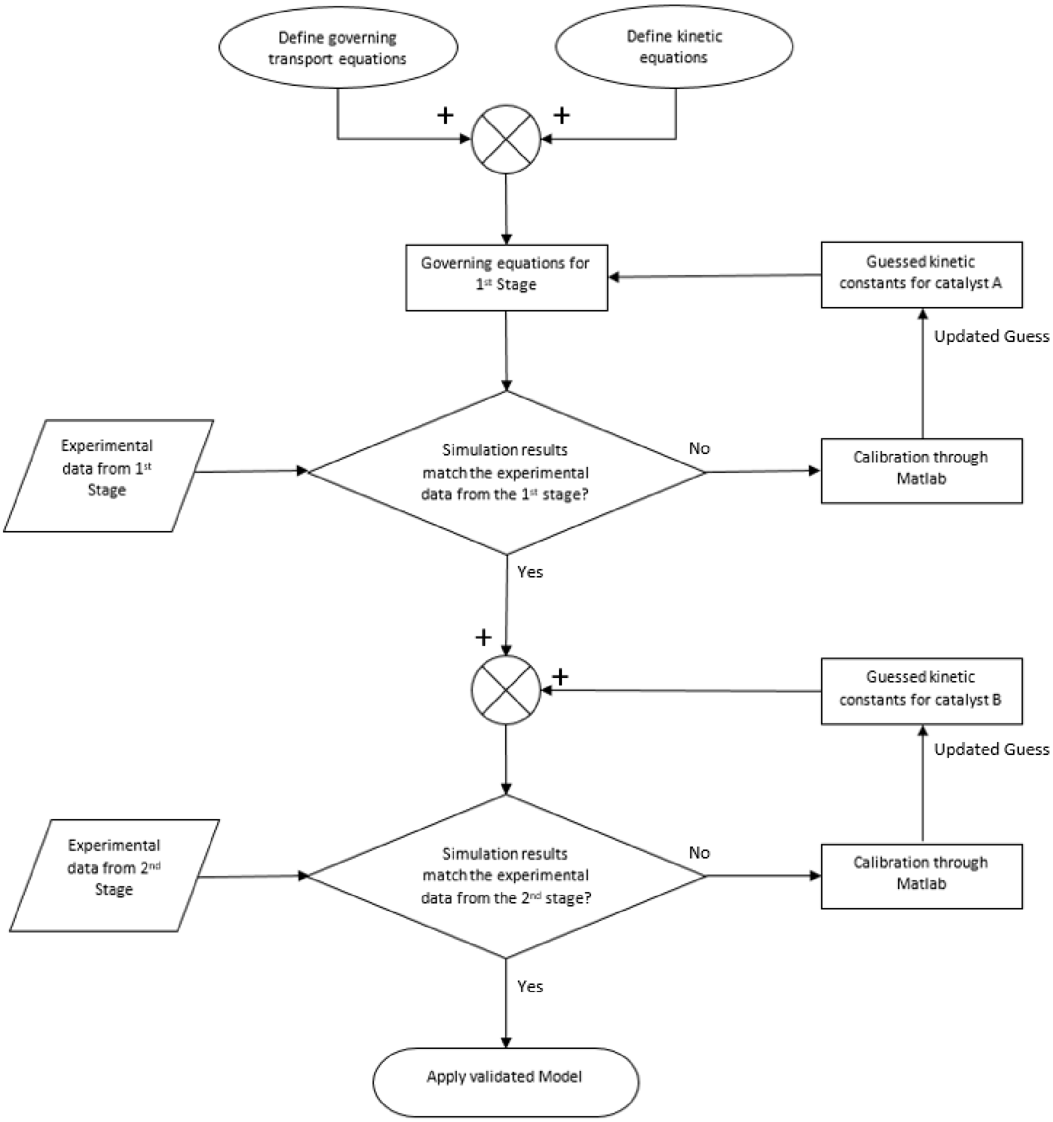

Figure 4.2: Flow chart of the modelling procedure.

In order to study how the concentrations of reactants and products vary across the plug flow reactor, a mass balance is performed on a control volume which encloses a section of the PFR of infinitesimally small thickness, dx. Since the thickness is small, we can assume that the fluid in that region of the PFR is perfectly mixed.

4.2.1 Mass Balance

One of the fundamental laws of physics states conservation of mass and it can neither be produced nor destroyed. Thus, given a control volume (dV) the sum of mass entering the system will be equal to the exiting mass or accumulation fractions within the system. [14] The main assumptions of this model are that it presents an uniform cross section concentration and there is no mixing in the axial direction, or no axial dispersion. Also, the fluid is assumed to transit at steady-state, therefore resulting in no accumulation. Given these assumptions, the mass balance is given by:

$$\text{IN - OUT +/- GENERATION} = \xcancel{\text{ACCUMULATION}} = 0$$

or

$$W_{j0} - W_j + \sum(a_{j,i} * r_i) \cdot dV = 0 \tag{4.1}$$

As the component j can be involved in many reactions, each reaction is indicated by i (i = 1, 2, 3), with each one being associated with his own kinetic coefficient a_j, i. The W is denoted as the mass flow rate and can be defined in function of the volumetric flow rate and concentration ($W = Q \cdot C$). Taking into account that the reaction takes place on the surface of the catalyst, so the reaction rate (r_i) is determined in function of the mass of catalyst, represented by $\rho_c \cdot dV$.

The mass balance represented in Equation 4.1 is applied over the the control volume obtaining Equation 4.2.

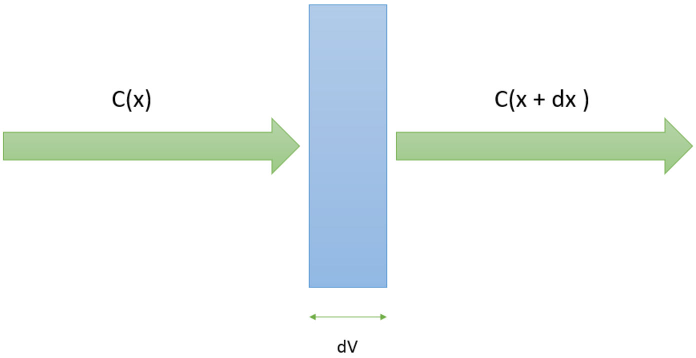

Figure 4.3: Specific control volume in the plug flow reactor

$$Q \cdot C(x) - Q \cdot C(x + dx) - r \cdot \rho_c \cdot dV = 0 \tag{4.2}$$

where,

Q = volumetric flow rate [m^3/s]
C = concentration [mol/m^3]
ρ_c = bulk density of the catalyst [kg/m ^3]
dV = Differential volume [m^3]

Noting that the control volume is given by $dV = S \cdot dx$, through Taylor's expansion, the Equation 4.2 can be rearranged as:

$$\frac{dC_j}{dx} = -\frac{S \cdot \rho_c}{Q} \cdot r \tag{4.3}$$

where S is the area of the cross section and r is the reaction rate of the chemical reaction of the system.

Chemical reactions are balanced according to their stoichiometry and are represented in the following structure:

$$aA + bB \longrightarrow dD + eE \tag{4.4}$$

with the respective reaction rate being defined as a function of the concentration, in this case C_A and C_B, and also the temperature:

$$r = k(T) \cdot (C_A)^a \cdot (C_B)^b \tag{4.5}$$

The specific rate of reaction, k(T), is described by the Arrhenius equation, presented in Equation 4.6.

$$k(T) = k_0 \cdot e^{\frac{-E_{act}}{R \cdot T}} \tag{4.6}$$

where,

k_0 = pre-exponential
E_a = energy of activation [J/mol]
R = gas constant [J/mol.K]
T = absolute temperature [K].

4.2.2 Simplified kinetic model

This model takes into account the hydrodeoxygenation and hydrodenitrogenation of biocrude in the presence of a catalyst, with both reactions being irreversible. Simplifying these reactions, they can be written in following way:

Reaction 1 $O + H_2 \longrightarrow \mathrm{H_2}O$
Reaction 2 $N + \frac{3}{2}H_2 \longrightarrow \mathrm{NH_3}$

This means that two pseudo-components, O and N, were defined, with each one representing the total amount of oxygen and nitrogen in the biocrude, respectively. As described in the before, a large number of different reactions occur during the both oxygen and nitrogen removal, making it impossible to evaluate and model them all. For this reason, the simplification made is a necessary approach to obtain a feasible model.

The Equation 4.3 has to be written in function of the different compounds in the system, in this case oxygen, nitrogen and hydrogen. Doing that, the following ordinary differential equation (ODE) system is obtained:

$$\begin{cases} \frac{dC_O}{dx} = -\frac{S \cdot \rho_c}{Q} \quad k_{0,1} \cdot e^{\frac{-E_{act,1}}{R \cdot T}} \cdot C_O \cdot C_{H_2} \\ \\ \frac{dC_N}{dx} = -\frac{S \cdot \rho_c}{Q} \quad k_{0,2} \cdot e^{\frac{-E_{act,2}}{R \cdot T}} \cdot C_N \cdot (C_{H_2})^{\frac{3}{2}} \\ \\ \frac{dC_{H_2O}}{dx} = +\frac{S \cdot \rho_c}{Q} \quad k_{0,1} \cdot e^{\frac{-E_{act,1}}{R \cdot T}} \cdot C_O \cdot C_{H_2} \\ \\ \frac{dC_{NH_3}}{dx} = +\frac{S \cdot \rho_c}{Q} \quad k_{0,2} \cdot e^{\frac{-E_{act,2}}{R \cdot T}} \cdot C_N \cdot (C_{H_2})^{\frac{3}{2}} \\ \end{cases} \tag{4.7}$$

The hydrogen that reacts with the oxygen and nitrogen within the biocrude is a dissolved gas in the liquid oil. Since the hydrogen in the system is provided in excess, the concentration of dissolved hydrogen in the oil is assumed to be constant across the length of the reactor and that reactions are not limited by mass transfer of H_2 into the oil. The objective is, knowing both the initial and final concentrations of the compounds, to estimate the kinetic coefficients $k_{0,n}$ and $E_{act,n}$. To do that, the remaining parameters of the ODE system must be determined from the biocrude characteristics and the operating conditions of the hydrotreating process.

Calculations

Through the elemental composition of the biocrude, where the weight percentage of both oxygen and nitrogen is provided, their concentrations in the biocrude is possible to calculate using the Equation 4.8:

$$C_x = \frac{wt_x\%}{100} \cdot \frac{\rho_{Biocrude} \cdot 1000}{M_x} \tag{4.8}$$

where,

C_x = Concentration of compound x [mol/m^3]
$wt_x\%$ = Weight percentage of compound x in the biocrude
$\rho_{biocrude}$ = bulk density of the biocrude [Kg/m ^3]
M_x = Molar mass of compound x [g/mol]

As mentioned above, it is not the gaseous hydrogen that reacts with the oxygen and nitrogen, but rather the hydrogen that dissolved in the biocrude. To calculate the concentration of dissolved hydrogen in the biocrude, the Henry's Law is utilized, which states that the amount of dissolved gas in a liquid is proportional to its partial pressure above the liquid. This translates in the following equation:

$$C_{H_2} = H^{cp} \cdot P \tag{4.9}$$

where,

C_{H_2} = Concentration of hydrogen dissolved in biocrude [mol/m^3]
H^{cp} = Henry's solubility constant [mol/(m^3 · Pa)]
P = Pressure of the system [Pa]

For the Henry's solubility constant, the value $7.7 \cdot 10^{-6}$ mol/(m^3 · Pa) was used, which is the Henry's constant of hydrogen in water at a temperature of 640K [15]. More data was investigated for more temperatures, with the values of the Henry's constant being very similiar, between 7.7 and 7.9 $\cdot 10^{-6}$ mol/(m^3 · Pa) for temperatures between 490 and 640K.

The bulk density of the catalyst is calculated through Equation 4.10:

$$\rho_c = \frac{m_c}{V_{CatBed}} \tag{4.10}$$

where,

ρ_c = bulk density of the catalyst [kg/m ^3]
m_c = mass of catalyst [kg]
V_{CatBed} = Volume of the catalyst bed [m ^3]

The volumetric flow rate is calculated through the operating condition WHSV, explained in Equation 2.1, using the following equation :

$$Q = \frac{WHSV \cdot m_c}{\rho_{biocrude} \cdot 3600} \tag{4.11}$$

where,

Q = Volumetric flow rate [m^3 / s]
$WHSV$ = Weight hourly space velocity [h^(-1)]
m_c = Mass of catalyst (kg)
$\rho_{biocrude}$ = bulk density of the biocrude [Kg/m ^3]

Chapter 5

Model Implementation&Calibration

As the kinectic constants, $k_{0,n}$ and $E_{act,n}$, are unknown for the ODE system presented in Equation 7.1, it is impossible to solve the ODE without first estimating these coefficients. This chapter will explain how the model was calibrated, using experimental data, in order to obtain values for the coefficients that fit the experimental observations. The model was created using Matlab, with commands of this programme being mentioned during this chapter.

5.1 First Stage Model

With a function containing the ODE system presented in Equation 7.1, a second function is created which uses the command ***ode45*** to solve the system. This command is used to integrate the ODE system for the space (length of reactor, from x=0 to x=0.7m), using the concentrations presented in Table 5.1 as the initial conditions. This values are obtained from Table 4.2, using Equation 4.8.

Table 5.1: Initial concentrations of oxygen and nitrogen for the raw biocrude.

	Concentration (mol/m^3)			
	O	**N**	**H2O**	**NH3**
Algae Biocrude	3971.5	5318.6	0	0

However, the ODE system can not be determined without the kinetic constants being estimated. To do this, the command ***lsqcurvefit*** is utilized, which estimates the unknown constants This command solves the ODE system presented in Equation 7.1 with an initial guess (guessed by the used) and compared to the experimental data shown in Table 5.2, in which the oxygen and nitrogen concentrations are calculated, using Equation 4.8, from Table 4.3. This command consists of an iterative method, where the ODE is solved until the difference between the calculated concentration and experimental concentration is minimum.

Following reactions 1 and 2, presented in subsection 4.2.2, the concentrations of water and ammonia are determined by the difference between the concentrations of oxygen and nitrogen in the raw biocrude and after the hydrotreating, respectively.

Table 5.2: Concentrations of oxygen and nitrogen on the biocrude plus water and ammonia after one-stage hydrotreating at the presented temperatures.

Temperature	**Concentration (mol/m^3)**			
(°C)	**O**	**N**	**H2O**	**NH3**
200	3605.8	5318.6	365.7	0
250	2304.5	5318.6	1666.6	0
300	0	4514.5	3971.5	804.1
320	0	3936.2	3971.5	1382.4
340	0	2973	3971.5	2345.6

The estimated kinetic coefficients are presented in Table 5.3. From the revised literature, it was seen that the values for the pre-exponential factor k_0 has an extremely wide range of values, basically having no restrictions besides being non-negative, while the energy of activation for deoxygenation and denitrogenation showed more or less of a boundary, being limited, roughly, between $10 \cdot 10^3$ and $30 \cdot 10^4$. [29] [69]

For this reason, the initial guesses for the pre-exponential factor and energy of activation were 1 $[\frac{m^3}{mol \cdot s}$ for reaction 1 & $(\frac{m^3}{mol})^{3/2} \cdot \frac{1}{s}$ for reaction 2] and $10 \cdot 10^4$ $[J/mol]$, respectively, for both reactions.

Table 5.3: Estimated kinetic coefficients for catalyst A.

Kinectic Constants	**Estimation**
$k_{0,1}$	2.12 $[\frac{m^3}{mol \cdot s}]$
$Eact_1$	93174.7 $[\ J/mol\ ]$
$k_{0,2}$	0.029 $[(\frac{m^3}{mol})^{3/2} \cdot \frac{1}{s}\ ]$
$Eact_2$	98321.6 $[\ J/mol\ ]$

The results show that the deoxygenation, represented by reaction 1, possesses a higher specific rate of reaction than the denitrogenation, reaction 2, which was expected, as previously described in Subsection 2.3.1. Following Equation 4.6, this higher specific rate of the reaction 1 can be seen by the fact that its pre-exponential factor is higher and its energy of activation is lower comparing to the reaction 2. Moreover, the energies of activation are within the ranges investigated. Figure 5.1 shows the fitting of the obtained concentrations functions with the experimental data, for different temperatures at constant pressure and space velocity, 100 bar and 0.5 h^{-1} respectively.

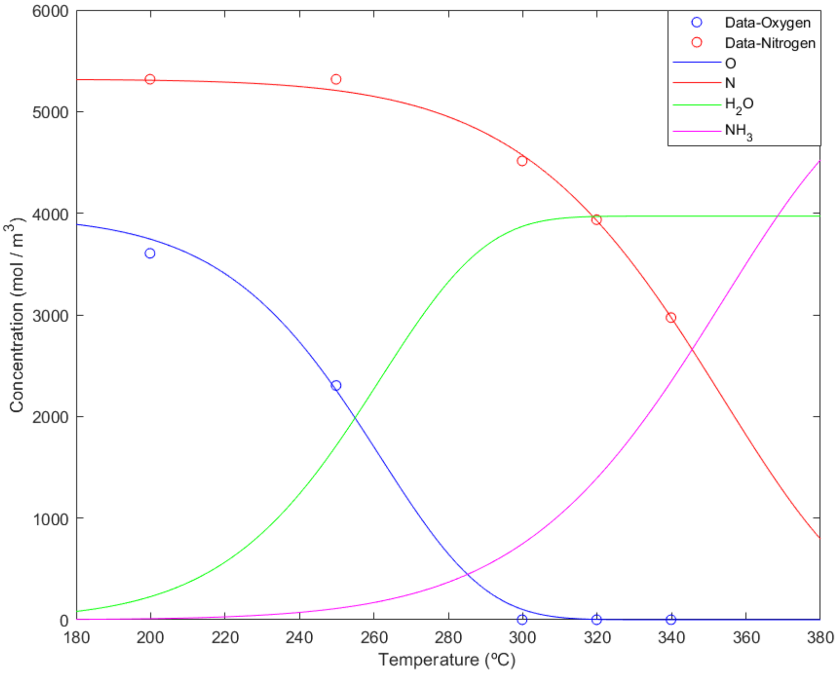

Figure 5.1: Fitting for concentrations after first stage hydrotreating for different temperatures. The points represent the experimental data used to estimate the kinetic coefficients.

As it can be seen in Figure 5.1, the fitting for the first stage model is extremely satisfactory, with the calculated values being very close to the experimental ones.

With the values for the kinetic constants estimated, the ODE system can now be integrated across the length of the reactor. Figure 5.2 presents the concentration profile of the different compounds throughout the reactor, at a temperature of 340ºC. This temperature was selected due to being the one used as feedstock for the second stage. As complete deoxigenation is obtained at 0.3 m and the main purpose of the first stage is to remove the highest quantity of oxygen possible in order to stabilize the oil, it leads to believe that the first reactor may be oversized.

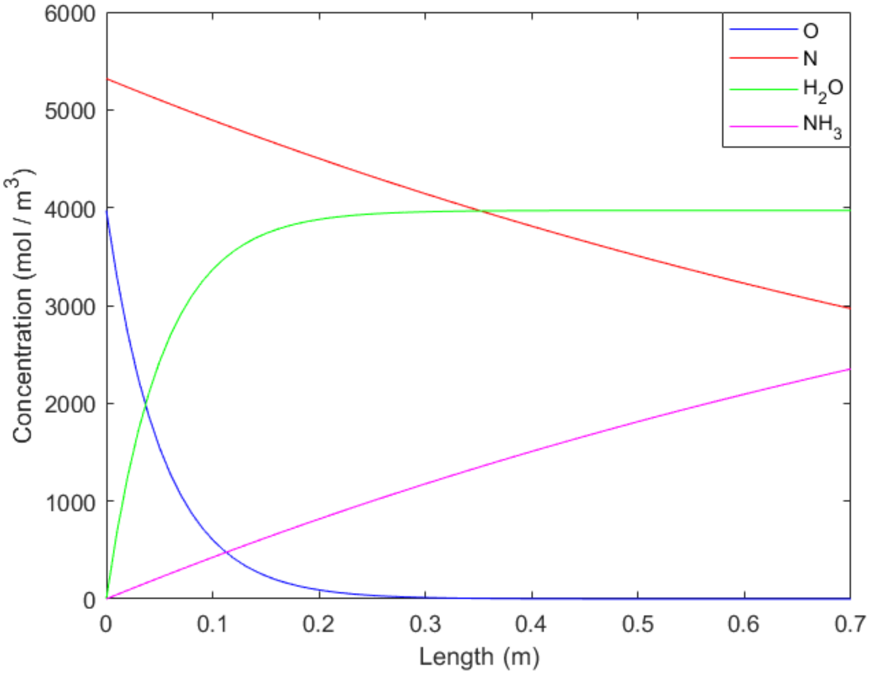

Figure 5.2: Variation of concentrations along the Reactor 1 for temperature of 340ºC, pressure of 100 bar and space velocity of $0.5h^{-1}$.

5.2 Second Stage Model

As presented in Figure 4.1, the reactor 2 contains two different catalysts, A and B. The length of the reactor is 0.59 m and the heights of catalyst A and B are 0.39 m and 0.20 m respectively. This model will follow the same methodology as the first stage, with the difference being that the kinetic constants for the first 0.39 m of the reactor 2 are the same as the for reactor 1. As the estimated kinetic parameters are for the reactions taking place on the surface of the catalyst, the parameters are assumed the same for identical catalysts.

So, for this model, two different functions using the ***ode45*** command are created, one for the catalyst A, which the kinetic parameters are known, and another for the catalyst B, where the kinetic parameters are unknown and the command ***lsqcurvefit*** will once again be used to estimate these constants.

The ODE system is integrated and solved for the catalyst A, spanning from x=0 to x=0.35 and with the initial concentrations being the ones presented in Table 5.2 for a temperature of 340ºC. These results will be the initial concentrations for the ODE system for the catalyst B, which is integrated spanning from x=0.39 to x=0.59.

The data used for the calibration of the second model for the catalyst B is presented in Table 5.4, which was calculated, using Equation 4.8, based on the values from Table 4.4.

Table 5.4: Concentrations of oxygen and nitrogen on the biocrude plus water and ammonia for two-stage hydrotreating at the presented temperatures.

Temperature (°C)	**Concentration (mol/m^3)**			
	O	**N**	**H2O**	**NH3**
340	0	1468.7	3971.5	3849.9
370	0	629.4	3971.5	4689.2
400	0	560.0	3971.5	4758.6

The estimated kinetic parameters are presented in Table 5.5. The same initial guesses were used as in the first stage model, and since the oxygen content had already reached zero, the kinetic parameters for the deoxygenation simply resulted in the guesses, which have no impact in the model. Regarding the kinetic parameters for the reaction 2 in catalyst, as both the pre-exponential factor and the energy of activation dropped, a clear reduction or increase in the specific reaction rate is very hard to evaluate just by the numbers.

Table 5.5: Estimated kinetic coefficients for catalyst B.

Kinectic Constants	**Estimation**
$k_{0,1}$	1.00 $[\frac{m^3}{mol \cdot s}]$
$Eact_1$	100000 $[\ J/mol\ ]$
$k_{0,2}$	1.56*10^{-5} $[(\frac{m^3}{mol})^{3/2} \cdot \frac{1}{s}]$
$Eact_2$	58265.78 $[\ J/mol\ ]$

Figure 5.3 shows the the concentrations of the reacting compounds after the second-stage hydrotreating in function of the temperature used, with the used data also being presented to evaluate the fit of the model.

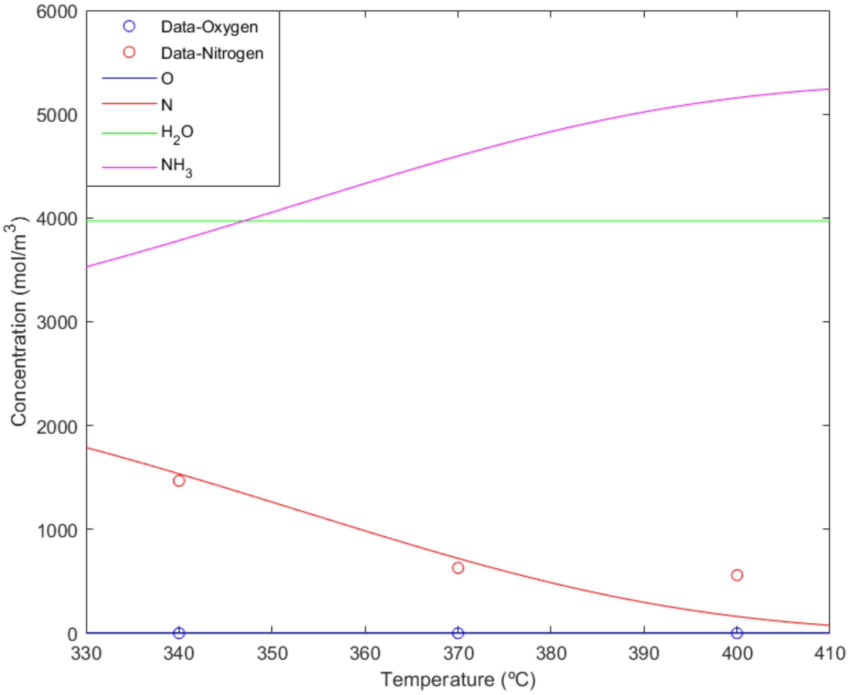

Figure 5.3: Fitting for concentrations after the second stage hydrotreating for different temperatures. The points represent the experimental data used to estimate the kinetic coefficients.

Figure 5.4 presents the concentration profile of the different reacting compounds for the 0.59 m of the reactor 2, at a temperatue of 370ºC. With this graphic, it is possible to see that the reaction rate of the denitrogenation increased, visualized by the difference of slopes from the point x=0.39 m on.

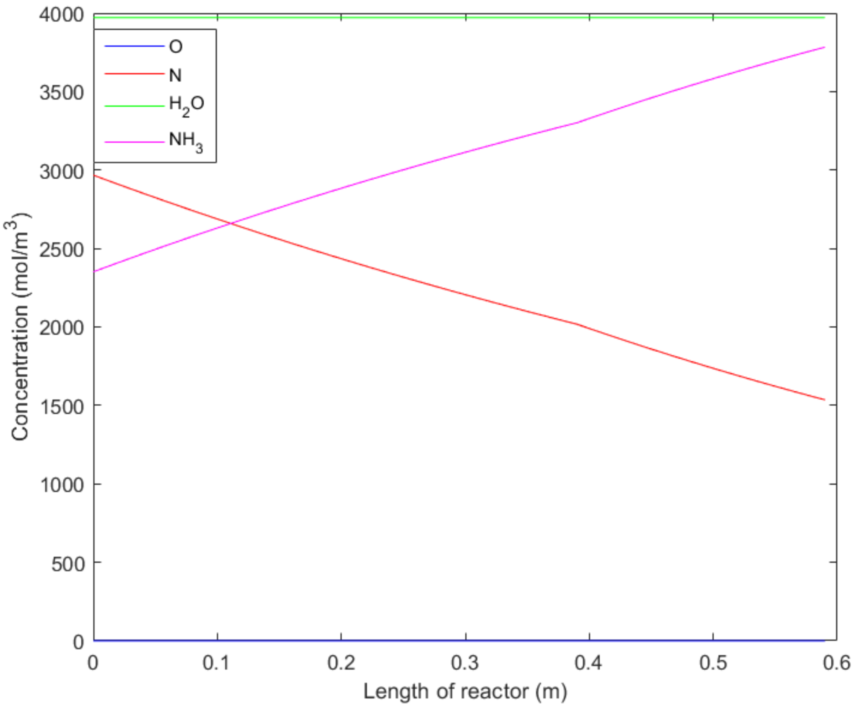

Figure 5.4: Variation of concentrations along the Reactor 2 for temperature of 370°C, pressure of 100 bar and space velocity of $0.5h^{-1}$.

Chapter 6

Model Validation

In order to validate the full model, that takes into consideration both catalysts in the second reactor, and to check its improvement, a simplified model in which the reactor 2 only contains catalyst A is created. Both models are evaluated for different temperatures, space velocities and pressures (with the other parameters being constant for each case), with the structure being the following:

- Different temperatures at constant pressure and space velocity of 100 bar and 0.5 h^{-1}, respectively.
- Different space velocities at constant temperature and pressure of 340°C and 100 bar, respectively.
- Different pressures at constant temperature and space velocity of 370°C and 0.5 h^{-1}, respectively.

The fits for the three cases being evaluated based on experimental data from an AAU two-stage hydrotreating campaign presented on the Appendix Figure A.1. At the end of the chapter, a parity plot for both cases is presented, using all the available experimental data points and their equivalent modelled values, with the objective of obtaining a better visualization of the errors of each model.

As the calibration was done using experimental data of the oxygen and nitrogen concentrations, in this chapter the figures will show a close-up for just the nitrogen and oxygen, neglecting the ammonia and the water produced, in order to better visualize the difference between the modelled points in the presented functions and the experimental data points, which translate the errors. It is also important to mention that, as total deoxygenation was achieved during the first-stage at temperature of 340°C, pressure of 100 bar and space velocity of 0.5 h^{-1} (the feedstock for the second-stage), the oxygen content will be zero throughout this chapter.

The statistical indicators to evaluate the fitting of the models used were the R-squared and the Root Mean Square Error (RMSE) between the experimental and the modelled values for the concentrations of oxygen and nitrogen, which can be described as the following:

- **R-Squared:** It can be defined as a statistical measure that determines the proportion of variance in the dependent variable that can be explained by the independent variable. This means that the R-squared evaluates the goodness of fit for a regression model. It ranges from 0 to 1 and, even though it can provide useful insight on the regression model, the assessment of a statistical model should not rely only on the R-squared, significating that the R-Squared should be analyzed along with other statistical parameters. The formula of R-squared can be expressed as:

  $$R - Squared = 1 - \frac{SS_{Regression}}{SS_{Total}} \tag{6.1}$$

  Where $SS_{Regression}$ represents the sum of squares due to regression, which evaluates how well the regression model describes the data that was used for modelling, and SS_{Total} represents the total sum of squares, which measures the variation in the data used for the regression model.

- **RMSE:** It is the standard deviation of the residuals, which are a measure of how far the data points are from the regression line, making the RMSE a measure of how spread around the residuals are. The lower the value of RMSE is, the more concentrated the data point will around the line of best fit. It is defined as the square root of the average of squared differences between prediction and actual values and is expressed as:

  $$RMSE = \sqrt{\frac{1}{N}\sum_{j=1}^{N}(PREDICTED_j - ACTUAL_j)} \tag{6.2}$$

  where N represents the sample size.

6.1 Simplified Model

As mentioned above, this models assumes catalyst A for all the length of reactor 2. This means that, as the both reactors use the same catalyst, the kinetic constants are assumed the same for both cases, as what is being done is estimating the kinetic parameters of the reaction taking place on the surface of the catalyst. This means that only the kinetic parameters for the catalyst A, presented in Table 5.3, are used in this section.

6.1.1 Results for different Temperatures

The concentrations of nitrogen and oxygen after the second-stage, using only catalyst A, for varying temperature, are presented in Figure 6.1. In an ideal case, the functions would coincide with the experimental points, also presented in the figure. The difference of values between them represents the error.

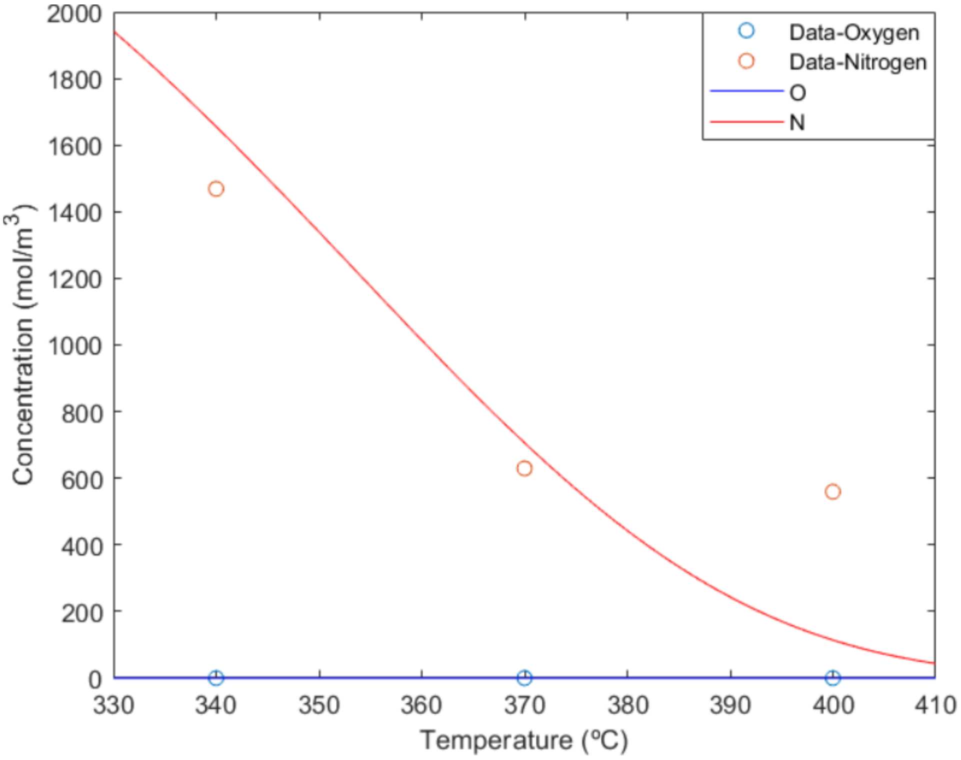

Figure 6.1: Concentrations after second stage hydrotreating, assuming only catalyst A for the reactor 2 total length, for different temperatures. The experimental data points presented are accounting for both catalysts A and B.

As it can be seen by the experimental data, the difference between 370°C and 400°C is very low, showing that the concentration function should flatten earlier. The simplifications taken have a big impact on this, as all the nitrogen-containing compounds are assumed as a single component "N", not dividing them by their reactivity, which would translate in different reaction rates. Overall, the fit has a R-squared value of 0.9002 and a root mean square error (RMSE) value of 282.41.

6.1.2 Results for different Space Velocities

Following the same structure, the concentrations of nitrogen and oxygen after the second-stage hydrotreating, for varying space velocity, are shown in Figure 6.2.

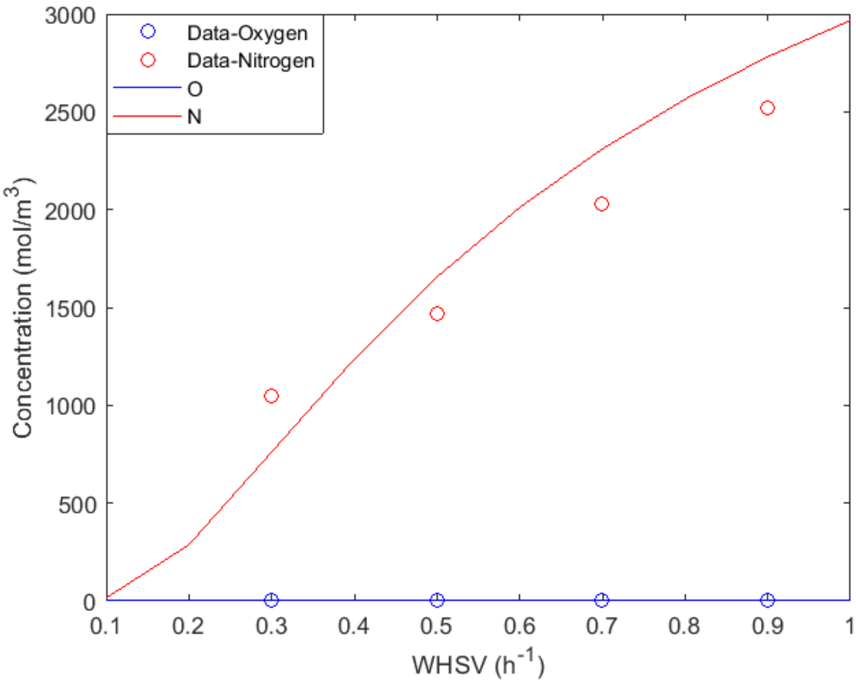

Figure 6.2: Concentrations after second stage hydrotreating, assuming only catalyst A for the reactor 2 total length, for different space velocities, at 340°C and 100 bar. The experimental data points presented are accounting for both catalysts A and B.

For the case shown in Figure 6.2, the model obtains higher concentrations than the experimental values, with the exception of WHSV=0.3 h^{-1}, the most severe condition, where the model achieves a much lower value than the experimental one. This fit has a R-squared value of 0.8407 and a RMSE value of 389.13.

6.1.3 Results for different Pressures

For varying pressure, the concentrations of the nitrogen and oxygen after the secon-stage hydrotreating are presented in Figure 6.3.

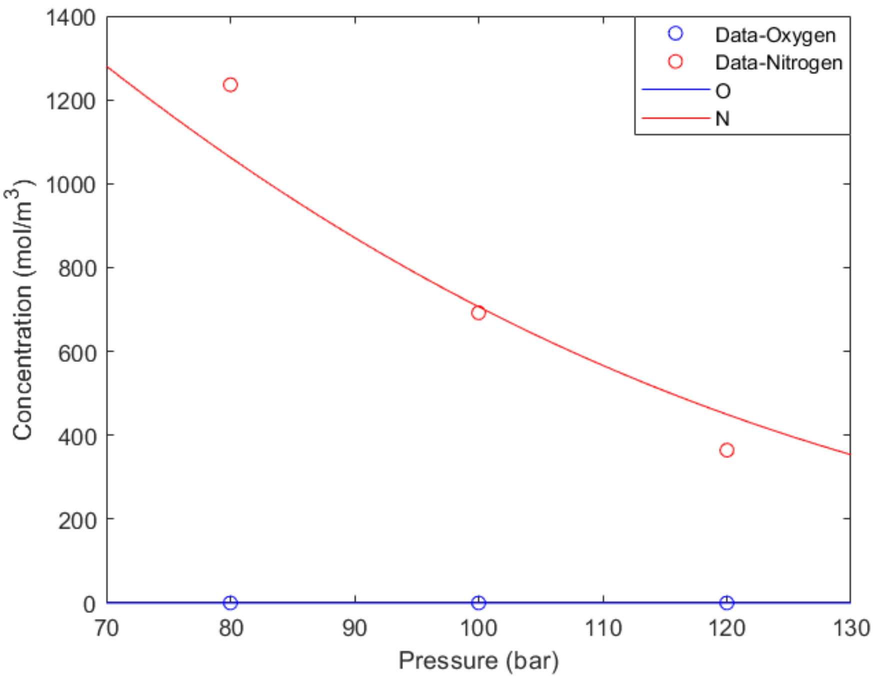

Figure 6.3: Concentrations after second stage hydrotreating, assuming only catalyst A for the reactor 2 total length, for different pressures, at 370°C and 0.5 h-1. The experimental data points presented are accounting for both catalysts A and B.

From the three tested pressures, the model obtained the best results for the 100 bar case, probably because the calibration was performed for different temperatures at this pressure. The fit possesses a R-squared value of 0.9977 and a RMSE of 111.72, showing to be the best fit of three.

6.2 Full Model

This model will follow the set-up used for the experimental data, which is presented in Figure 4.1, where the Reactor 2 contains both catalyst A and catalyst B. Therefore, the kinetic constants for catalyst A, presented in Table 5.3, are used for the first 0.39 m of the reactor, with the kinetic constants for catalyst B, shown in Table 5.5, are utilized for the remaining 0.20 m.

6.2.1 Results for different Temperatures

The concentrations of nitrogen and oxygen after the second-stage hydrotreating with both catalyst A and B, for varying temperature, are presented in Figure 6.4.

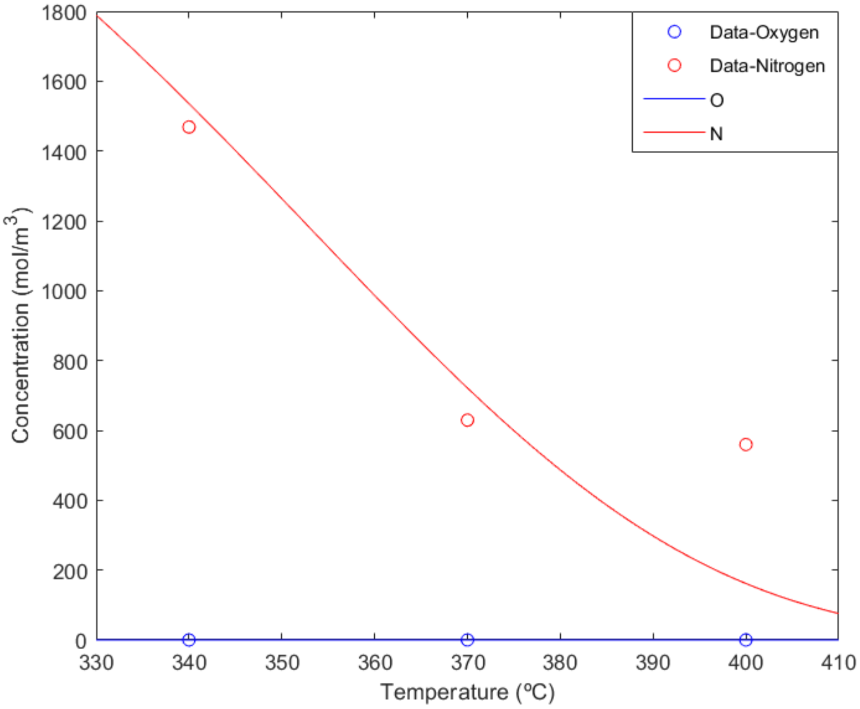

Figure 6.4: Concentrations after second stage hydrotreating, for both catalysts on reactor 2, for different temperatures. The experimental data points presented are accounting for both catalysts A and B.

This fit showed a R-squared value of 0.8836, which worsen compared to the simple case, and a RMSE value of 238.89, which, oppositely, shows improvement comparing to the simple case. Just like the simple model, the function should flatten earlier, which does not happen due to the fact that the compounds are not divided by their reactivity, which would make different reactions predominant at different temperature ranges and, consequently, change the curvature of the function.

6.2.2 Results for different Space Velocities

For varying space velocity, the concentrations of nitrogen and oxygen after the second-stage hydrotreating, using both catalysts, are shown in Figure 6.5.

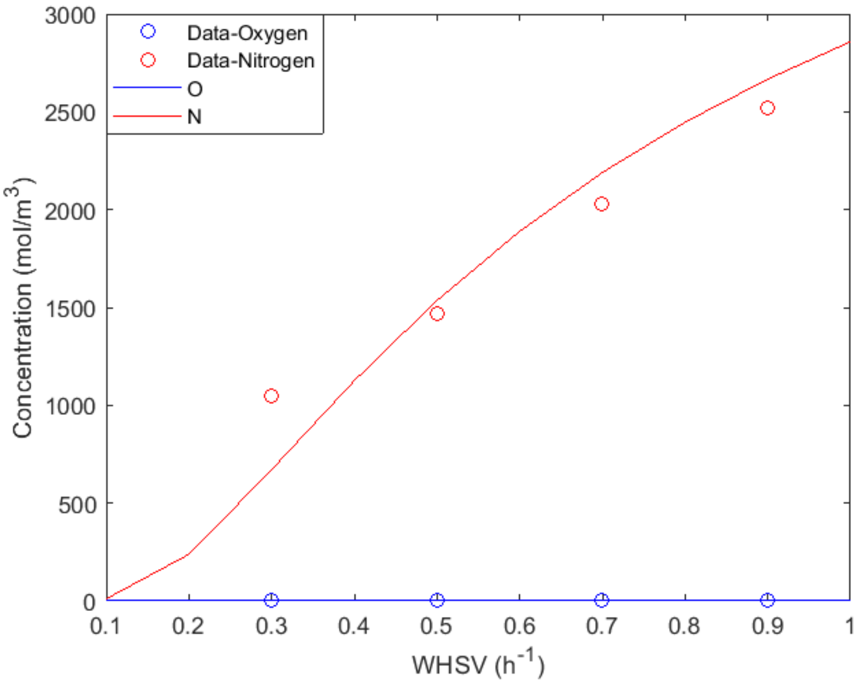

Figure 6.5: Concentrations after second stage hydrotreating, for both catalyst in reactor 2, for different space velocities, at 340°C and 100 bar. The experimental data points presented are accounting for both catalysts A and B.

The fitting shows a smaller error compared to the simplified scenario, for every WHSV value, where estimated values approaches the experimental data. This results can been seen in the statistic parameters, the R-squared presents a value of 0.8487 and a RMSE value of 386.66, which shows a very slight improvement compared to the simple model.

6.2.3 Results for different Pressures

The concentrations for nitrogen and oxygen after the second-stage hydrotreating, for varying pressure, are presented in Figure 6.6.

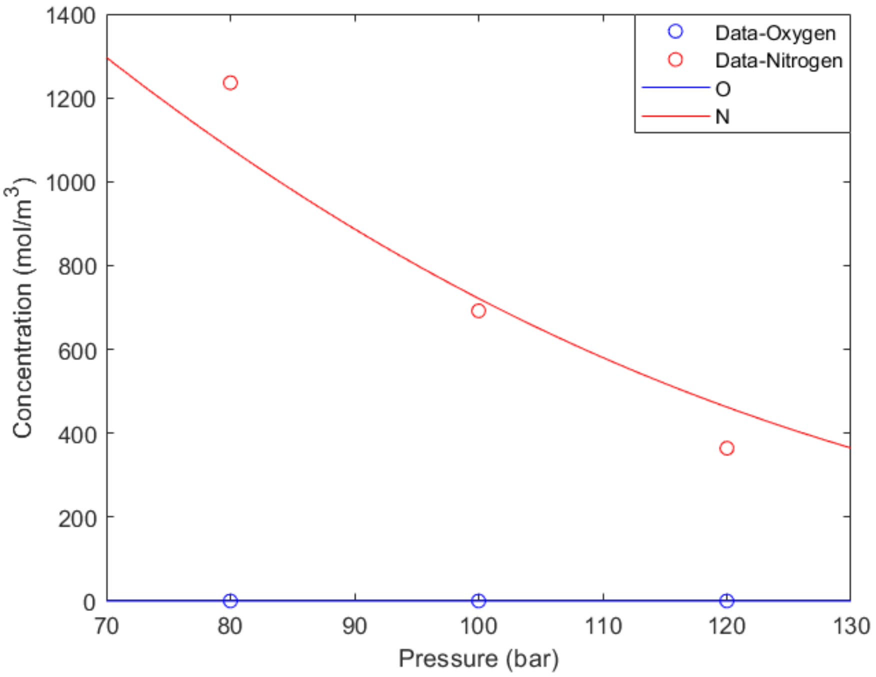

Figure 6.6: Concentrations after second stage hydrotreating, for both catalysts in reactor 2, for different pressures, at 370ºC and 0.5 h-1. The experimental data points presented are accounting for both catalysts A and B.

As expected, the estimated concentration at 100 bar show similar results to the experimental values, due to the fitting being done for that pressure value. Comparing to the simplified scenario, the fitting did not show significant improvements obtaining a R-squared value of 0.9975 and a RMSE value of 108.42, values very similar to the ones obtained from the simplified scenario.

6.3 Overall Evaluation for both scenarios

The parity plot for both cases is presented in Figure 6.7, where it can be seen that the models are quite similar, with the simplified model showing, for most cases, a higher concentration than the full model, which leads to conclude that the catalyst B has a slightly higher reaction than catalyst A.

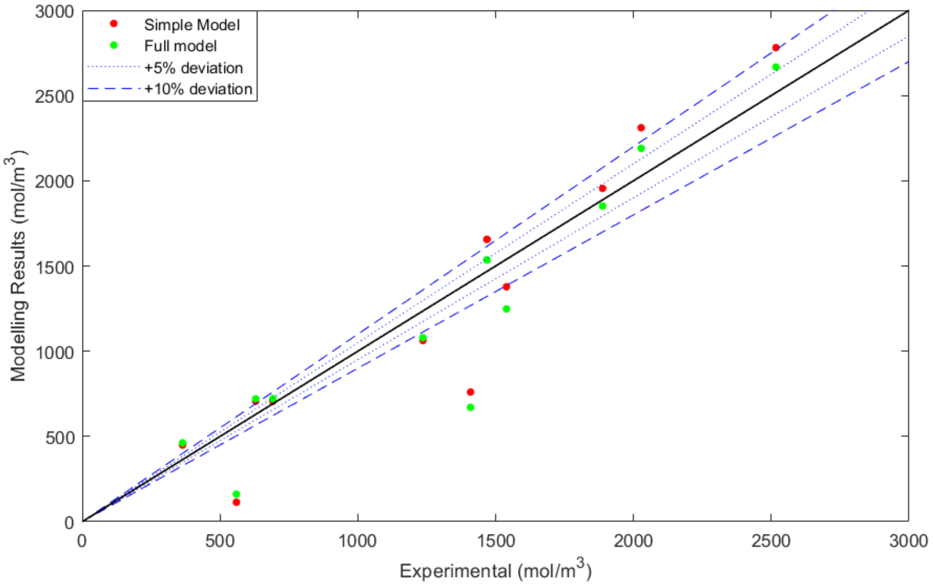

Figure 6.7: Parity plot for both Simplified and Full models.

The R-squared and RMSE values obtained for the fits in each case are presented in Table 6.1. Comparing these values, it can be concluded that the full model barely shows any improvement comparing to the simplified model.

Table 6.1: Statistic results for the different cases in each model.

	R-Squared		**RMSE [in mol/m^3]**	
	Simplified model	**Full model**	**Simplified model**	**Full model**
Temperature	0.90	0.88	282.4	238.9
WHSV	0.84	0.85	389.1	386.7
Pressure	1.00	1.00	111.7	108.2

It is important to mention that, since complete deoxygenation was reached in the first reactor, these statistical indicators take only the nitrogen data points in consideration, which means that the presented R-squared values only evaluate the goodness of fit of the denitrogenation (reaction 2), as well as the RMSE, which only evaluates how far the nitrogen data points are from the reaction 2 function.

For the temperature profiles, there is a possibility of the point for 400ºC to be an outlier, as it is already dealing with small quantities of nitrogen (wt% lower than 1%), which makes the fit to loose quality. Moreover, the fact that all the nitrogen compounds are agglomerated as a single component "N" and not divided by their reactivity may cause higher conversions at more severe conditions, as seen in the plots for both temperature and space velocity, where the most severe conditions resulted in much lower concentrations than the experimental values obtained. Due to these reasons, an optimization on the model will be performed in the next chapter, where the nitrogen will be divided in two different components, one for faster kinetics (high reactivity nitrogen-containing compounds) and one for slower kinetics (low reactivity nitrogen-containing compounds).

Chapter 7

Model Optimization & Application

In the previous chapter it could be seen that, for more severe conditions in the second reactor, the fit for the denitrogenation reaction was not satisfactory. For this reason, a possible optimization for the denitrogenation modelling will be presented, with the objective of creating two pseudo-components, "high reactivity" N and "low reactivity" N, instead of just one single component in which all the nitrogen-containing compounds were lumped into. Although still being a simplification, as dividing in "high" and "low" reactivities is a very rough definition, it is expected to improve the model, as having N compounds with a slower reaction rate may flatten the nitrogen concentration function for more severe conditions, since the "high" reactivity will already be in small concentrations and the rate of the "low" reactivity will be the predominant one.

Moreover, possible applications for the created model are presented, which include evaluations on the reactors set-up, including their dimensions, and on the operating conditions used during the hydrotreating process. This will be performed following the idea behind the two-stage hydrotreating approach, where the first stage has the objective of stabilizing the oil, this means (mostly) oxygen removal, in order for the second stage to be performed at more sever conditions with less probability of coking reactions, among other issues related with biocrude instability.

7.1 Optimized Model

The biocrude is composed by thousands different compounds, that don't react in the same way, with some of them being easier to convert and others more difficult. For the case of nitrogen, compounds such as fatty amides and non-heterocylic nitrogen compounds are relatively easy to remove, while heterocyclic nitrogen-containing compounds are much harder to remove, as can been seen in Figure 1.13. This provided extra motivation to split the nitrogen in two pseudo-components, "high reactivity" N and "low reactivity" N.

In order to divide the N compounds, it was assumed that, by the time that the biocrude reaches the catalyst B in the second reactor, all the "high reactivity" compounds were converted. Also it was assumed that only 10% of the "low reactivity" was converted on the first reactor, at 340°C. Through a trial and error process and after various ratios were tested in order to fulfill the assumptions, the nitrogen was divided in 55% of "high reactivity" and 45% of "low reactivity". The conversion of the "low reactivity" nitrogen compounds during the stabilization phase (first stage) and the ratio between "high" and "low" reactivity were obtained based on the data provided by the AAU campaign for continuous hydrotreating of algae HTL biocrude, which means that for other scenarios where different feedstocks and/or different operating conditions are utilized, these values would have to be adjusted.

Separating the N component in "low reactivity" and "high reactivity", the ODE system obtained is now defined as:

$$\begin{cases} \frac{dC_O}{dx} = -\frac{S\cdot\rho_c}{Q} \quad k_{0,1}\cdot e^{\frac{-E_{act,1}}{R\cdot T}}\cdot C_O\cdot C_{H_2} \\ (\frac{dC_N}{dx})_{HIGH} = -\frac{S\cdot\rho_c}{Q} \quad k_{0,2}\cdot e^{\frac{-E_{act,2}}{R\cdot T}}\cdot C_N\cdot (C_{H_2})^{\frac{3}{2}} \\ (\frac{dC_N}{dx})_{LOW} = -\frac{S\cdot\rho_c}{Q} \quad k_{0,3}\cdot e^{\frac{-E_{act,3}}{R\cdot T}}\cdot C_N\cdot (C_{H_2})^{\frac{3}{2}} \\ \frac{dC_{H_2O}}{dx} = +\frac{S\cdot\rho_c}{Q} \quad k_{0,1}\cdot e^{\frac{-E_{act,1}}{R\cdot T}}\cdot C_O\cdot C_{H_2} \\ \frac{dC_{NH_3}}{dx} = +\frac{S\cdot\rho_c}{Q} \quad k_{0,2}\cdot e^{\frac{-E_{act,2}}{R\cdot T}}\cdot C_N\cdot (C_{H_2})^{\frac{3}{2}} + \frac{S\cdot\rho_c}{Q} \quad k_{0,3}\cdot e^{\frac{-E_{act,3}}{R\cdot T}}\cdot C_N\cdot (C_{H_2})^{\frac{3}{2}} \end{cases} \tag{7.1}$$

In the first reactor the deoxygenation kinetic constant remained practically the same, as expected, while for the nitrogen, "high reactivity" N present a much higher specific rate of reaction, compared to the "low reactivity", as can presented in Table 7.1

Table 7.1: Estimated kinetic coefficients for catalyst A.

Kinectic Constants	**Estimation**
$k_{0,1}$	$2.11\ [\frac{m^3}{mol \cdot s}]$
$Eact_1$	$93173.5\ [\ J/mol\ ]$
$k_{0,2high}$	$1.6\ [(\frac{m^3}{mol})^{3/2} \cdot \frac{1}{s}\ ]$
$Eact_{2high}$	$114780.2\ [\ J/mol\ ]$
$k_{0,3low}$	$0.003\ [(\frac{m^3}{mol})^{3/2} \cdot \frac{1}{s}\ ]$
$Eact_{3low}$	$96034.7\ [\ J/mol\ ]$

The fitting obtained in the first reactor is presented in Figure 7.1, where N represents the sum of the high reactivity N and the low reactivity N. Figure 7.2 shows the same, but with the high and low reactivity N separated.

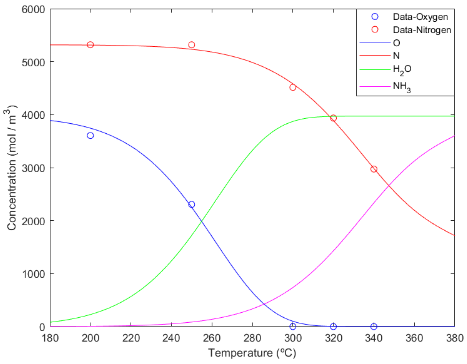

Figure 7.1: Fit of the reactor 1 for the optmized model, with N being the sum of the high and low reactivity nitrogen compounds.

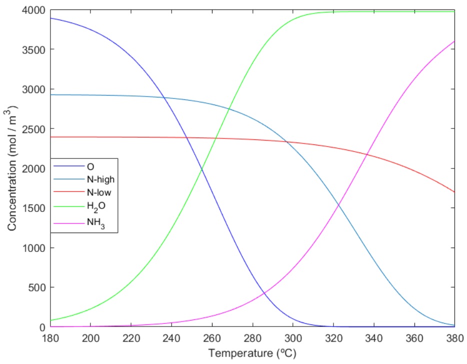

Figure 7.2: Fit of the reactor 1 for the optmized model, with the high and low reactivity N shown separately.

Following the same process for the catalyst B, the kinetics parameters are obtained and showed in Table 7.2.

Table 7.2: Estimated kinetic coefficients for catalyst B.

Kinectic Constants	**Estimation**
$k_{0,1}$	$1\ [\frac{m^3}{mol \cdot s}]$
$Eact_1$	$100000\ [\ J/mol\ ]$
$k_{0,2high}$	$1\ [(\frac{m^3}{mol})^{3/2} \cdot \frac{1}{s}\ ]$
$Eact_{2high}$	$100000\ [\ J/mol\ ]$
$k_{0,3low}$	$0.000003\ [(\frac{m^3}{mol})^{3/2} \cdot \frac{1}{s}\ ]$
$Eact_{3low}$	$48144.0\ [\ J/mol\ ]$

Overall, the optimized model showed a better goodness of fit than the full model presented in the previous chapter. Even through rough estimations, dividing the nitrogen component showed to increase the quality of the model, which can be seen by the significant decrease of the RMSE, presented in Table 7.3, as well as visually by Figures 7.3, 7.4 and 7.5. It is also important to refer that this case showed the necessity of dividing the nitrogen component due to being an algae biocrude, which contains considerable amount of nitrogen and a low content of oxygen.

Table 7.3: Statistic results for the optimization model.

	R-Squared		RMSE [in mol/dm^3]	
	Full model	Optimized model	Full model	Optimized model
Temperature	0.88	0.87	238.9	150.7
WHSV	0.97	0.98	221.5	105.2
Pressure	1.00	1.00	108.2	153.7

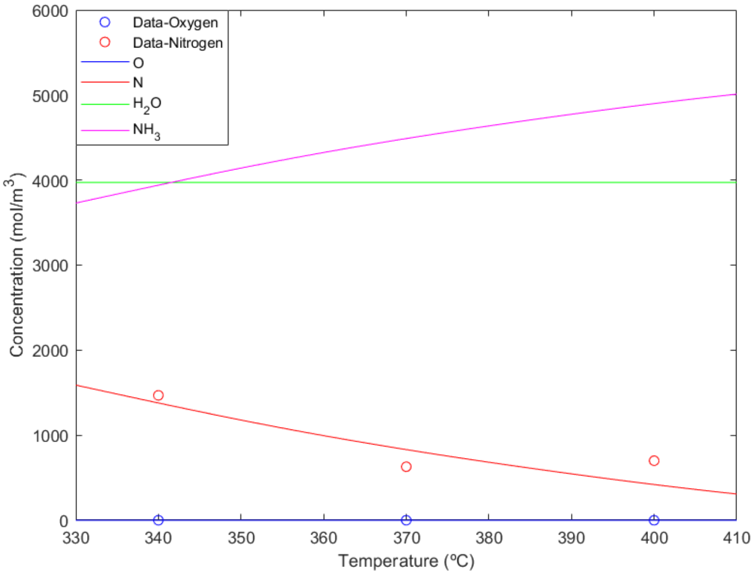

Figure 7.3: Fit between the experimental data for different temperatures, at 100 bar and 0.5 h^{-1}, and the optimized model

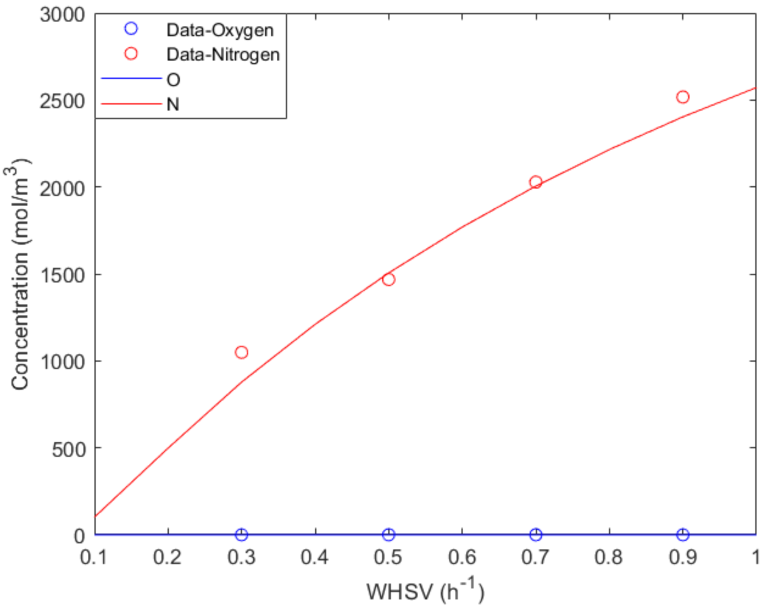

Figure 7.4: Fit between the experimental data for different space velocities, at 100 bar and 340°C, and the optimized model.

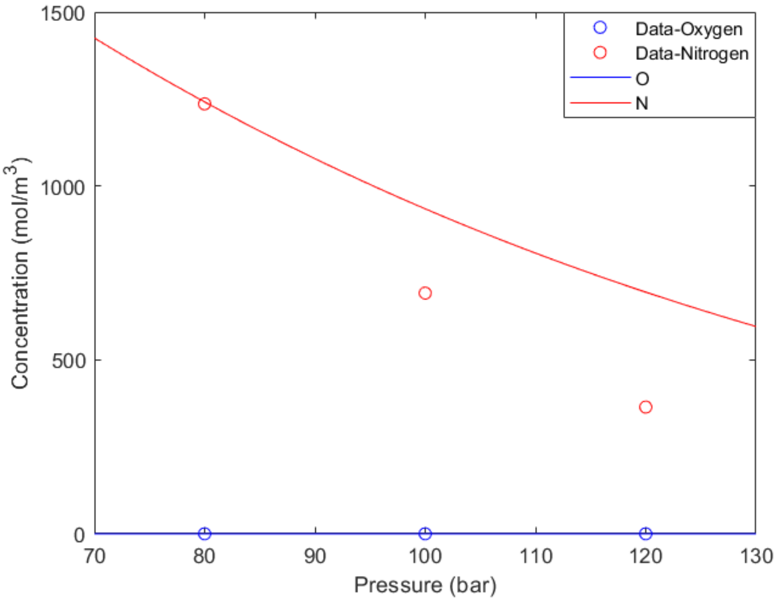

Figure 7.5: Fit between the experimental data for different pressures at 370°C and 0.5 h^{-1} and the optimized model

The parity plot presented in Figure 7.6 is for the full model and the optimized one, where it can be seen that for high concentration, the optimized presents better results, however at severe conditions, that result in low concentration, the model is still not able to predict accurately.

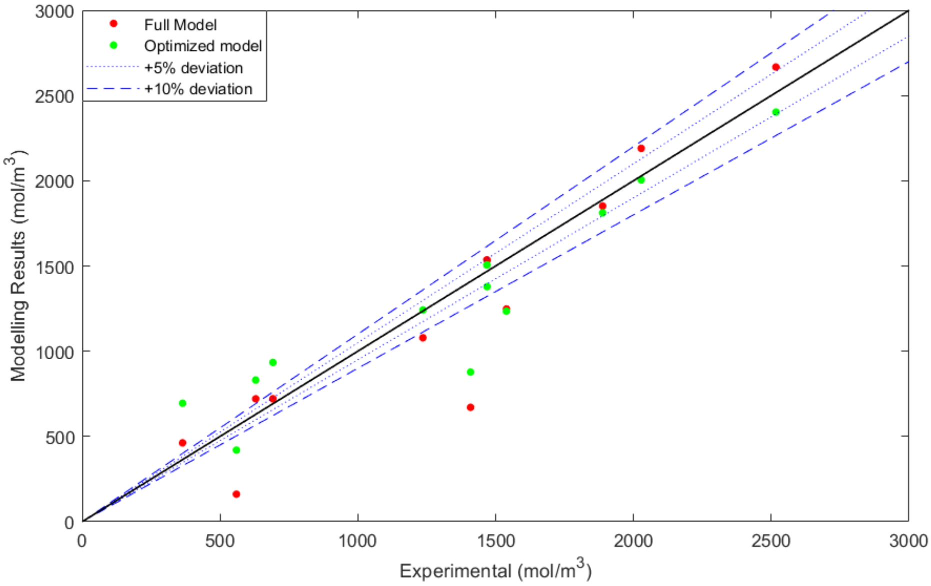

Figure 7.6: Parity plot for both Full model and Optimized model

Chapter 8

Conclusion

Extensive literature was investigated regarding the hydrotreating process for biocrude upgrading. Unlike the process for petroleum, in which there is much more knowledge due to longer period of study, a lot of questions remain for biocrude, especially on how to describe the deoxygenation and denitrogenation of these oils, which strongly vary depending on the feedstock and the operating conditions used during the biocrude production and upgrading.

As the initial plan was to perform experimental work on the hydrotreating of mischantus HTL biocrude, special interest at the start was placed on lignocellulosic biomass. Being a HTL biocrude with a very high content of oxygen, which indicates its instability, the objective was to investigate how a two-stage hydrotreating would enhance the upgrading of mischantus biocrude. Only three experiments for single stage hydrotreating could be performed, however it served as extra motivation to investigate a two-stage hydrotreating process, as for the case at 350ºC the oil completely coked. The objective would be to stabilize the oil at mild conditions in a first stage and then proceed with more severe conditions on the second stage.

As lab work became impossible, the study changed its course to model a two-stage hydrotreating. This model was created based on experimental data obtained in a AAU campaign for algae biocrude and its purpose is to estimate the kinetic parameters for the deoxygenation and denitrogenation that take place during the process. To make this possible, all the oxygenates are lumped into a single component "O", with the same being done for all the nitrogen-containing compounds as "N", and the multiple reactions that occur are simplified into just one for each deoxygenation and denitrogenation.

The model showed good results, except for the most severe conditions. As the algae biocrude possesses a low content of oxygen and it ends quite fast, the single component "O" did not create issues for the model, but the "N" removal ended up being overestimated for the most severe conditions, which lead to an optimization for the model where the "N" component is divided in "high reactivity N" and "low reactivity N".

As it the kinetics for denitrogenation of biocrude are unknown, different proportions for each N component were tested, along with an assumption that the "high reactivity N" finish before reaching the catalyst B. This optimized model showed improvements, although it was obtained using rough estimations and various tests for the used experimental data.

As already described, even showing some flaws for more severe conditions, the created model after validation showed results with very low errors for conditions up to 370°C in the temperature case and 0.5 h^{-1} for the space velocity. Knowing this, the full model presented in Section 6.2 can be used to evaluate the system utilized for the hydrotreating process that produced the experimental data provided in the Appendix A. Depending on specific targets and different objectives, all the values used as inputs to the system, as the reactors dimensions, mass and height of the catalysts, operating conditions utilized, etc, can be played with in order to obtain optimal conditions.

For example, if the objective is to use the first stage as the stabilization phase, where the objective is solely to obtain complete deoxygenation, costs could be lowered using different approaches. For instance, analyzing Figure 5.1, it is possible to see that total deoxygenation is obtained at temperatures between 300 and 320°C (at 100bar and 0.5 h^{-1}). This means that the temperature used during the first-stage at the AAU campaign, which was 340°C, would be to high, following this target, and could be lowered down with the objective of decreasing the energy consumption. Other approach could be analyzing the reactors length. As seen in Figure 5.2, when operating at 340°C, 100bar and 0.5 h^{-1}, complete deoxygenation is reached already at x=0.3m of the first reactor, which indicates that it would be way oversized for this purpose. This is important information for a system assembly, where the costs for the reactors set-up would be smaller due to the lower size.

The same logic and methodology could used for different targets, also with other approaches. This shows how important it is to understand the behavior of the different reactions that will take place on the investigated process.

Chapter 9

Future Work

Followed the presented study, the future work can be divided in two different categories, one relating to experimental work and the other connected to the model, more specifically to the kinetics of deoxygenation and denitrogenation:

- **Experimental Work:** The initial objective of this study still remains to investigate. The mischanthus biocrude, due to its high instability, should have an enhanced upgrading if a two-stage hydrotreating procedure is performed. Initially, more single stage experiments may be necessary, in order to better understand the behavior of this specific biocrude for different operating conditions, before starting the two-stage experiments. After the optimal conditions for the first stage had been determined (possibly the more severe conditions possible without any signs of coking), the same process would be performed, now to check the conditions in which the biocrude would reach the highest degree of both deoxygenation and denitrogenation. After that, possible continuous hydrotreating tests could be done in order to investigate the feasibility of upgrading mischantus biocrude at larger scale.
- **Kinetics investigation:** First of all, more literature around the kinetics of both deoxygenation and denitrogenation should have been investigated. If this was the original purpose of the thesis, a bigger focus would have been placed on the kinetics of the reactions and the different types of both oxygen and nitrogen containing compounds existent in biocrude. As explained during the modelling, knowing the specific types of compounds present on the biocrude will give information regarding their reactivity, which makes a possible division of the oxygenates and the nitrogen containing compounds in the biocrude more feasible. An enhanced division of the compounds into more pseudo-components would improve the model, as it would have a more detailed information regarding the different reactions and their respective rates during the hydrotreating process. Also the thermal part of the process

is an area of interest, since the hydrotreating process involves exothermic reactions can lead to deactivation of the catalyst and thus disable the hydrotreating process.

Bibliography

[1] Venkatesh Balan. "Current challenges in commercially producing biofuels from lignocellulosic biomass". In: *ISRN biotechnology* 2014 (2014).

[2] David Beckman et al. *Techno-economic assessment of selected biomass liquefaction processes*. 1990.

[3] P Biller and AB Ross. "Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content". In: *Bioresource technology* 102.1 (2011), pp. 215–225.

[4] Patrick Biller and AB Ross. "Production of biofuels via hydrothermal conversion". In: *Handbook of biofuels production*. Elsevier, 2016, pp. 509–547.

[5] Patrick Biller et al. "Hydroprocessing of bio-crude from continuous hydrothermal liquefaction of microalgae". In: *Fuel* 159 (2015), pp. 197–205.

[6] Ortwin Bobleter. "Hydrothermal degradation of polymers derived from plants". In: *Progress in polymer science* 19.5 (1994), pp. 797–841.

[7] Anthony V Bridgwater. "Renewable fuels and chemicals by thermal processing of biomass". In: *Chemical Engineering Journal* 91.2-3 (2003), pp. 87–102.

[8] Anthony V Bridgwater. "Review of fast pyrolysis of biomass and product upgrading". In: *Biomass and bioenergy* 38 (2012), pp. 68–94.

[9] Marion Carrier et al. "Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass". In: *Biomass and bioenergy* 35.1 (2011), pp. 298–307.

[10] Daniele Castello, Muhammad Salman Haider, and Lasse Aistrup Rosendahl. "Catalytic upgrading of hydrothermal liquefaction biocrudes: Different challenges for different feedstocks". In: *Renewable Energy* 141 (2019), pp. 420–430.

[11] Daniele Castello, Thomas Pedersen, and Lasse Rosendahl. "Continuous Hydrothermal Liquefaction of Biomass: A Critical Review". In: *Energies* 11 (2018), p. 3165.

[12] European Comission. *2030 climate energy framework*. URL: `https://ec.europa.eu/clima/policies/strategies/2030_en`.

[13] Keziah Copeland. *Catalytic Hydrocracking*. visited: 18-03-2020. `https://www.slideserve.com/keziah/chapter-7-catalytic-hydrocracking`, 2017.

[14] Tapas K Das. *Industrial Environmental Management: Engineering, Science, and Policy*. John Wiley & Sons, 2020.

[15] John Aurie Dean. *Lange's handbook of chemistry*. New york; London: McGraw-Hill, Inc., 1999.

[16] Ayhan Demirbas. "Use of algae as biofuel sources". In: *Energy conversion and management* 51.12 (2010), pp. 2738–2749.

[17] Susan van Dyk et al. "Potential synergies of drop-in biofuel production with further co-processing at oil refineries". In: *Biofuels, Bioproducts and Biorefining* 13.3 (2019), pp. 760–775.

[18] Douglas C Elliott. "Historical developments in hydroprocessing bio-oils". In: *Energy & Fuels* 21.3 (2007), pp. 1792–1815.

[19] Douglas C Elliott et al. "Hydrothermal liquefaction of biomass: developments from batch to continuous process". In: *Bioresource technology* 178 (2015), pp. 147–156.

[20] Mohamed A Fahim, Taher A Al-Sahhaf, and Amal Elkilani. *Fundamentals of petroleum refining*. Elsevier, 2009.

[21] Edward Furimsky. "Catalytic hydrodeoxygenation". In: *Applied Catalysis A: General* 199.2 (2000), pp. 147–190.

[22] Michael J Girgis and Bruce C Gates. "Reactivities, reaction networks, and kinetics in high-pressure catalytic hydroprocessing". In: *Industrial & Engineering Chemistry Research* 30.9 (1991), pp. 2021–2058.

[23] Alexander N Glazer and Hiroshi Nikaido. *Microbial biotechnology: fundamentals of applied microbiology*. Cambridge University Press, 2007.

[24] José Goldemberg and Patricia Guardabassi. "The potential for first-generation ethanol production from sugarcane". In: *Biofuels, Bioproducts and Biorefining: Innovation for a sustainable economy* 4.1 (2010), pp. 17–24.

[25] ARK Gollakota, Nanda Kishore, and Sai Gu. "A review on hydrothermal liquefaction of biomass". In: *Renewable and Sustainable Energy Reviews* 81 (2018), pp. 1378–1392.

[26] Parsa Haghighat et al. "Hydrotreating of Hydrofaction$^{\text{TM}}$ biocrude in the presence of presulfided commercial catalysts". In: *Sustainable energy & fuels* 3.3 (2019), pp. 744–759.

[27] Muhammad Salman Haider et al. "Catalytic hydrotreatment of microalgae biocrude from continuous hydrothermal liquefaction: Heteroatom removal and their distribution in distillation cuts". In: *Energies* 11.12 (2018), p. 3360.

[28] Bianca Hanganu et al. "The Study of Natural Saponification Processes in Preservation of Human Corpses". In: *REVISTA DE CHIMIE* 68.12 (2017), pp. 2948–2951.

[29] L Hermida et al. "Deoxygenation of Palmitic Acid to Produce Diesel-like Hydrocarbons over Nickel Incorporated Cellular Foam Catalyst: A Kinetic Study". In: *J Adv Chem Eng* 6.1 (2016), pp. 1–8.

[30] Charles G Hill and Thatcher W Root. *An introduction to chemical engineering kinetics & reactor design*. Wiley Online Library, 1977.

[31] Jessica Hoffmann, Claus Uhrenholt Jensen, and Lasse A Rosendahl. "Co-processing potential of HTL bio-crude at petroleum refineries–Part 1: Fractional distillation and characterization". In: *Fuel* 165 (2016), pp. 526–535.

[32] Jacqueline M Jarvis et al. "Assessment of hydrotreatment for hydrothermal liquefaction biocrudes from sewage sludge, microalgae, and pine feedstocks". In: *Energy & Fuels* 32.8 (2018), pp. 8483–8493.

[33] Jacqueline M Jarvis et al. "Hydrothermal liquefaction biocrude compositions compared to petroleum crude and shale oil". In: *Energy & Fuels* 31.3 (2017), pp. 2896–2906.

[34] Claus Uhrenholt Jensen, Jessica Hoffmann, and Lasse A Rosendahl. "Co-processing potential of HTL bio-crude at petroleum refineries. Part 2: A parametric hydrotreating study". In: *Fuel* 165 (2016), pp. 536–543.

[35] Claus Uhrenholt Jensen et al. "Hydrofaction^{TM} of forestry residues to drop-in renewable transportation fuels". In: *Direct Thermochemical Liquefaction for Energy Applications*. Elsevier, 2018, pp. 319–345.

[36] Binbin Jin et al. "Co-liquefaction of micro- and macroalgae in subcritical water". In: *Bioresource technology* 149C (Sept. 2013), pp. 103–110. DOI: `10.1016/j.biortech.2013.09.045`.

[37] Li Jingyan, Chu Xiaoli, and Tian Songbai. "Research on determination of total acid number of petroleum using mid-infrared attenuated total reflection spectroscopy". In: *Energy & fuels* 26.9 (2012), pp. 5633–5637.

[38] David SJ Jones and Peter P Pujadó. *Handbook of petroleum processing*. Springer Science & Business Media, 2006.

[39] Sergios Karatzos, James D McMillan, and Jack N Saddler. "The potential and challenges of drop-in biofuels". In: *Report for IEA Bioenergy Task* 39 (2014).

[40] Sergios Karatzos et al. "Drop-in biofuel production via conventional (lipid/fatty acid) and advanced (biomass) routes. Part I". In: *Biofuels, Bioproducts and Biorefining* 11.2 (2017), pp. 344–362.

[41] Sanjib Kumar Karmee and Carol Sze Ki Lin. "Valorisation of food waste to biofuel: current trends and technological challenges". In: *Sustainable Chemical Processes* 2.1 (2014), p. 22.

[42] Y Kim and W Parker. "A technical and economic evaluation of the pyrolysis of sewage sludge for the production of bio-oil". In: *Bioresource technology* 99.5 (2008), pp. 1409–1416.

[43] Roland Arthur Lee and Jean-Michel Lavoie. "From first- to third-generation biofuels: Challenges of producing a commodity from a biomass of increasing complexity". In: *Animal Frontiers* 3.2 (Apr. 2013), pp. 6–11. ISSN: 2160-6056. DOI: `10.2527/af.2013-0010`. eprint: `https://academic.oup.com/af/article-pdf/3/2/6/32409932/6.pdf`. URL: `https://doi.org/10.2527/af.2013-0010`.

[44] Zhiqiang Ma and Jeroen van Bokhoven. "Thermal conversion of biomass–pyrolysis and hydrotreating". In: *Catalysis* 26 (2014), pp. 249–272.

[45] P Manara and A Zabaniotou. "Towards sewage sludge based biofuels via thermochemical conversion–a review". In: *Renewable and Sustainable Energy Reviews* 16.5 (2012), pp. 2566–2582.

[46] M. Karol Michalski. *Design of experiments and optimization of algae bio-crude hydrotreating for biofuel production*.

[47] L. Nazari et al. "Recent advances in energy recovery from wastewater sludge". English. In: (2018), pp. 67–100. DOI: `10.1016/B978-0-08-101029-7.00011-4`. URL: `https://sfx.aub.aau.dk/sfxaub?sid=google&auinit=L&aulast=Nazari&atitle=Recent+advances+in+energy+recovery+from+wastewater+sludge&id=doi:10.1016/B978-0-08-101029-7.00011-4`.

[48] OER. *Chemical Properties of Alkenes*. visited: 18-03-2020. `https://courses.lumenlearning.com/suny-orgbiochemistry/chapter/chemical-properties-of-alkenes/`, 2016.

[49] Bhabani Prasanna Pattanaik and Rahul Dev Misra. "Effect of reaction pathway and operating parameters on the deoxygenation of vegetable oils to produce diesel range hydrocarbon fuels: A review". In: *Renewable and Sustainable Energy Reviews* 73 (2017), pp. 545–557.

[50] Igor Pioro and Sarah Mokry. "Thermophysical properties at critical and supercritical pressures". In: *Heat Transfer-Theoretical Analysis, Experimental Investigations and Industrial Systems*. InTech, 2011.

[51] Jerome A Ramirez, Richard J Brown, and Thomas J Rainey. "A review of hydrothermal liquefaction bio-crude properties and prospects for upgrading to transportation fuels". In: *Energies* 8.7 (2015), pp. 6765–6794.

[52] Paul R Robinson. "Petroleum processing overview". In: *Practical advances in petroleum processing*. Springer, 2006, pp. 1–78.

[53] Lasse Rosendahl. *Direct thermochemical liquefaction for energy applications*. Woodhead Publishing, 2017.

[54] Rawel Singh et al. "Hydrothermal liquefaction of agricultural and forest biomass residue: comparative study". In: *Journal of Material Cycles and Waste Management* 17.3 (2015), pp. 442–452.

[55] Marina Oliveira de Souza Dias et al. "Sugarcane processing for ethanol and sugar in Brazil". In: *Environmental Development* 15 (2015), pp. 35–51.

[56] Statista. *Daily demand for crude oil worldwide from 2006 to 2019 (in million barrels)*. URL: `https://www.statista.com/statistics/271823/daily-global-crude-oil-demand-since-2006/`.

[57] Jilu Lizy Stephen and Balasubramanian Periyasamy. "Innovative developments in biofuels production from organic waste materials: a review". In: *Fuel* 214 (2018), pp. 623–633.

[58] Paul Tanger et al. "Biomass for thermochemical conversion: targets and challenges". In: *Frontiers in plant science* 4 (2013), p. 218.

[59] S. S. Toor. *Course information and introduction to future fuel conversion scenarios*. Lecture. 2019.

[60] Saqib Sohail Toor, Lasse Rosendahl, and Andreas Rudolf. "Hydrothermal liquefaction of biomass: a review of subcritical water technologies". In: *Energy* 36.5 (2011), pp. 2328–2342.

[61] Saqib Sohail Toor et al. "lignocellulosic biomass—thermal pre-treatment with steam". In: *Pretreatment Techniques for Biofuels and Biorefineries*. Springer, 2013, pp. 59–75.

[62] Ngoc Trung Trinh. "Fast pyrolysis of lignin, macroalgae and sewage sludge". PhD thesis. 2013.

[63] Usman. *Petroleum Refining Engineering-II*. visited: 27-09-2019. `https://www.slideshare.net/MuhammadRashidUsman1/petroleum-refinery-engineeringpart230july2016`, 2016.

[64] Stanislav V Vassilev and Christina G Vassileva. "Composition, properties and challenges of algae biomass for biofuel application: an overview". In: *Fuel* 181 (2016), pp. 1–33.

[65] C Luke Williams et al. "Sources of biomass feedstock variability and the potential impact on biofuels production". In: *BioEnergy Research* 9.1 (2016), pp. 1–14.

[66] Yuan Xue et al. "A review on the operating conditions of producing bio-oil from hydrothermal liquefaction of biomass". In: *International Journal of Energy Research* 40.7 (2016), pp. 865–877.

[67] Changyan Yang et al. "Pyrolysis of microalgae: A critical review". In: *Fuel Processing Technology* 186 (Apr. 2019), pp. 53–72. DOI: `10.1016/j.fuproc.2018.12.012`.

[68] Bo Zhang, Hua-Jiang Huang, and Shri Ramaswamy. "Reaction kinetics of the hydrothermal treatment of lignin". In: *Biotechnology for Fuels and Chemicals*. Springer, 2007, pp. 487–499.

[69] S Zhang et al. "Lumping kinetic model for hydrotreating of bio-oil from the fast pyrolysis of biomass". In: *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 31.8 (2009), pp. 639–645.

[70] Zhanying Zhang et al. "Biofuels from food processing wastes". In: *Current opinion in biotechnology* 38 (2016), pp. 97–105.

Appendix A

Appendix A

Table A.1: Elemental balance of the two-stage hydrotreating products

Temperature (°C)	Pressure (bar)	WHSV (h^-1)	Elemental Balance (wt.%)			
			C	H	O	N
340	100	0.3	83.8	14.7	0	1.5
340	100	0.5	83.5	14.3	0	2.1
340	100	0.7	83.1	14	0	2.9
340	100	0.9	82.8	13.7	0	3.6
340	120	0.5	83.3	14.5	0	2.2
340	80	0.5	83.2	14.1	0	2.7
370	80	0.5	83.8	14.8	0	1.3
370	120	0.5	84	15.2	0	0.8
340	100	0.5	83.5	14.3	0	2.1
370	100	0.5	83.8	15.3	0	0.9
400	100	0.5	84.2	15.1	0	0.8