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# Master's Thesis

Techno-Economic Analysis of  
catalytic hydroprocessing of  
Fast Pyrolysis Bio-Oil to ma-  
rine biofuel



Utrecht University



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by

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# Abstract

The global shipping industry is responsible for 2-3% of the world's greenhouse gas emissions. The International Maritime Organization has set a target to reduce shipping emissions by 50% in 2050 compared to 2008 levels. Biofuels have the potential to reduce the emissions of the shipping sector. A potentially affordable and scalable biofuel for the shipping sector is hydroprocessed Fast Pyrolysis Bio-Oil (FPBO), produced from lignocellulosic biomass. To produce transportation fuels from lignocellulosic biomass two processing steps are needed. The first step is fast pyrolysis, which is in the early commercial stage. The second step is hydroprocessing, which is still in the development stage. The Dutch company Biomass Technology Group (BTG) has developed a multi-stage catalytic hydroprocessor to convert FPBO into marine fuel. The aim of this thesis is to assess the techno-economic potential of an FPBO to marine fuel via multi-stage hydroprocessing. Also, a first estimation of the emission factor of the fuel will be made.

BTG has provided a design for a demo and commercial plant. This design formed the basis for the development of a chemical process simulation in Aspen Plus. The simulation led to four outcomes: mass balance, energy balance, equipment costs and output product characterisation. These outcomes were combined with the Standardized Cost Estimation of New Technologies methodology, to calculate the production costs of both plants, the average emission factors and test whether the output products characteristics meet the marine fuel requirements.

The marine fraction, which is the main output product of the process, complies with the technical requirements of marine fuel. The total lifetime costs of the demo plant are slightly above the 22 M€. The MFSP for the commercial plant was 29,50 €/GJ, which is affected most by the PICULA catalyst lifetime and FPBO costs. The average emission factor of the products of the demo and commercial plant is 22,01 kg CO<sub>2</sub>/GJ and 23,28 kg CO<sub>2</sub>/GJ, respectively.

To conclude, the multi-stage hydroprocessing of FPBO shows potential from the technical, economic and emission factor perspective. The results of this thesis can contribute to the decarbonisation of the shipping sector.



# Contents

|   |     |
|---|-----|
| Abstract  | iii |
| 1 Introduction  | 1   |
| 2 Theoretical background                              | 3   |
| 2.1 Marine (bio)fuel                                  | 3   |
| 2.2 Cetane Number                                     | 4   |
| 2.3 Fast Pyrolysis Bio-Oil                            | 5   |
| 2.4 Catalytic hydroprocessing                         | 6   |
| 2.5 Chemical process modelling                        | 7   |
| 2.5.1 Properties                                      | 7   |
| 2.5.2 Simulation                                      | 7   |
| 2.5.3 Aspen Economic Analyser                         | 7   |
| 2.5.4 Aspen Energy Analyser                           | 7   |
| 2.6 Linear programming                                | 8   |
| 2.7 Standardised Cost Estimation for New Technologies | 8   |
| 2.8 Minimum Fuel Selling Price                        | 13  |
| 2.9 Sensitivity analysis                              | 13  |
| 2.10 Emission factor analysis                         | 13  |
| 3 Materials and methods                               | 15  |
| 3.1 Source of data                                    | 16  |
| 3.2 BTG design  | 16  |
| 3.2.1 Process design                                  | 16  |
| 3.2.2 Input and output characterisation               | 19  |
| 3.2.3 Catalysts                                       | 20  |
| 3.3 Linear programming                                | 21  |
| 3.3.1 Decision variables                              | 21  |
| 3.3.2 Objective function                              | 21  |
| 3.3.3 Constraints                                     | 22  |
| 3.4 Chemical process simulation                       | 23  |
| 3.4.1 Properties                                      | 23  |
| 3.4.2 Simulation                                      | 24  |
| 3.4.3 Aspen Economic Analyser                         | 27  |
| 3.4.4 Aspen Energy Analyser                           | 27  |
| 3.5 Cetane number                                     | 30  |
| 3.6 Standardised Cost Estimation for New Technologies | 30  |
| 3.6.1 Equipment Costs                                 | 30  |
| 3.6.2 Utility costs                                   | 30  |
| 3.6.3 Raw material costs                              | 31  |
| 3.7 Minimum Fuel Selling Price & lifetime costs       | 32  |
| 3.8 Emission factor analysis                          | 32  |
| 4 Results   | 35  |
| 4.1 Technical results output products                 | 35  |
| 4.1.1 Marine fraction                                 | 36  |
| 4.1.2 Light fraction                                  | 36  |
| 4.1.3 Gas fraction                                    | 37  |

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|       |  |    |
|-------|--|----|
| 4.2   | Economic results . . . . .   | 37 |
| 4.2.1 | Lifetime costs demo plant . . . . .                                | 38 |
| 4.2.2 | MFSP commercial plant . . . . .                                    | 38 |
| 4.2.3 | Sensitivity analysis on the input factors . . . . .                | 39 |
| 4.2.4 | Sensitivity analysis on the value of the output products . . . . . | 40 |
| 4.3   | Emission factor . . . . .  | 41 |
| 4.3.1 | Sensitivity on type of hydrogen . . . . .                          | 42 |
| 5     | Discussion . . . . .   | 43 |
| 5.1   | Comparison with existing literature. . . . .                       | 44 |
| 5.1.1 | Output products comparison . . . . .                               | 44 |
| 5.1.2 | MFSP comparison . . . . .  | 44 |
| 5.1.3 | Emission factor comparison . . . . .                               | 45 |
| 5.2   | Limitations and future research. . . . .                           | 46 |
| 6     | Conclusion . . . . .   | 47 |
|       | Bibliography . . . . .   | 49 |
| A     | Appendix . . . . .   | 55 |
| A.1   | Components per Reactor of Solver Model. . . . .                    | 55 |
| A.2   | Overall molar balance simulation. . . . .                          | 55 |
| A.3   | Pseudo Components in MTF . . . . .                                 | 56 |
| A.4   | SCENT calculations . . . . .                                       | 57 |



# Acronyms

**BTG** Biomass Technology Group.

**CAPEX** Capital Expenditures.

**CC** Composite Curves.

**CCS** Carbon Capture and Storage.

**ETS** Emission Trading System.

**FAME** Fatty Acid Methyl Ester.

**FCI** Fixed Capital Investment.

**FPBO** Fast Pyrolysis Bio-Oil.

**GCC** Grand Composite Curves.

**GHG** Greenhouse Gas.

**HEN** Heat Exchanger Network.

**HVO** Hydrotreated Vegetable Oil.

**ILUC** Indirect Land Use Change.

**IMO** International Maritime Organization.

**ISBL** Inside Battery Limits.

**LCA** Life Cycle Assessment.

**LHV** Lower Heating Value.

**LPG** Liquefied Petroleum Gas.

**MFSP** Minimum Fuel Selling Price.

**MGO** Marine Gas Oil.

**MTF** Mix of Transportation Fuels.

**NPV** Net Present Value.

**OPEX** Operational Expenditures.

**OSBLS** Outside Battery Limits.

**SCC** Shifted Composite Curves.

**SCENT** Standardized Cost Estimation for New Technologies.

**SMR** Steam Methane Reforming.

**SPO** Stabilised Pyrolysis Oil.

**TAN** Total Acid Number.

**TCI** Total Capital Investment.

**TDEC** Total Delivered Equipment Costs.

**TEA** Techno-Economic Analysis.

**TPEC** Total Purchased Equipment Costs.

**UCO** Used Cooking Oil.

**WHSV** Weight Hourly Space Velocity.

# 1

## Introduction

The global shipping industry is responsible for 2-3% of the world's Greenhouse Gas (GHG) emissions [27]. Over the last few years, there has been an increasing interest in this topic. The International Maritime Organization (IMO) has implemented a 0,5% Sulphur fuel cap and announced a GHG reduction target. This Sulphur cap decreases the allowed percentage of Sulphur in marine fuels from 3,5% to 0,5% [24]. The GHG target aims to reduce the total annual GHG emissions by at least 50% by 2050 compared to 2008 levels [24]. Biofuels can help achieve both the cap and the target, however one of the challenges is supply.

Biofuels that are currently available and can be used in diesel engines are esters and hydroprocessed fatty acids like Fatty Acid Methyl Ester (FAME) and Hydrotreated Vegetable Oil (HVO). These fuels are produced from feedstocks such as palm oil, edible oil, Used Cooking Oil (UCO) and animal fat, which are unsustainable or limited in supply. Palm oil and edible oils often have low or even no GHG reduction due to Indirect Land Use Change (ILUC)<sup>1</sup>. UCO and animal fats are not scalable as there is just a limited production of these feedstocks per capita<sup>2</sup>. FAME and HVO can be categorised as distillate diesel fuels and are compatible with road diesel engines. This means they are high in quality<sup>3</sup> and therefore more expensive compared to most fuels used in shipping engines. Ships have the ability to deploy lower quality fuels. This is because most of the ocean going ships have the capability to heat up and purify the fuel to get it into an optimal form so it can be used by the engines. This ability calls for the development of low cost marine biofuels that may be of lower quality.

According to the World Bioenergy Association, lignocellulosic biomass is abundantly available and one of the most promising feedstocks to contribute to the decarbonisation of the energy sector [17]. This feedstock would therefore be a scalable option to produce marine biofuels from. Before this feedstock can be used, it is crucial to develop conversion routes to bridge the price gap between fossil fuels and current biofuels.

One of the potential technologies to convert solid lignocellulosic biomass into liquid fuel is pyrolysis. This technology recently became commercial due to the efforts of the Dutch company Biomass Technology Group (BTG). The Fast Pyrolysis Bio-Oil (FPBO), which is the end product of their conversion route, can however not directly be used as a transportation fuel as it is not compatible with the current combustion engines. Before it can be used, the impurities (e.g. high oxygen content) need to be removed. It has been demonstrated on lab-scale that this can be done by multi-stage catalytic hydroprocessing [65]. Hydroprocessed FPBO is expected to be relatively cheap (14-24 USD<sub>2005</sub>/GJ) compared to other biofuel routes like oil plant based renewable diesel (15-30 USD<sub>2005</sub>/GJ) [9].

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<sup>1</sup>ILUC occurs when biofuels are produced on existing agricultural land. The demand for food and feed crops remains and may lead to the production of food and feed on other land. For example, forest may be changed into agricultural land, leading to the release of a substantial amount of CO<sub>2</sub> emissions into the atmosphere [7].

<sup>2</sup>The RED-II has set a cap on these feedstocks to avoid the production of waste on purpose. Already most of the UCO is imported from outside Europe (e.g. China) [14].

<sup>3</sup>The quality of a fuel in the shipping industry is related to the transparency, sulphur content, viscosity and density of the fuel [19]. A fuel which is transparent, has no sulphur, is viscous at ambient temperature and has a density of around 780-850 kg/m<sup>3</sup> is considered as a high quality fuel.

Globally multiple parties are investigating the catalytic hydroprocessing of FPBO, but commercial implementation has not yet been achieved [1, 4, 44, 52, 65–67]. Since the hydroprocessing of FPBO to marine fuel has not been commercialised, a Techno-Economic Analysis (TEA) is required to provide guidance for investments in this technology. Several TEAs have been conducted on the production of fuels from FPBO [8, 18, 22, 29, 30, 48]. These TEAs are focused on the production of jet- and road biofuel, and not on the production of marine biofuel. Because marine diesel may be of a lower quality than jet and road fuel, it is easier to meet the marine requirements than the road or jet fuel requirements. For this reason it would be a logical step to start focusing on the marine market during the early developments of this conversion route. Therefore, the aim of this thesis is to assess the techno-economic potential of an FPBO to marine fuel via multi-stage hydroprocessing. Also, a first estimation of the emission factor of the fuel will be made.

The thesis is based on a Dutch case study from the company BTG. BTG has developed a plant design for multi-stage hydroprocessing FPBO. Together with GoodFuels, a sustainable marine fuel pioneer, they are planning to build the world's first refinery for an advanced marine biofuel [20]. It is planned that this demo will have an input capacity of 500 kg FPBO per hour and starts with the production before the end of 2023. After a hopefully successful demo, a commercial plant with an input capacity of 10 tonne per hour is planned to be built. This case study provides technical information based on a real design, which reflects the actual technological status of this conversion route. To investigate the techno-economic potential of this design the following research questions are answered:

- Can the main output product of the Fast Pyrolysis Bio-Oil multi-stage hydroprocessor comply with the technical requirements of a marine fuel?
- What are the total lifetime costs for the demo plant?
- What is the minimum fuel selling price of the output products of the commercial plant, and what factors influence this price the most?
- What is the average emission factor of the output products of the demo and commercial plant?

The answers of these research questions give up to date and realistic (as this thesis is based on a real design) information on the technological, economical and environmental potential of FPBO to marine biofuel via multi-stage hydroprocessing. As there was no research performed on the specific field of marine fuels, it contributes theoretically to literature. This thesis also provides background information needed for decisions regarding future investments in this technology. Since this technology is planned to be used in a demo plant that should start producing within three years from now, this thesis also contributes practically [20].

As mentioned above, the scope of this thesis is based on a Dutch case study by BTG. The Port of Rotterdam is their preferred location, therefore, the geographical scope of this thesis is the Netherlands. The temporal scope is the year 2020 as the development of this project has already begun and insights in the techno-economic and carbon footprint of the technology are needed now. The technological scope is set on only the hydroprocessing of the FPBO. The technology is evaluated within the possibilities of the chemical engineering software Aspen Plus.

This thesis will be structured as follows: in addition to the introduction, an overview of marine biofuels, Fast Pyrolysis Bio-Oil, catalytic hydroprocessing and the tools that will be used for the analysis are given. Hereafter, the methodology that is used to answer the research question is discussed extensively, followed by the results. Then a discussion is given, followed by the conclusion of this thesis and ending with the references and appendices.

# 2

## Theoretical background

### 2.1. Marine (bio)fuel

In general, ships only use fuels in their engines that are compliant with fuel standards. The ISO 8217 is globally the most used marine standard. The ISO standard specifies the requirements for fuels for the use in marine diesel engines and boilers, prior to conventional onboard treatment (settling, centrifuging, filtration). In the standard, the term “fuels” is used to include the following:

- Hydrocarbons from petroleum crude oil, oil sands and shale.
- Hydrocarbons from synthetic or renewable sources, similar in composition to petroleum distillate fuels.
- Blends of the above with a fatty acid methyl ester(s) component.

The standard specifies seven categories of distillate fuels and six categories of residual fuels [46]. The most important parameters of the most commonly used fuels are presented in Table 2.1 below. Besides the characteristics a typical Lower Heating Value (LHV) of a marine fuel ranges around 42 MJ/kg. A biofuel should not have a much lower (e.g. < 35 MJ/kg) LHV than this 42 MJ/kg because this would lead to an under supply of energy to the engine. The engines can often inject more fuel which would reduce the problem, however, this injection increase is limited to the maximum capacity of the fuel pumps and injectors. Typically an increase up to 10-20% is possibly dependent on the design of the onboard fuel infrastructure.

Table 2.1: Important ISO 8217:2017 specifications for marine fuels.

| Characteristics             | Unit              | Limit | DMA   | DMB    | RMA   | RMB   | RMK    |
|-----------------------------|-------------------|-------|-------|--------|-------|-------|--------|
| Kinematic viscosity @ 40 °C | cSt               | Max   | 6,000 | 11,000 | 10,0  | 30,0  | 700,0  |
|                             |                   | Min   | 2,000 | 2,000  | -     | -     | -      |
| Density at 15 °C            | Kg/m <sup>3</sup> | Max   | 890,0 | 900,0  | 920,0 | 960,0 | 1010,0 |
| Cetane number               |                   | Min   | 40    | 35     | -     | -     | -      |
| Flash point                 | °C                | Min   | 60,0  | 60,0   | 60,0  | 60,0  | 60,0   |
| Water                       | Volume %          | Max   | -     | 0,3    | 0,3   | 0,5   | 0,5    |
| Total Acid Number (TAN)     | mg KOH/g          | Max   | 0,5   | 0,5    | 2,5   | 2,5   | 2,5    |

*DMA, DMB, RMA RMB and RMK are the fuel quality grades. Where DM stands for Distillate Marine and RM stands for Residual Marine. The third letter (A, B and K) stands for the quality grade where A is the highest and K is the lowest quality.*

The ISO 8217 is developed as a standard for petroleum derived fuels. To meet the requirements of the standard, a fuel should be predominantly petroleum derived (>50% petroleum derived). This means that 100% biofuels, which are not petroleum derived, can never meet this standard. However, this standard is just a guideline to ensure a consistent quality of a marine fuel, but is not mandatory to follow by regulation. Although it is just a guideline, engine manufactures often only give warranty on their engines when ISO8217 compliant fuels are used. GoodFuels, the world's first company that commercialised a dedicated marine bio-fuel, does deliver 100% biofuels to the shipping sector. According to GoodFuels, the predominately petroleum derived parameter of the ISO8217 is not crucial [19]. The parameters like the ones in Table 2.1 however are. Therefore, it is in this thesis assumed that a biofuel that meets the technical parameters of this standard meets the requirements a marine biofuel [19].

## 2.2. Cetane Number

A parameter in the distillate marine fuels standard (ISO 8217) is the Cetane number. This number rates the quality of the combustion of a fuel. The Cetane number can precisely be calculated with the results of combustion tests. However, there are also methods that allow the calculation of the Cetane number using the fuel density and its volatility. Those methods give an estimation rather than a specific number. The method used for fossil fuels is specified in the ISO 4264 standard [47]. The method is applicable to fuels containing non-petroleum derivatives from tar sand and oil shale, but is not applicable to pure hydrocarbons or distillate fuels derived from coal. The Cetane number can be calculated using equation 2.1 presented below.

$$CI = 45,2 + 0,0892 * T_{10N} + (0,131 + 0,901B) * T_{50N} + (0,0523 - 0,42B) * T_{90N} + \dots \quad (2.1)$$

$$\dots + 0,00049 * (T_{10N}^2 - T_{90N}^2) + 107 * B + 60 * B^2$$

Where:

$$\begin{aligned} T_{10N} &= T_{10} - 215 \\ T_{50N} &= T_{50} - 215 \\ T_{90N} &= T_{90} - 215 \\ T_{10} &= \text{the 10 \% (V/V) distillation recovery temperature [}^\circ\text{C]} \\ T_{50} &= \text{the 50 \% (V/V) distillation recovery temperature [}^\circ\text{C]} \\ T_{90} &= \text{the 90 \% (V/V) distillation recovery temperature [}^\circ\text{C]} \\ B &= [\exp(-0,0035 * D_N)] - 1 \\ D_N &= D - 850 \\ D &= \text{the density @ 15 }^\circ\text{C [kg/m}^3\text{]} \end{aligned}$$

In Table 2.2, the fuel characteristic ranges are given for which the method is most suitable. According to the ISO 4264 document, the expected error of the prediction via the Cetane number equation will be less than  $\pm 2$  Cetane numbers for fuel with a Cetane index between 32,5 and 56,5. But it should be noted that this standard was originally developed for fossil fuels.

Table 2.2: The optimal ranges for the input factor of the Cetane number calculation according to the ISO 4264.

| Fuel Property                                | Unit              | Minimum | Maximum |
|--|-------------------|---------|---------|
| Cetane number                                |                   | 32,5    | 56,5    |
| Density @ 15 °C                              | kg/m <sup>3</sup> | 805     | 895     |
| 10 % (V/V) distillation recovery temperature | °C                | 171     | 259     |
| 50 % (V/V) distillation recovery temperature | °C                | 212     | 308     |
| 90 % (V/V) distillation recovery temperature | °C                | 251     | 363     |

## 2.3. Fast Pyrolysis Bio-Oil

Fast pyrolysis is a thermal cracking process of organic material. During the process, the biomass is heated rapidly to a high temperature (typically around 500-600°C) in the absence of oxygen. The high temperature evaporates the biomass in long carbon chains. These gasses are then cooled to obtain a liquid oil. Overall, fast pyrolysis results in three products: gas (non-condensable syngas), liquid (FPBO) and solid (char). When optimal settings are used, approximately 60-70% of the energy content of the biomass ends up in the FPBO which is the main product of the process.

The FPBO is a viscous mixture of compounds with a wide range of molecular weights. This FPBO has multiple applications like power generation, commodity chemical and polymers [3]. The technology is scaled-up in the last decade to an industrial level by parties like BTG. Examples of projects are the Empyro plant by BTG-BTL in the Netherlands and the Green Fuel Nordic plant in Finland [59].

It is a technology with a high potential because of multiple reasons:

- FPBO is one of the cheapest liquid fuels produced from biomass today. It has been shown to be two to three times cheaper than biomass conversion technologies based on fermentation and gasification processes [66].
- A primary benefit of fast pyrolysis over other thermochemical pathways, such as liquefaction and gasification, is that it converts solid biomass into liquid biomass [70].
- Fast pyrolysis could serve the transportation fuels market using feedstocks, like lignocellulosic biomass, which are outside the food chain [3]. Lignocellulosic biomass is the most abundant and inexpensive sustainable source of carbon [66].
- As biomass residues and waste can be used as input for the process, the GHG reduction potential is high. The FPBO also has a lower sulphur content compared with fossil fuels and, therefore, also leads to lower local SO<sub>x</sub> emissions [70].
- The upgraded end-product is rich in aromatics and cycloparaffins, has outstanding cold flow properties and is expected to be ideally miscible with petroleum derived fuels [23].

Table 2.3 shows the typical characteristics of FPBO. As mentioned before, the FPBO on itself is a low-quality fuel that cannot be used in conventional gasoline and diesel engines [66]. This is primarily due to the high oxygen content, resulting in the oil being immiscible with petroleum-derived fuels. The oil must be substantially or completely deoxygenated before it can substitute petroleum. The oil is also very acidic which could harm the fuel infrastructure and the engine of a vehicle. To be able to use this oil, the acidity should be reduced by a factor of 100. Furthermore, it has a high water content (approximately 20-25%) which decreases the lower heating value. Lastly, the phase stability of the oil is low which means that the chemical structure of the fuel changes overtime [44].

Table 2.3: Fast Pyrolysis FPBO typical properties [23].

| Characteristics   | Unit              | Value |
|-------------------|-------------------|-------|
| Water content     | Wt%               | 25    |
| Solids content    | Wt%               | 0.02  |
| Density           | Kg/m <sup>3</sup> | 1170  |
| LHV               | MJ/kg             | 20    |
| pH                |                   | 2.8   |
| MCRT              | Wt%               | 17    |
| Viscosity @ 40 °C | cSt               | 30    |

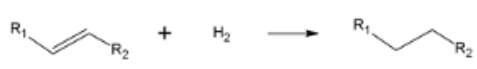


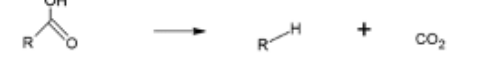
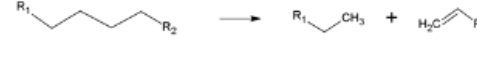

## 2.4. Catalytic hydroprocessing

Ideally, pyrolysis oil should be deoxygenated and upgraded to a mixture of organic molecules that are compatible with the current fuel infrastructure. Multi-stage catalytic hydroprocessing is a way to deoxygenate and upgrade the FPBO. This is a chemical process in which oxygenated compounds react with hydrogen in the presence of catalysts to produce hydrocarbons. This process can reduce the oxygen concentration below 1% while also bringing the components in the oil to an appropriate molecular weight range for useful liquid fuels. First studies on hydroprocessing have already been conducted in the eighties [11]. Nowadays hydroprocessing is still in the development phase and requires considerable efforts before it turns commercial.

An option could be to use the existing catalytic hydroprocessors of the petroleum industry to co-refine FPBO (up to  $\approx 5\%$ ) with fossil crude oil [23]. Only a little modification is needed to overcome the acidity and corrosives problem [48]. The current units are used for hydrodesulfurization of petroleum derived fuels. For higher concentration than  $\approx 5\%$  it is not possible to use the existing units as the lifetime of the catalysts will decrease dramatically. New hydrotreating process need to be developed with a multistage process that uses multiple catalysts and operates on multiple temperatures and pressures [23].

The two main steps in multi-stage hydroprocessing are 1) stabilization and 2) upgrading of the FPBO. In both steps, the FPBO is deoxygenated in the form of water, carbon dioxide and carbon monoxide. The chemical reactions during the FPBO hydrotreating process are very complex, as shown in Table 2.4. Overall, most of the FPBO is deoxygenated by decarboxylation and hydrodeoxygenation. There are two main challenges that need to be overcome before multi-stage hydroprocessing becomes technically suitable. The first challenge is finding a catalyst for the stabilization process, with an economically visible lifetime. The second challenge is finding the correct number of processing steps, temperatures and pressures.

Table 2.4: Examples of reactions during catalytic hydroprocessing of FPBO [29].

| Name                             | Reaction   |
|----------------------------------|--|
| Hydrogenation                    |   |
| Hydrodeoxygenation / dehydration |  |
| Decarbonylating                  |  |
| Decarboxylation                  |  |
| Cracking                         |  |
| Hydrocracking                    |  |

A general concern in hydroprocessing of FPBO is carbon deposition. Carbon deposition on the surface of solid catalysts is a common problem in hydrocarbon processing. Carbon deposits can impede the activity of the catalysts as well as block the flow of the liquid/gas through the catalyst bed. About eight years ago lifetimes of much more than 200 hours were not achieved for hydroprocessing FPBO [38]. In the last decade, much research was done to improve the lifetime of the catalyst. It is believed that dedicated catalyst under the 'PICULA' group should be able to live longer [33]. BTG has developed a catalyst themselves which will be discussed later.



## 2.5. Chemical process modelling

This study is based on the development of an Aspen Plus simulation model of a conceptual demo and commercial scale plant. Aspen Plus is widely used in the petroleum and chemicals industry for mass and energy balance. It simulates steady-state chemical process reactions and calculated mass and energy balances based on reactions or experimentally derived operating conditions [59]. The software has proven its capability in modelling whole plant simulations such as fast pyrolysis of biomass [45, 50, 53, 68]. A chemical concept is often analysed simultaneously with the technological concept and a rough economic analysis. It is therefore possible to use the heat and energy balances generated by the model to calculate the economics and complete a techno-economic assessment.

### 2.5.1. Properties

The process design in Aspen Plus starts with initializing the properties of all components that are used in the process. This can be done in the properties environment. There are different types of properties that can be used. Examples are conventional, non-conventional, solid, pseudo components, blends, assays and more. In most cases, conventional components like hydrogen are used and can be obtained from the Aspen Plus database. But not all molecules exist in the database. When a specific molecule cannot be found in the database a possibility is to upload the molecular structure together with the molecular weight as a user-defined component. Aspen Plus will then calculate the most important characteristics of the components. As Aspen Plus was initially not built for biomass processing, a lot of the biomass components are missing. The user-defined components option gives the user the possibility to upload components themselves and still simulate their (biomass) process.

After initialising the feedstock properties, a property method needs to be chosen. A property method is a collection of models and methods used to calculate physical properties. Each property method in the Aspen Physical Property System is based on either the activity coefficient method or the equation-of-state method for phase equilibrium calculations. The equilibrium method determines how other thermodynamic properties, such as enthalpies and molar volumes, are calculated.

### 2.5.2. Simulation

After defining the properties, the simulation model can be built in the simulation environment. There are two levels of dept in the simulation environment. The first level is the overall model, including all product streams and all operating units (heat exchangers, reactors, separators and columns). This overall mode allows the user to evaluate the model as a whole. In the second level, the operating units can be evaluated independently. This level allows parameters (e.g. temperature and pressure) to be adjusted for each separate operating unit.

### 2.5.3. Aspen Economic Analyser

The Aspen Economic Analyzer is the cost estimating software that provides Capital Expenditures (CAPEX) estimates and Operational Expenditures (OPEX) estimates for comparing and screening multiple process schemes. It allows the user to estimate the equipment costs per operating unit. Also, the size and material of the equipment, the operating temperatures and the pressure are considered. The main downsides of the integrated Aspen Economic Analyzer is that it is not transparent on the calculations behind the costs.

### 2.5.4. Aspen Energy Analyser

In the chemical process, there are product streams that either need to be cooled down or heated up. This used to be done only by utilities such as refrigerated water or steam. Nowadays almost in any industrial plant, the processes are designed with heat integration in mind. Heat integration is the usage of hot streams (that need to be cooled down) to heat up cooler streams (that need to be heated up) and vice versa. By doing this, the process needs fewer utilities since it uses its own energy excess/deficit, resulting in fewer operational costs. Cost optimisation often is the main reason for heat integration, but environmental reasons start to play a bigger role as well. The environmental impact of the utilities is mostly based on the gas used for the heaters, as this leads to  $CO_2$  emissions. Heated cooling water may also have a negative environmental impact as it could disrupt the local ecosystem.

Additionally, Aspen Plus provides an energy analyser. This software allows the user to design an optimal Heat Exchanger Network (HEN) for the process designed in Aspen. The technique that this energy analyser uses to optimize the HEN is called a Pinch Point analysis. This is the most widely used technique to optimize heat integration for a process. In this method, a hot and a cold composite curve, where the temperature is set out against enthalpy, are constructed. The hot composite curve represents all hot streams where heat needs to be removed. The cold composite curve represents all the cool streams where heat needs to be added. The Pinch Point is the point where the temperature difference between the hot and the cold composite curves are the lowest. The pinch point divides the composite curve into a part above and a part below the pinch point. In the Pinch analysis no heat can be transferred across the pinch point temperature. When the hot and cold streams above the pinch point are not in balance, utilities will be added to heat the cold streams or cool the hot streams.

## 2.6. Linear programming

Linear programming, also called linear optimization, is a method to achieve the best outcome in a mathematical model whose requirements have linear relationships. One of the software programs that allows the use of linear programming is Excel solver. This Microsoft software is used to optimise one formula cell (the objective function), based on multiple constraints. In this thesis, the linear programming method Simplex LP in the Excel solver is used. The Solver optimises the objective cell to a minimum, maximum or particular value. The optimum is based on the changing variable cells and the constraints. The constraints determine the boundaries of the objective cell. Changing variable cells have an influence on the outcome of the objective cell. When the solver runs, these changing variable cells are changed in the way that the model fits all constraints and optimises the objective cell.

## 2.7. Standardised Cost Estimation for New Technologies

This thesis uses the Standardized Cost Estimation for New Technologies (SCENT) methodology developed by Ereev and Patel (2012) for the cost estimation. In this methodology, the capital costs for chemical process plants are based on the estimate of the cost of major equipment items such as heat exchangers, columns, reactors, pumps and separators. The other costs can be calculated based on a factor of these major equipment costs. The advantage of the methodology is that the cost estimation can be done with a limited amount of data. Therefore, the methodology is most suitable for new establishing chemical technologies. The theoretical accuracy of the prepared estimates is within  $\pm 30\%$ . This accuracy rate is considered in the sensitivity analysis. The goal of the methodology is to determine the production costs of the product. The production costs are the costs required for the plant to manufacture the product. They are often expressed in cost per unit or per time (e.g hourly). The production costs are often expressed as (semi-)variable and fixed costs. The (semi-)variable costs are the costs fully or partially proportional to the facility's load factor. The fixed costs are all the costs independent of the load factor. The full list of production costs is presented in Table 2.5.

Table 2.5: Classification of production costs [15].

| <b>(Semi-)variable costs</b>           | <b>Fixed costs</b>            |
|--|-------------------------------|
| Raw materials                          | Local taxes                   |
| Operating labour                       | Insurance                     |
| Direct supervisory and clerical labour | General plant overhead        |
| Utilities                              | Administrative costs          |
| Maintenance and repairs                | Distribution and marketing    |
| Operating supplies                     | Research and Development      |
| Laboratory charges                     | Capital recovery <sup>a</sup> |
| Patents, royalties                     |                               |

*a. Annualized percentage of Total Capital Investment (including interest)*

One of the most important fixed costs is the capital costs which included tall buildings, machinery and equipment needed for daily operations (Table 2.6). The annual costs are referred to as capital recovery costs, which are fixed costs and based on the type of depreciation on the investment.

Table 2.6: Classification of costs objects constituting the total capital investment [15].

| Total Capital Investment           |                           |                             |
|------------------------------------|---------------------------|-----------------------------|
| Fixed Capital Investment           |                           | Working Capital             |
| Direct costs                       | Indirect costs            |                             |
| <i>Inside Battery Limits costs</i> | <i>Other direct costs</i> | Engineering and supervision |
| Equipment, including delivery      | Buildings                 | Construction expenses       |
| Equipment installation             | Service facilities        | Contractor's fee            |
| Piping, electrical work            | Land                      | Legal                       |
| Insulation, painting               | Yard works                | Start-up capital            |
| Instrumentation and control        |                           | Contingency <sup>a</sup>    |

a. There is an additional "allowance" called contingency capital which is usually a percentage of the value of the whole project. This capital is meant to cover any unforeseen events, such as unpredicted delays due to weather conditions strikes, transportation issues, etcetera.

For process industry plants, the fixed-capital investment can be divided in two parts: Inside Battery Limits (ISBL) and the Outside Battery Limits (OSBLs). The battery limit is the imaginary or real geographical boundary around the area of the processing plant. The ISBL may be defined as all direct costs. This includes the expenses for the equipment (including delivery and installation), piping, electrical work, insulation, painting, instrumentation and control. One may say that the ISBL is the processing subsystem of the plant, where the utilities and raw material flow in and out (figure 2.1). Other direct costs are the OSBLs costs, commonly referred to as 'off-sites'. Next to the direct costs, there are indirect costs.

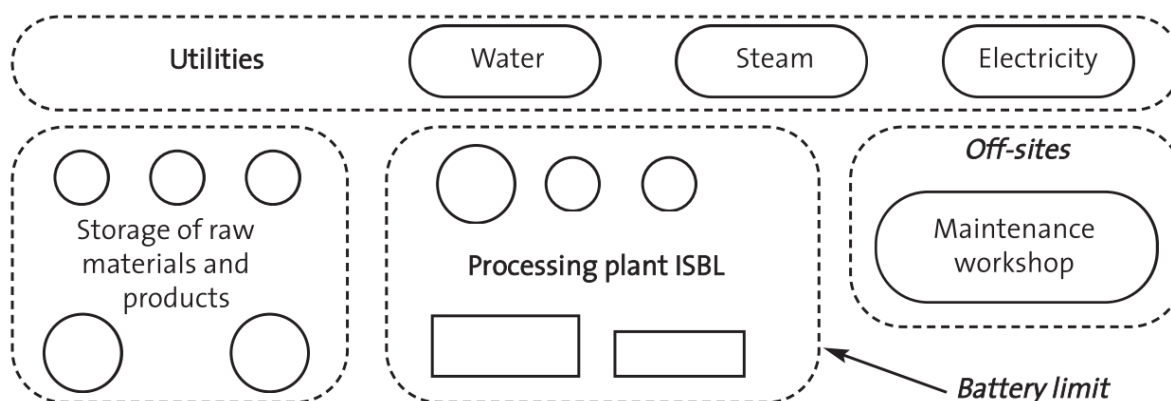


Figure 2.1: An example of a manufacturing plant: it shows the inside battery limits and the off-sites which are the outside battery limits [15].

For the daily operations of the plant also a certain amount of money is required. This needs to cover expenses such as utility bills, salaries, raw material costs and other supplies. The sum of those costs is called the working capital, which is not available for another purpose and is therefore part of the capital investment. The working capital ensures the liquidity of the firm behind the process plant.

As mentioned earlier the capital costs for chemical process plants are often based on the estimate of the cost of the major equipment items. There are also some costs which cannot be estimated on the basis of the equipment costs. These are the cost of the utilities and the raw materials. Those costs need to be obtained from the material and energy balances.

The steps that need to be taken to calculate the Total Capital Investment (TCI) are:

1. Estimate the Total Purchased Equipment Costs (TPEC).
2. Calculate the Total Delivered Equipment Costs (TDEC) and the installation costs.
3. Determine the Fixed Capital Investment (FCI), including all direct and indirect costs.
4. Estimate the working capital based on the FCI.
5. Determine the utility and raw material costs based on the material and energy balance.
6. Estimate the labour costs.
7. Estimate the total production costs including all fixed and (semi-)variable costs.

### 1. Estimate the cost of the equipment

The cost of the equipment can be determined by the economic analyser of Aspen Plus. This function within the software gives a cost estimation per operation unit of the design. As the design in Aspen Plus represents the scale of the plant, no scaling has to be done. Aspen Plus also considered the additional requirements for high pressures and temperatures. Therefore, no additional factors are used to represent these extra requirements.

### 2. Purchased equipment and installation costs

Additional costs that needs to be considered is the charge for the delivery of the equipment. These includes transportation, insurance, duties and taxes. These costs are very hard to determine, therefore, a cost factor of 10% is often used.

The installation factor depends on the labour and the material costs. The installation and construction costs vary in different geographical locations. In this methodology two assumptions are made: 1) the equipment is bought from a global market and is therefore not depended on the geographical location, and 2) the labour costs between countries do differ from each other and therefore need a correction factor<sup>1</sup>. A ratio between labour and material costs allows the user to develop a simple country-specific factor. The country specific correction factor for the Netherlands is assumed to be 1.28 [15].

### 3. Fixed Capital Investment

The cost objects within the FCI are commonly estimated by multiplication factors. Those factors depend on the type of material (solids, fluids or a mix) that is processed. Table 2.7 presents the factors as a factor of either TDEC or TPEC for a fluid processing plant.

Table 2.7: Factor for estimation of the direct and indirect costs of the fixed-capital investment (based on fluid processing).

| Type of cost                 | Unit      | Value |
|------------------------------|-----------|-------|
| Instrumentation and controls | % of TDEC | 36%   |
| Building                     | % of TPEC | 45%   |
| Service facilities           | % of TDEC | 70%   |
| Engineering and supervision  | % of TDEC | 33%   |
| Construction expenses        | % of TDEC | 41%   |
| Contractors fee              | % of TDEC | 22%   |
| Legal expenses               | % of TDEC | 4%    |
| Contingency                  | % of TDEC | 44%   |
| Land                         | % of TDEC | 6%    |
| Yard improvements            | % of TDEC | 10%   |

<sup>1</sup>The SCENT methodology uses the United States as the default country. No correction factors are needed when the plant is built in the United States.

#### 4. Working capital

For new technologies including new end-products, there is a high uncertainty regarding the sales. Therefore, a high working capital is needed, this value ranges typically between 15% and 30% of the TCI. When the end-product is sold at a relatively constant and uniform yearly rate, the working capital can be lower. When the sales vary during the year a higher working capital is needed.

#### 5. Utility and raw material costs

The cost of the utilities and the raw material are depended on the material and energy balance. In this section it is important to use data that is representative for the geographical location of the plant. Most chemical plants are located on a site where utilities are provided by an infrastructure. The price of the utility is mainly determined by the operating costs of generation and transmitting the utility stream. The utility consumption of a process can only be estimated accurately when the energy requirement is known [63]. The heating requirement can be fulfilled with hot oil, fired heat, high pressure steam, medium pressure steam or low pressure steam. Steam is the heat source that is most most widely used in chemical plants, because it has a number of advantages:

- Steam gives a high heat output per weight at a constant temperature (compared to hot oil and flue gas);
- The temperature at which the steam is released can be controlled by controlling the pressure of the steam. This enables precise temperature control. Condensing steam has a high heat transfer coefficient, which leads to cheaper heat exchangers;
- Steam is nontoxic and nonflammable which is preferred from a safety perspective.

Steam is mostly supplied at three levels: high, medium and low pressure. High pressure steam is at 40 bar, corresponding to a saturation temperature of 250 °C. For medium pressure steam these numbers are 20 bar and 212 °C and 6 bar and 159 °C for low pressure steam. The furnace efficiency of the boiler used to produce the steam is 80-90% [63]. Fired heat is used for heating duties above the highest temperature that can be reached with high pressure steam, typically around 250 °C. The cost of this fired heat can be calculated from the price of the fuel that is used (e.g. Natural Gas). The furnace efficiency that typically is used fired heaters is 85% [63]. Hot oil is often used as heat source in situations where fired heat or steam is not suitable. Hot oil can heat up to 440 °C. A hot oil heater usually uses both the radiant and convective sectors of the heater and have a heater efficiency of 80-85% [63]. Water is often used for cooling. The heat capacity and density of water is 4,1570 kJ \* kg<sup>-1</sup> \* °C<sup>-1</sup> and 998,23 kg/m<sup>3</sup> at 20 °C, respectively [60]. In case 1 m<sup>3</sup> of cooling water has an inlet temperature of 20 °C and an outlet temperature of 30 °C, the water can provide 41,72 MJ of cooling. To calculate the cost of the heating requirement equation 2.2 can be used.

$$C_{yr,x} = P_{NG} * Hr * \frac{D_x}{\eta_x} \quad (2.2)$$

Where:

- $C_{yr,x}$  = the cost per year for heat transfer fluid x  
 $P_{NG}$  = the price of natural gas  
 $Hr$  = the annual operation hour of the plant  
 $D_x$  = the required duty of heat transfer fluid x  
 $\eta_x$  = the efficiency of the boiler/heater used to produce heat transfer fluid x

## 6. Labour costs

The labour costs are divided into two groups: 1) the operating labour costs and 2) direct supervisory and clerical labour costs. Wessel (1952) developed an equation to estimate the number of employee-hours that is needed for the production of 1000 kg of end-product [15]. The equation is as follows:

$$\log Y = -0,0783 * \log X + 1,252 + B \quad (2.3)$$

Where:

- $Y$  = the operating labour in operator-hours per ton (short) per processing step
- $X$  = the plant capacity in tons (short) per day
- $B$  = a constant depended on the type of process

Note that the used ton is a short ton, not a Metric tonne (1 short ton = 0.907 Metric tonne). The different B factors per type of process are presented in Table 2.8. Once the number of required employees is estimated, the value needs to be multiplied by the earlier mentioned country specific labour cost factor. The direct supervisory and clerical labour can then be calculated with a factor of 15% compared to the operating labour costs.

Table 2.8: Different B factors per type of process in Wessel (1952) labour cost methodology.

| Type of process                      | B factor |
|--------------------------------------|----------|
| Batch operation                      | 0,132    |
| Average labour requirements          | 0,000    |
| Well-instrumented continuous process | -0,167   |

## 7. Total production costs

The total production costs can now be calculated using the above calculated values in combination with the factors from table 2.9. Research and Development is not included in the SCENT method as these costs are expected to be inaccurate for emerging technologies.

Table 2.9: Factors for estimation of (semi-)variable and fixed production costs.

| Type of cost                       | Based on:                   | Low value | Average value | High value |
|------------------------------------|-----------------------------|-----------|---------------|------------|
| Direct supervisory clerical labour | % of operating labour       | 10%       | 15%           | 20%        |
| Operating supplies                 | % of maintenance            | 10%       | 15%           | 20%        |
| Patents and royalties              | % of production costs       | 10%       | 15%           | 20%        |
| Laboratory charges                 | % of operating labour       | 1%        | -             | 2%         |
| Local taxes                        | % of FCI                    | 3%        | -             | 4%         |
| Insurance                          | % of FCI                    | 1%        | 1%            | 1%         |
| General plant overhead             | % of labour and maintenance | 50%       | 60%           | 70%        |
| Administrative costs               | % of operating labour       | 15%       | 20%           | 25%        |
| Distribution and marketing         | % of total production costs | 2%        | 11%           | 20%        |

## 2.8. Minimum Fuel Selling Price

The MFSP is the price of the fuel when a zero equity Net Present Value (NPV) is achieved. The equity NPV is the sum of the future cash that comes from and flow to the equity holders. The MFSP can be calculated by using the equation below [31].

$$MFSP = \frac{\sum_{t=-1}^L \frac{I_t * E + D_t + T_t + COP_t}{(1+r)^t}}{\sum_i q_i \sum_{t=-1}^L \frac{P_{i,t}}{(1+r)^t}} \quad (2.4)$$

Where:

|           |   |   |
|-----------|---|---|
| $t$       | = | the financial year  |
| $I_t$     | = | the investment expenditures in year t                       |
| $E$       | = | the equity share of the investment                          |
| $D_t$     | = | principle and interest payment in year t                    |
| $T_t$     | = | tax payments in year t                                      |
| $COP_t$   | = | cost of production in year t                                |
| $i$       | = | is the fuel product (e.g. light fraction or marine biofuel) |
| $P_{i,t}$ | = | production of fuel product i in year t                      |
| $q_i$     | = | ratio of fuel product i with respect to marine biofuel      |
| $r$       | = | the discount rate   |
| $L$       | = | the project lifetime  |

## 2.9. Sensitivity analysis

A sensitivity analysis is performed to examine the impact of the input on the costs. A single input factor varies within its expected minimum and maximum boundaries. By doing this it is possible to see which input factor has the highest influence on the costs, and how much the costs can change.

## 2.10. Emission factor analysis

The Renewable Energy Directive II specifies a methodology and rules to calculate the GHG impact of biofuels, bioliquids and their fossil fuel equivalents [16]. The equation that this methodology specifies to calculate the total emission from the use of the biofuel is as follows:

$$e = e_{ec} + e_l + e_p + e_{td} + e_u - e_{sca} - e_{ccs} - e_{ccr} \quad (2.5)$$

Where:

|           |   |  |
|-----------|---|--|
| $e$       | = | the emission factor of the fuel  |
| $e_{ec}$  | = | the emission factor from the extraction or cultivation of raw materials                        |
| $e_l$     | = | the emission factor from carbon stock changes caused by land-use change                        |
| $e_p$     | = | the emission factor from processing  |
| $e_{td}$  | = | the emission factor from transport and distribution  |
| $e_u$     | = | the emission factor from the fuel in use   |
| $e_{sca}$ | = | the emission factor savings from soil carbon accumulation via improved agricultural management |
| $e_{ccs}$ | = | the emission factor savings from $CO_2$ capture and geological storage                         |
| $e_{ccr}$ | = | the emission factor savings from $CO_2$ capture and replacement                                |

Some important points that need to be taken into account during the total emission calculation are:

- The GHG emission from biofuels should be expressed in terms of  $g\ CO_2eq / MJ$  of fuel.
- The emissions of biofuels,  $e_u$ , should be taken as zero for biofuels.
- For the use of electricity during the conversion process of the feedstock to fuel, the local emission intensity should be used.
- The GHG taken into account for  $CO_2$  equivalents are  $CO_2$ ,  $N_2O$  and  $CH_4$ . The gasses do have a different Global Warming Potential (GWP) which is related to the level of heat a GHG traps in the atmosphere up to a specific time horizon, relative to  $CO_2$ . See Table 2.10 for the factor for each of the GHG.

Table 2.10: Global warming potential (GWP) per type of GHG [16].

| GHG    | Factor |
|--------|--------|
| $CO_2$ | 1      |
| $N_2O$ | 298    |
| $CH_4$ | 25     |

BTG recently performed a Life Cycle Assessment (LCA) on the production of FPBO[57]. This was the first full LCA using real data from a demo plant scale. They found a result of 376  $g\ CO_2\ eq$  for 1 tonne of FPBO from forestry residues. The GHG shaving from biofuels may be calculated as follows:

$$S = \frac{E_{F(t)} - E_B}{E_{F(t)}} \quad (2.6)$$

Where:

- $S$  = biofuel saving compared to fossil fuel comparators
- $E_B$  = total emissions from the biofuel
- $E_{F(t)}$  = total emissions from the fossil fuel comparator for transport



# 3

## Materials and methods

This section describes the steps that are taken to answer the research questions. Figure 3.1 shows the used methodology. The process design of BTG forms the basis of the thesis. From this starting point, a chemical process simulation model was built in the chemical engineering software Aspen Plus. To build a model in Aspen Plus, one of the following variables has to be known:

- The kinetics and stoichiometry of the reactions that take place.
- The composition of all streams between the unit operators.

In this case, it was unknown which exact reactions take place in the reactors. Therefore, in this thesis, the composition of the streams had to be used to build the model. The composition of the incoming and outgoing streams was available. However, information of the composition of the streams between the unit operators, hereafter referred to as intermediate streams, was missing (black box). To determine the composition of all intermediate streams, parallel to the Aspen Plus model, a linear programming model (using Excel Solver) was built. Earlier studies, like Tews et al. that ran into the same black box problem have also used linear programming to determine the composition of intermediate streams [59]. This Solver model is able to determine the optional composition of the intermediate streams based on a target function and multiple constraints. With the information of the intermediate streams, it is possible to build the simulation in Aspen Plus. Additionally, heat integration was performed to minimise the utility demand. The chemical process simulation leads to four outcomes:

1. **Energy balance:** which was obtained from the Aspen Energy Analyser and gives insight into the demand for electricity, heating and cooling.
2. **Mass balance:** which was obtained from the design of BTG was validated in Aspen Plus.
3. **Equipment costs:** which was obtained from the Aspen Economic Analyser. This estimation is based on the condition of the process (e.g. mass flow, pressure and temperature) and of the size of the equipment.
4. **Product characterisation:** which was obtained from the Aspen Plus stream summary. This characterisation gives information on the potential application of the output products.

The production costs of the design can be estimated using the SCENT methodology [15], using the energy balance, mass balance and equipment costs. The economic results of the demo plant are presented in the form of lifetime costs. The economic results of the commercial plant are presented as MFSP, which shows the price of the marine biofuel when a zero equity (NPV) is achieved. Besides providing the information for the economic results, the energy and mass balance also provides information for the average emission factor calculations of the output products.

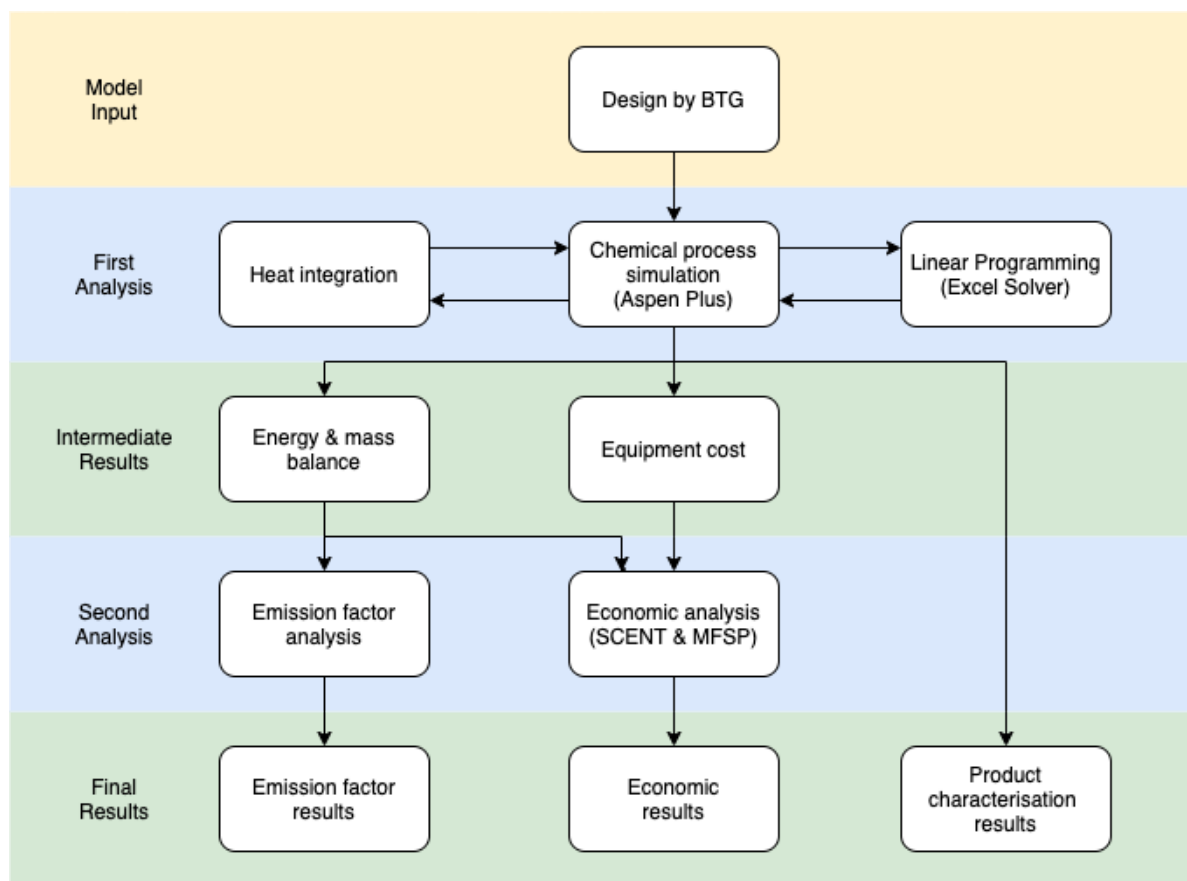


Figure 3.1: Overview of the methodology of the thesis.

### 3.1. Source of data

This thesis used experimental data provided by BTG, which was obtained from their lab-scale test setup. The provided data gave insight into the multi-stage hydroprocessing design and the characteristics of the feed and product streams. The data required for the economic assessment is mostly obtained from the SCENT methodology and supplemented where necessary with data from literature and regional specific databases (e.g. Eurostat and Statline). The data for the environmental analysis is mostly taken from literature.

### 3.2. BTG design

This section discusses all the data obtained from BTG, related to their multi-stage catalytic hydroprocessing design. The information discussed in this section consists of a simplified overview of the process design, the known information on process streams, and information on the catalysts.

#### 3.2.1. Process design

Figure 3.2 presents a simplified overview of the design of the multi-stage catalytic hydroprocessor. The demo and commercial design are equal in terms of process design. Therefore, only one process design was built. Only the mass flows of the two designs differ from each other. Table 3.1 presents the input, intermediate and output mass flows for both the demo and commercial plants. As shown in Figure 3.2, the process can be divided into five technical areas:

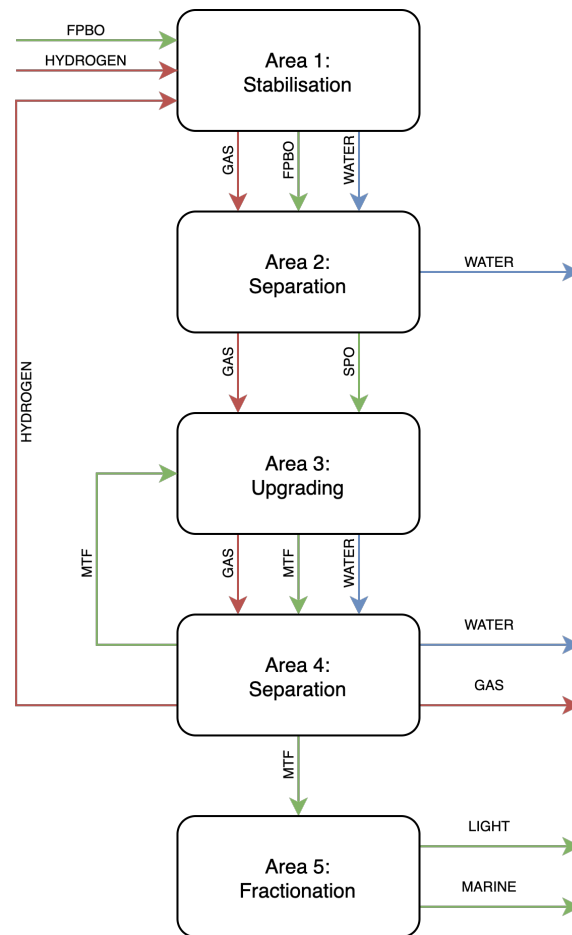


Figure 3.2: A simplified overview of the FPBO hydroprocessing process.

1. The first area of the process is the FPBO stabilisation stage. In this stage, FPBO and hydrogen is fed to four stabilisation reactors. The process requires 5% of hydrogen compared to the inlet weight of FPBO. The reactors operate on different temperatures ranging from 80-200 °C, and a pressure of 200 bar. The main aim of this first area is to stabilise the FPBO and remove approximately half of its oxygen content in the form of water.
2. In the second area the gas, water and oil fractions are separated from each other. Approximately 30% of the weight of the FPBO inlet weight is removed in the form of water. This water contains 5% of biogenic carbon. Stabilised Pyrolysis Oil (SPO) is the oil that remains after the first area. This SPO together with the separated gas in then fed to the third area.
3. In the third area, the mixture is again fed to four upgrading reactors. These reactors operate on a lower pressure (130 bar) than the stabilisation reactors. However, the temperatures are higher and range between 250-340 C. In these reactors a commercial NiMo(S) catalyst is used. The main purpose of this area is to remove the leftover oxygen content from the SPO.
4. In the fourth area, the leftover water, gas fraction and hydrogen is separated from the oil. The hydrogen is then recycled and send back to the first area. The leftover oil is oxygen-free and labelled as Mix of Transportation Fuels (MTF). Lastly, this MTF is sent to the fifth area.
5. In the fifth area, the MTF is divided into two fractions. This is need to increase the flashpoint of the MTF, in order to meet the ISO 8217 requirements. Experimental data has shown that fractionation of approximately 15% is enough to increase the flashpoint to be sufficient for a marine fuel.

Table 3.1: Main design properties and assumptions.

| Parameter                            | Unit  | DEMO | Commercial |
|--------------------------------------|-------|------|------------|
| FPBO inlet stream                    | Kg/hr | 500  | 10.000     |
| Hydrogen inlet stream                | Kg/hr | 25   | 500        |
| SPO intermediate stream              | Kg/hr | 350  | 7.000      |
| Hydrogen recycle intermediate stream | Kg/hr | 41,7 | 833,3      |
| Waste water outlet stream            | Kg/hr | 260  | 5200       |
| Gas fraction outlet stream           | Kg/hr | 90   | 1800       |
| Light fraction output                | Kg/hr | 25   | 500        |
| Marine fraction output               | kg/hr | 150  | 3.000      |

During the stabilisation and upgrading of the FPBO there are three phases in the system: 1) aqueous, 2) gaseous and 3) liquid. The amount of carbon (C), hydrogen (H) and oxygen (O) in those three phases combined is always equal before and after a reactor. However, the amount of C, H and O within one phase can change, as atoms can move from one phase to another phase during reactions in the reactor. In Figure 3.3 below, the O/C and H/C ratio of the liquids (bio-oil) is shown, as well as three red arrows. These arrows represent the three steps of stabilisation and upgrading of the bio-oil. The FPBO starts is the north-east top of the plot. During the process the O/C ratio continuously decreases. The H/C ratio, on the other hand, decreases first, but increases again after a certain point. During the entire process, water is produced from the hydrogen and the oxygen from the bio-oil. The first step of stabilisation and upgrading is sugar chemistry where oxygen and hydrogen is removed from the bio-oil. The second step is dehydration, where water is removed from the oil. The final step is the lignin chemistry, which is lignin hydrocracking. The sugar and lignin chemistry are two total different processes happening under different pressures, temperatures and catalysts. In the south-east side of the plot the MTF comes out of the system. After the three steps the bio-oil has consumed all the input hydrogen and is almost oxygen free (<1 wt%). [23]

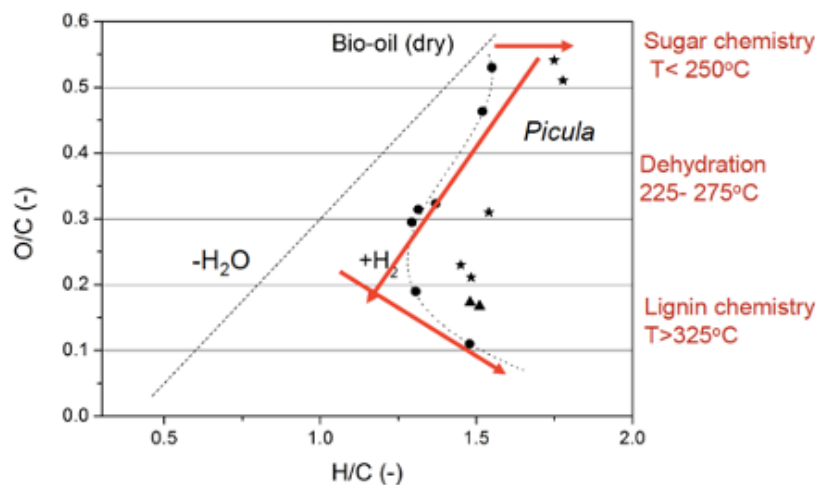


Figure 3.3: Van Krevelen plot illustrating the O/C and H/C ratio during stabilisation and upgrading of the FPBO, where the markers (circle, star and triangle) represent experimental data [23].

### 3.2.2. Input and output characterisation

BTG has provided information on the characteristics of the following streams which are discussed separately.

- FPBO (input stream):** in this thesis, sawdust is considered as the primary feedstock for the production of the FPBO. The main reason for this choice is that Empyro, a Dutch pyrolysis oil plant owned by BTG-BTL, produces FPBO from sawdust. The FPBO of Empyro is used for the lab-scale test setup of BTG. Therefore, this FPBO is chosen to represent the FPBO of the multi-stage hydoprocessing design. The organic products of FPBO are a complex mixture of hundreds of compounds and are considered hard to define. In previous literature, the properties of FPBO were defined via a number of model compounds that represent a compound group [29, 35, 48]. Typical compound groups in FPBO are acids, ketones, aldehydes, carbohydrates - sugars, pyrolytic lignin, extractives and water. BTG has provided the composition of two samples as presented in Table 3.2. Those samples were not the samples used for the hydroprocessing experiments, but no better representation of the FPBO was available. The CHO-balance of the input sample has a lot of influence on the total mass balance of the system. It was expected by BTG that the FPBO (wet basis) should have a carbon content close to 46-47%, hydrogen content close to 7,5-8% and oxygen content close to 45-46,5%. The FPBO also contains water with an estimated content between 20-25%. However, using the two provided samples, it was not possible to make a correct CHO-balance for the whole system. Since, the CHO-content of all in- and output streams except the FPBO were pre-defined, the FPBO was the only stream which could be adjusted to make the CHO-balance of the system correct. Therefore, an optimisation of the FPBO composition was performed to make the CHO-balance of the whole system correct. The optimised composition is shown in Table 3.2 under 'optimised' [23]. The adjusted composition has a CHO-content (wet basis) of respectively 45,6%, 8% and 46,4%. The water content of this wet basis FPBO was 24,25%. The CHO-balance and water content of this optimised composition was comparable with the earlier described expectations of BTG [23].

Table 3.2: FPBO (saw dust) composition, dry basis [23].

| Compound group            | Model compound                  | Formula   | Sample 1 | Sample 2 | Optimised |
|---------------------------|---------------------------------|---|----------|----------|-----------|
| Acids                     | Crotonic acid                   | C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>    | 0.0557   | 0.0889   | 0.0411    |
| Alcohols                  | 1,4-benzenediol                 | C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>    | 0.0697   | 0.0898   | 0.0305    |
| Ketones                   | Hydroxy acetone                 | C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>    | 0.0829   | 0.0363   | 0.0476    |
| Aldehydes                 | 3-methoxy-4-hydroxybenzaldehyde | C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>    | 0.0697   | 0.0652   | 0.0607    |
| Guaiacols                 | Isoeugenol                      | C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>  | 0.0498   | 0.0435   | 0.0553    |
| Low MW sugars             | Levoglucosan                    | C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>   | 0.0597   | 0.1698   | 0.0332    |
| High MW sugars            | Cellobiose                      | C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> | 0.3386   | 0.3518   | 0.3266    |
| Low MW lignin compound A  | Dimethoxy stilbene              | C <sub>16</sub> H <sub>16</sub> O <sub>2</sub>  | 0.1095   | 0.00     | 0.1095    |
| Low MW lignin compound B  | Dibenzofuran                    | C <sub>12</sub> H <sub>8</sub> O                | 0.0221   | 0.00     | 0.0349    |
| Extractives               | Dehydroabietic acid             | C <sub>20</sub> H <sub>28</sub> O <sub>2</sub>  | 0.0299   | 0.041    | 0.1499    |
| High MW lignin compound A | Oligomeric compounds            | C <sub>20</sub> H <sub>26</sub> O <sub>8</sub>  | 0.0915   | 0.056    | 0.0913    |
| High MW lignin compound B | Phenylcoumaran compounds        | C <sub>21</sub> H <sub>26</sub> O <sub>8</sub>  | 0.0199   | 0.0577   | 0.0193    |

- SPO (intermediate stream):** the water content of the SPO was 7,5%.
- MTF (intermediate stream):** from BTGs experimental data there were some characteristics of MTF identified. A CHO-balance of respectively, 88,4%, 12,7% and 0,0% was found. Moreover, almost no sulphur and a TAN of approximately 0,01 mg KOH/g was found in the MTF [23]. The MTF is fully miscible with fossil diesel which means that it should be compatible with the current fuel infrastructure. Another source of information was a report written by Ajam et al. (2013) [1]. They extensively analysed the chemical properties and constructed a distillation curve of the MTF provided by BTG (Figure 3.4).
- Waste water (output stream):** experimental data has shown that waste water from the process is not pure water. It is estimated that the water contains approximately 5% biogenic carbon [23]. For modelling purposes a component acetic acid was added to the water, to represent the 5% biogenic carbon share. Acetic acid is a colourless liquid organic compound with the chemical formula  $CH_3COOH$ . This component was chosen because it is a common component in wastewater from biochemical processes [37].
- Gas fraction (output stream):** the gas fraction as presented in Table 3.3 was obtained from experimental data.

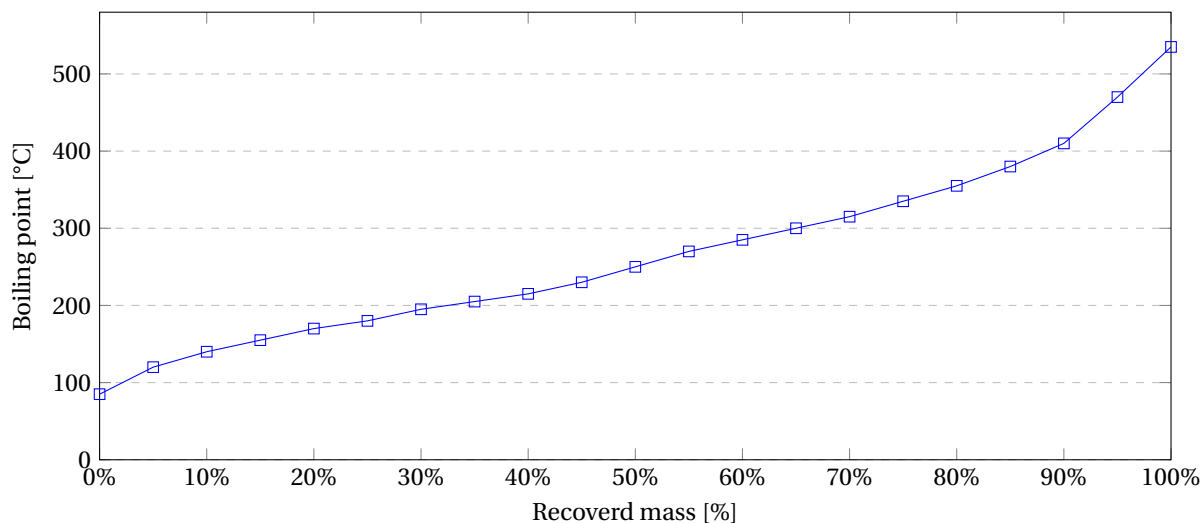


Figure 3.4: The distillation curve of the MTF derived from wood-based FPBO [1].

Table 3.3: The gas fraction components with weight shares [23].

| Component   | Fraction |
|-------------|----------|
| $CO$        | 0.5 wt%  |
| $CO_2$      | 19 wt%   |
| $CH_4$      | 27 wt%   |
| $C_2H_6$    | 24 wt%   |
| $C_3H_8$    | 19 wt%   |
| $C_4H_{10}$ | 10 wt%   |

### 3.2.3. Catalysts

The lifetime of the catalyst is an important factor in the stabilisation process. Therefore, a specially developed catalyst is used, named PICULA. The PICULA catalyst is an improved Ni-Cu catalyst, which is patented by BTG. The expectation is that this catalyst has a lifetime between 3-12 months in the demo plant. After some improvements, it should have a lifetime between 12-24 months in the commercial plant. The Weight Hourly Space Velocity (WHSV) of this catalyst in the stabilisation reactors is  $0.3 \text{ h}^{-1}$ . In the demo and commercial plant, 1,7 tonne and 33 tonne of PICULA catalyst is required, respectively. In the upgrading reactors, a commercial NiMo(S) catalyst is used. The WHSV of this catalyst is  $0,5 \text{ h}^{-1}$  in the demo plant and  $1 \text{ h}^{-1}$  in the commercial plant. In the demo plant, 0,7 tonne of NiMo(S) catalyst is required and in the commercial plant 7 tonne. [23]

### 3.3. Linear programming

As described above, some information was available on the input, output and intermediate streams of the design. However, it is unknown which reactions exactly happen within the eight reactors. The characteristics of the input and output streams, the mass flows of all the streams including the mass flow of waste water removal, and the O/C and H/C pathway of the bio-oil from Figure 3.3 are known. With this information and keeping the CHO-balance in mind<sup>1</sup>, an estimation of the yield of each of the eight reactors can be made. It is assumed that only the 22 components presented in Table 3.4 can be present in the system. Those 22 components represent the FPBO, the gas fraction, the waste water and the MTF<sup>2</sup>. For modelling purposes, it is assumed that no other components exist in the reactors as this would make the model much more complex<sup>3</sup>. A simple linear programming model (in Excel solver) was built to simulate the yield of the eight reactors. While calculating the yield of the reactors, the model needs to meet the CHO-balance requirement, meet the mass flow requirements, and the bio-oil should follow the O/C and H/C pathway. Over the eight reactors, the FPBO and hydrogen are converted step by step into aqueous products, gaseous products and MTF. Below a detailed description of the model with its decision variables, objective function and constraints is given.

#### 3.3.1. Decision variables

The decision variables are the variables that the solver model changes in order to satisfy the constraints. In this model the decision variables are the output mass of the 22 components of each reactor.

Table 3.4: The 22 components used in the solver model.

| Aqueous     | Gaseous         | FPBO                            | MTF |
|-------------|-----------------|---------------------------------|-----|
| Water       | Hydrogen        | Crotonic Acid                   | MTF |
| Acetic-Acid | Carbon-Monoxide | 1,4-Benzenediol                 |     |
|             | Carbon-Dioxide  | Hydroxyacetone                  |     |
|             | Ethane          | 3-Methoxy-4-Hydroxybenzaldehyde |     |
|             | Methane         | Isoeugenol                      |     |
|             | Propane         | Levoglucofan                    |     |
|             | Butane          | Cellobiose                      |     |
|             |                 | Dimethoxy Stilbene              |     |
|             |                 | Dibenzofuran                    |     |
|             |                 | Dehydroabiatic Acid             |     |
|             |                 | Oligomeric Compounds            |     |
|             |                 | Phenylcoumaran Compounds        |     |

#### 3.3.2. Objective function

The objective for the stabilisation reactors was to minimise the H/C ratio of the oil fraction as much as possible, while the objective of the upgrading reactors was to maximise the H/C ratio of the oil fraction. Therefore, the formula cell which calculates the H/C ratio was chosen to be the objective function of all reactors. Following Figure 3.3, the O/C ratio of the oil fraction decreased constantly over the eight reactors. The O/C ratio target was manually entered as a constraint for each reactor separately.

<sup>1</sup>The C, H and O mass flow of the reactor inlet should be in a perfect balance with the C, H and O mass flow of the reactor outlet.

<sup>2</sup>The MTF consists of an assay of pseudo components but is treated as a single component in the linear programming model.

<sup>3</sup>In reality there are more components which are not considered in this model.

### 3.3.3. Constraints

Some constraints are the same for all reactors. However, for some reactor there are additional specified constraints. The constraints used for all reactors are:

1. The molar mass of the input carbon needs to be equal to the molar mass of the output carbon.
2. The molar mass of the input hydrogen needs to be equal to the molar mass of the output hydrogen.
3. The molar mass of the input oxygen needs to be equal to the molar mass of the output oxygen.
4. The decision variables may not be negative.
5. The carbon content in the aqueous fraction should always be 5%.

The constraints for specific reactors are described below.

Reactor R1-4 (last reactor of stabilisation area) and reactor R2-4 (last reactor of upgrading area) need a specific amount of water in the mixture as specified in the design by BTG. This required amount of water is added as a constraint for these reactors. The amount of water required for both reactors in the demo plant is specified below. For the commercial plant this amount is exactly 20 times higher.

- The water output constraint of the R1-4 reactor is 176 kg/hr. Hereof, 150 kg/hr is separated out of the system and 26 kg/hr is required to meet the 7.5% water content in SPO.
- The water output constraint of the R2-4 reactor is 110 kg/hr.

Moreover, R2-4 output requires a certain amount of gas with a certain composition as shown in Table 3.3). The gas fraction also requires a certain amount of hydrogen. The amount of gas for the demo plant is specified below. For the commercial plant this amount is exactly 20 times higher.

- The gas output constraint of the R2-4 reactor is 90 kg/hr, as shown in Table 3.3).
- The hydrogen output constraint of the R2-4 reactor is 42 kg/hr, which will be recycled and sent back to the first stabilisation reactor.

Lastly, the output of the reactors R1-4 and R2-4 requires a certain amount of oil. The amount of oil for the demo plant is specified below. For the commercial plant this amount is exactly 20 times higher.

- The oil output constraint of the R1-4 reactor, is 324 kg/hr. The SPO (with a 7,5% of water content) is composed of this oil combined with the 26 kg/hr water described above.
- The oil (MTF) output constraint of the R2-4 reactor is 192,5 kg/hr. Hereof 175 kg/hr is sent to the fractionation section and 17,5 kg/hr is recycled.

In Table 3.5, the H/C and O/C ratio's per reactor are given after executing the models for all reactors. It also shows that the H/C ratio declines first and increases later, while the O/C ratio declines steadily. This is in line with the H/C-O/C ratio pathway obtained from experimental data (Figure 3.3). As the oxygen from the oil is mainly removed via water, the water content increases after every reactor. Between reactor R1-4 and R2-1 there is a decrease in water as water is separated from the oil and sent out of the system.



Table 3.5: Excel Solver H/C ratio, O/C ratio and total water content.

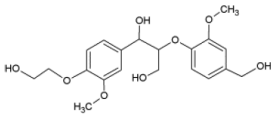
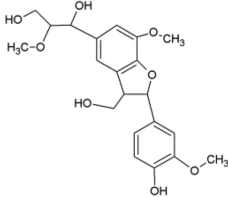
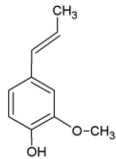
| Stream      | H/C ratio | O/C ratio | Water Content DEMO [t/hr] | Water Content Commercial [t/hr] |
|-------------|-----------|-----------|---------------------------|---------------------------------|
| R1-1 inlet  | 1,373     | 0,410     | 0,121                     | 2,420                           |
| R1-1 outlet | 1,373     | 0,401     | 0,135                     | 2,700                           |
| R1-2 outlet | 1,298     | 0,363     | 0,149                     | 2,980                           |
| R1-3 outlet | 1,285     | 0,326     | 0,163                     | 3,260                           |
| R1-4 outlet | 1,309     | 0,270     | 0,176                     | 3,520                           |
| R2-1 outlet | 1,370     | 0,166     | 0,047                     | 0,940                           |
| R2-2 outlet | 1,431     | 0,090     | 0,068                     | 1,360                           |
| R2-3 outlet | 1,555     | 0,050     | 0,089                     | 1,780                           |
| R2-4 outlet | 1,713     | 0,000     | 0,110                     | 2,200                           |

### 3.4. Chemical process simulation

#### 3.4.1. Properties

The optimised composition of the FPBO, as presented in Table 3.2, is used as input for chemical process simulation. Most of the FPBO compounds are found in the Aspen Plus thermodynamic database. High MW Lignin derived compound A, High MW Lignin derived compound B and Guaiacols were the only model compounds that were not present in the database. These compounds had to be defined manually into the Aspen Plus software using the molecular structures, physical and chemical properties (Table 3.6). The model compounds of the hydrogen<sup>4</sup>, waste water and gas fraction were also found in the Aspen Plus database. The distillation curve was used to make a representation of the MTF stream. Using this distillation curve, Aspen is able to make an assay of pseudo components that give a realistic representation of the MTF, as shown in Table A.3. This assay is used to represent the MTF in this thesis.

Table 3.6: Molecular structures and physical and chemical properties for user defined compounds [29].

| Parameter           | Unit      | High MW lignin derived compound A   | High MW lignin derived compound B  | Guaiacols   |
|---------------------|-----------|---|--|---|
| Formula             |           | C <sub>20</sub> H <sub>26</sub> O <sub>8</sub>                                      | C <sub>21</sub> H <sub>26</sub> O <sub>8</sub>                                       | C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>  |
| Molecular structure |           |  |  |  |
| TBP                 | F         | 1198,4  | 1172,4   | 507,2   |
| TC                  | F         | 1482,2  | 1468,2   | 987,5   |
| Pc                  | psia      | 241,9   | 243,7  | 476,4   |
| Vc                  | ft3/lbmol | 15,9  | 16   | 7,8   |
| Tm                  | F         | 218,3   | 252,3  | 57,2  |
| H                   | Btu/lbmol | -498806   | -496040  | -88516,7  |
| Δ G                 | Btu/lbmol | -297590   | -284159  | -16887,1  |

The property method that is used in this Aspen Plus simulation is the Soave- Redlich-Kwong (SRK) property method. This method uses the Kabadi-Danner mixing rules to account for hydrocarbon and water immiscibility. The NBS steam tables form the basis of this method. The SRK method has been used in recent bio-oil hydrotreating literature [35, 49] and is therefore used in this thesis as well.

<sup>4</sup>The hydrogen that is used is not produced on-site. For modelling purposes it is assumed that the hydrogen is 100% pure.

### 3.4.2. Simulation

An overview of the simulation built in Aspen Plus is shown in Figure 3.5. The simulation uses the results of the linear programming model presented in Tables A.1 and A.2<sup>5</sup>. Below a detailed description of all areas of the chemical process simulation is given.

- **Area 1:** at the beginning of the process, the FPBO is sent to a standard pressure pump. Here, the FPBO is pressurised to a pressure of 200 bar, leading to a temperature increase from 50 to 61 °C. The pressurised stream is then heated up in a heat exchanger to a temperature of 80 °C. Together with the new and recycled hydrogen, the FPBO is fed to the first reactor. In total the stabilisation area consists of four pairs of heat exchangers and reactors. The temperatures of these four reactors are 80, 120, 160 and 200 °C, respectively. An Aspen Plus User2 model is used to represent the stabilisation reactors. A User2 model offers the possibility to modify the yield of the reactor. The principle of this User2 model is the same as a yield reactor (a reactor where the user can define the yield of the input and output components). Yield reactors are often used in biomass conversion simulation in Aspen Plus [48, 54]. The only downside of a yield reactor is that it does not allow yielding pseudo components. As the MTF is based on pseudo components, the yield reactor cannot be used. Contrarily to the yield reactor, the User2 model can yield pseudo components. Each User2 model calculates the required duty per reactor and checks whether the in- and output streams are in balance. After the fourth reactor a mixture of gas, water and bio-oil is sent to the second area. It is important to know that the catalysts does not play a role in the Aspen Plus simulation, but is incorporated later in the economic analysis. The size of the reactors do play a role as this is important for the economic analysis. The size of the first four reactors are 200 and 2000 litres for the demo and commercial plant, respectively. These sizes were predetermined by the engineers of BTG [23].
- **Area 2:** in the second area, the first step is to separate the gas from the water and bio-oil. This gas is sent directly to area three. The water and bio-oil are then depressurised in a valve to approximately 1 bar. This low pressure mixture is then fed to a second separator where the water is evaporated from the mixture. This water contains approximately 5 wt% of carbon and has a mass flow that equals 30% of the FPBO inlet. The bio-oil which is sent to area three, is referred to as SPO.
- **Area 3:** at the inlet of the third area the gas and SPO from area two, together with a MTF recycle stream from area four, are merged together. These three streams are fed again to four pairs of heat exchangers and reactors. The pressure in these reactors is 130 bar and the inlet temperatures are 250, 300, 340 and 340 °C, respectively. A difference between these reactors and the reactors from area one, is that these reactors have a temperature increase between the inlet and the outlet. The increase in temperature is 20 °C, 40 °C, 0 °C and 60 °C in the reactors, respectively. In the heat integration section, the temperature changes in the reactors will be discussed further.
- **Area 4:** the inlet of Area 4 is the outlet stream of the last upgrading reactor. This stream consists of gaseous, aqueous and MTF components. These three groups are separated in a standard separator. The aqueous fraction, which again consists of 5% carbon, is removed and sent together with the waste water from section two, to a heat exchanger and then out of the system. In the heat exchanger some of the heat is recovered as will be discussed in the heat integration section. Another outlet stream from the separator is the MTF, this fraction is sent to area five. The last stream from the separator is the gaseous fraction which is sent to another separator. In this separator the hydrogen will be cleaned from the rest of the gas. The cleaned hydrogen will be recycled and sent to area 1. In this design for each kg FPBO, 1 Nm<sup>3</sup> hydrogen is recycled. Some of the heat of the recycled hydrogen is recovered as the inlet temperature of Area 1 should only be 80 °C. The leftover gas is 90 kg/hr for the demo plant and 1,8 ton/hr for the commercial plant. The leftover gas is sent to a heat exchanger to recover heat and then sent out of the system. The composition of this gas is given in Table 3.3.

<sup>5</sup>This table shows the flows for the demo plant, the flows of the commercial plant are exactly 20 times higher.

- **Area 5:** this is the last area of the design. In this area the main aim is to distillate a light fractions from the MTF with the goal to increase the flashpoint of the marine fraction. From experimental data, it was found that when the lightest 15% (hereafter labeled as light fraction) of the MTF is fractionated, the flashpoint of the heavier 85% (hereafter labeled as marine fraction) is increased above the required 60 °C (safety requirement from the marine fuel standard). The flashpoint of the light fraction is below 10 °C. After distillation 150 kg/hr and 3 tonne/hr of marine fuel is produced for the demo and commercial plant, respectively. Only 25 kg/hr and 500 kg/hr of light fraction is produced by the demo and commercial plant, respectively. Those streams are again sent to a heat exchanger to recover some of the heat before it goes out of the system.

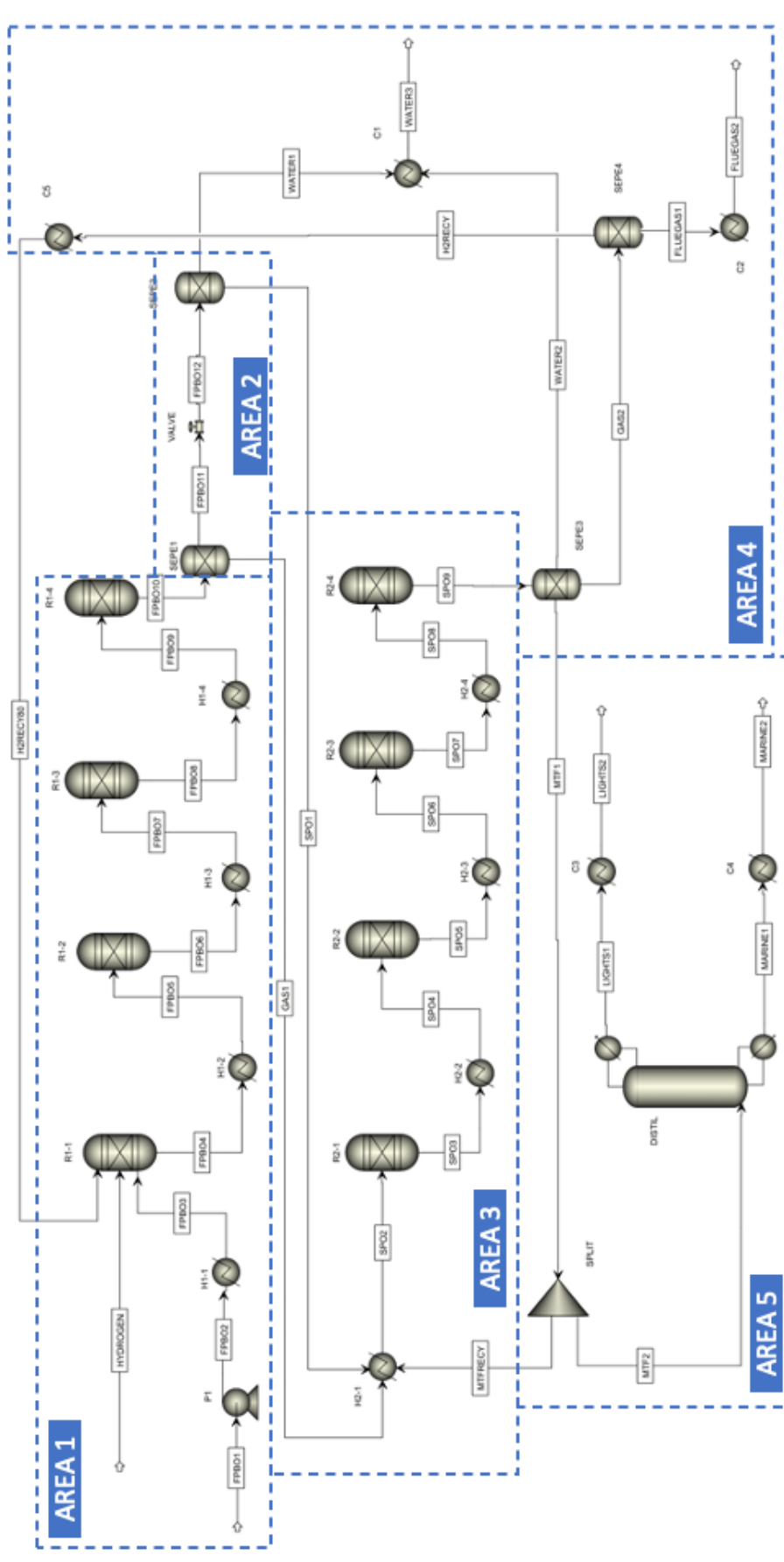


Figure 3.5: Main Aspen Plus Flowsheet with different Areas.

### 3.4.3. Aspen Economic Analyser

The equipment costs are given by the Aspen Economic Analyser based on the chemical process simulation. The size of the reactors had to be manually entered as those were sized by BTG [23]. The used sizes are shown in Table 3.7. In Table 3.8 a detailed cost overview of the equipment of both the demo and commercial plant is given. No other data was taken from the Aspen Economic Analyser. The total TPEC is the input for the SCENT method.

Table 3.7: The sizes for the reactors of the demo and commercial plant.

|          | Unit           | R1 demo | R2 demo | R1 commercial | R2 commercial |
|----------|----------------|---------|---------|---------------|---------------|
| Volume   | m <sup>3</sup> | 0,500   | 0,200   | 8,500         | 2,000         |
| Diameter | m              | 0,371   | 0,503   | 1,294         | 0,799         |
| Height   | m              | 1,853   | 2,515   | 6,468         | 3,993         |

Table 3.8: Equipment costs based on the Aspen Economic Analyser.

| Process unit ID | Type           | Unit | DEMO      | Commercial |
|-----------------|----------------|------|-----------|------------|
| P1              | Pump           | €    | 332.500   | 354.821    |
| H1-1            | Heat exchanger | €    | 3.333     | 10.268     |
| H1-2            | Heat exchanger | €    | 8.839     | 27.232     |
| H1-3            | Heat exchanger | €    | 13.929    | 103.304    |
| H1-4            | Heat exchanger | €    | 10.268    | 48.750     |
| H2-1            | Heat exchanger | €    | 7.500     | 12.679     |
| H2-2            | Heat exchanger | €    | 11.339    | 60.179     |
| C1              | Heat exchanger | €    | 7.679     | 17.321     |
| C2              | Heat exchanger | €    | 8.304     | 16.696     |
| C3              | Heat exchanger | €    | 6.198     | 8.661      |
| C4              | Heat exchanger | €    | 6.964     | 9.732      |
| C5              | Heat exchanger | €    | 9.732     | 23.036     |
| R1-1            | Reactor        | €    | 74.732    | 288.214    |
| R1-2            | Reactor        | €    | 74.554    | 288.214    |
| R1-3            | Reactor        | €    | 74.554    | 288.214    |
| R1-4            | Reactor        | €    | 95.089    | 288.214    |
| R2-1            | Reactor        | €    | 34.732    | 129.554    |
| R2-2            | Reactor        | €    | 34.732    | 132.143    |
| R2-3            | Reactor        | €    | 34.732    | 132.143    |
| R2-4            | Reactor        | €    | 34.732    | 160.089    |
| SEPE1           | Seperator      | €    | 54.286    | 78.661     |
| SEPE2           | Seperator      | €    | 13.661    | 13.661     |
| SEPE3           | Seperator      | €    | 64.464    | 92.143     |
| SEPE4           | Seperator      | €    | 65.179    | 65.179     |
| DISTIL          | Collumn        | €    | 46.875    | 81.786     |
| Total           |                | €    | 1.128.905 | 2.730.893  |

### 3.4.4. Aspen Energy Analyser

The thermodynamic data provide by the Aspen Energy Analyser is shown in Table 3.9. Only the pump (P1) needs electricity while all other unit operators need either heating or cooling. In an optimal scenario, all unit operators are included in the HEN. However for safety reasons, the reactors in this design are not included in the heat integration but cooled by utilities (i.e. cooling water or air). This to avoid accidents in case of failure of other parts of the system. When the reactors are not cooled properly, certain exothermic reactions can result in a so-called runaway causing an explosion eventually.

Table 3.9: Duty per unit operator for the demo and commercial plant.

| Process unit ID | Type           | Inlet temp. [C] | Outlet temp [C] | DEMO duty [kW] | Commercial duty [kW] | Heat integration |
|-----------------|----------------|-----------------|-----------------|----------------|----------------------|------------------|
| P1              | Pump           | 50,0            | 61,2            | 2,5            | 124,6                | No               |
| H1-1            | Heat exchanger | 61,2            | 80,0            | 4,0            | 127,6                | Yes              |
| H1-2            | Heat exchanger | 80,0            | 120,0           | 41,5           | 829,1                | Yes              |
| H1-3            | Heat exchanger | 120,0           | 160,0           | 49,5           | 989,1                | Yes              |
| H1-4            | Heat exchanger | 160,0           | 200,0           | 110,9          | 2217,7               | Yes              |
| H2-1            | Heat exchanger | 99,7            | 250,0           | 63,9           | 1277,1               | Yes              |
| H2-2            | Heat exchanger | 270,0           | 300,0           | 15,7           | 313,1                | Yes              |
| H2-3            | Heat exchanger | 340             | 340             | 0,0            | 0,0                  | No               |
| H2-4            | Heat exchanger | 340             | 340             | 0,0            | 0,0                  | No               |
| C1              | Heat exchanger | 99,7            | 50,0            | -85,7          | -1906,0              | Yes              |
| C2              | Heat exchanger | 400,0           | 50,0            | -19,8          | -421,3               | Yes              |
| C3              | Heat exchanger | 136,9           | 50,0            | -12,3          | -260,7               | Yes              |
| C4              | Heat exchanger | 205,8           | 50,0            | -23,0          | -539,2               | Yes              |
| C5              | Heat exchanger | 400,0           | 80,0            | -53,6          | -1071,1              | Yes              |
| R1-1            | Reactor        | 80,0            | 80,0            | -8,5           | -170,2               | No               |
| R1-2            | Reactor        | 120,0           | 120,0           | -26,2          | -524,6               | No               |
| R1-3            | Reactor        | 160,0           | 160,0           | -81,0          | -1620,9              | No               |
| R1-4            | Reactor        | 200,0           | 200,0           | -46,2          | -923,6               | No               |
| R2-1            | Reactor        | 250,0           | 270,0           | -56,2          | -1124,7              | No               |
| R2-2            | Reactor        | 300,0           | 340,0           | -28,6          | -571,1               | No               |
| R2-3            | Reactor        | 340,0           | 340,0           | -9,1           | -182,2               | No               |
| R2-4            | Reactor        | 340,0           | 400,0           | 12,6           | 251,1                | No               |
| SEPE1           | Seperator      | 200,0           | 177,3           | -27,8          | -556,5               | Yes              |
| SEPE2           | Seperator      | 68,6            | 68,6            | -61,6          | -1231,4              | Yes              |
| SEPE3           | Seperator      | 400,0           | 400,0           | -34,3          | -685,3               | Yes              |
| SEPE4           | Seperator      | 400,0           | 400,0           | -0,9           | -18,0                | Yes              |
| DISTIL          | Collumn        | 145,8           | 138,9           | -33,6          | -671,1               | Yes              |

The duty requirements from all unit operators, except the pump (electricity) and reactors (safety reasons), are used to develop the Composite Curves (CC), Shifted Composite Curves (SCC) and Grand Composite Curves (GCC). The minimum driving temperature ( $\Delta T_{min}$ ) that was used for this analysis was 20 °C, because it is a common used  $\Delta T_{min}$  in bio refining [54]. The plots in Figure 3.6 show the heat integration analysis of both the demo (left) and commercial (right) plant. In the top plots the CC of the hot and cold streams are presented. The hot streams CC are shifted as shown in the middle SCC plots. This is needed to allow heat transfer between the cold and hot streams. In the bottom two plots the GCC are presented. In these plots the pinch point of the HEN is located at 100 °C. From the GCC the minimum energy requirements for the cold and hot utilities of the HEN are determined. Table 3.10 shows the heating and cooling requirements.

Table 3.10: Heating and cooling requirements DEMO and Commercial design

|         | DEMO     |               |            | Commercial |               |            |
|---------|----------|---------------|------------|------------|---------------|------------|
|         | HEN [kW] | Reactors [kW] | Total [kW] | HEN [kW]   | Reactors [kW] | Total [kW] |
| Cooling | 163,7    | 255,9         | 419,6      | 3458,8     | 5117,4        | 8576,2     |
| Heating | 188,7    | 12,6          | 201,2      | 3902,1     | 251,1         | 4153,2     |

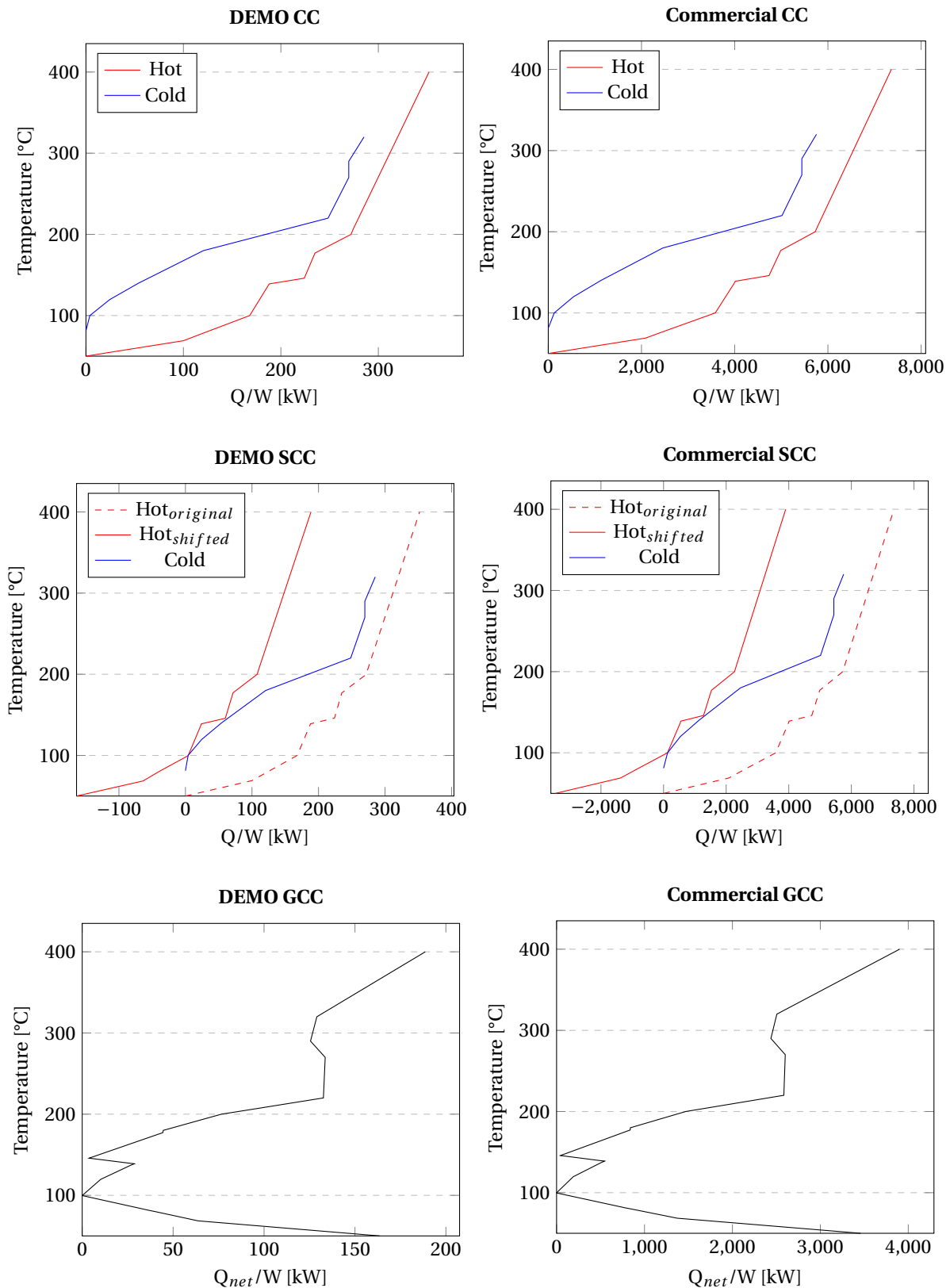


Figure 3.6: Heat integration (composite curve, shifted composite curve, grand composite curve) of the demo (left) and commercial (right) plant.

### 3.5. Cetane number

An estimation of the Cetane number of the marine fraction is calculated using the equation (Equation 2.1) specified in the ISO 4264. The distillation curve of the marine fraction is presented in Figure 3.7. The information from the marine fraction in combination with its density is the input for the calculation (see Table 3.11).

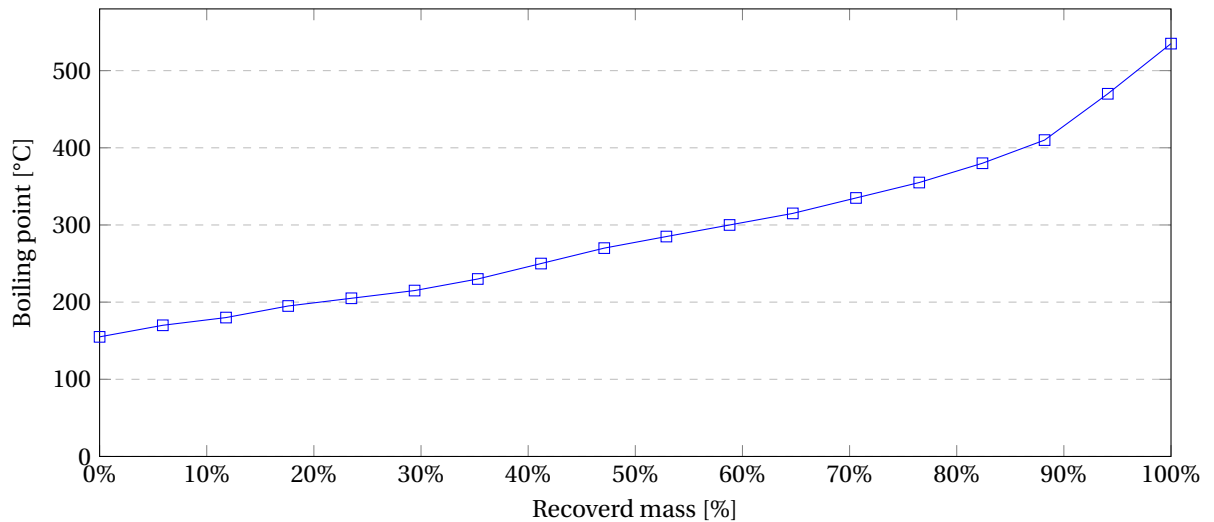


Figure 3.7: The distillation curve of the marine fraction after the distillation of 15% of the lights from the MTF.

Table 3.11: Input values for the ISO 4264 methodology to calculate the Cetane number.

| Parameter | Unit              | Value |
|-----------|-------------------|-------|
| T10       | °C                | 172   |
| T50       | °C                | 273   |
| T90       | °C                | 420   |
| Density   | kg/m <sup>3</sup> | 767,5 |

### 3.6. Standardised Cost Estimation for New Technologies

#### 3.6.1. Equipment Costs

The TPEC costs is presented in Table 3.8. For the demo plant this costs are €1.128.905 and for the commercial plant €2.730.893.

#### 3.6.2. Utility costs

The prices used for the utilities are presented in Table 3.12. To lower the cost for utilities and the carbon footprint, it is chosen to use a share of the output gas fraction for heating. For that reason, no external natural gas is needed for heating.

Table 3.12: Utility prices used for the SCENT calculations.

|                     | Unit             | Value | Source | Comment  |
|---------------------|------------------|-------|--------|--|
| Electricity         | €/kWh            | 0,059 | [58]   | This electricity price is the 2019 average price for the smallest non-household consumers. |
| Cooling Water       | €/m <sup>3</sup> | 0,05  | [31]   |  |
| Wastewater disposal | €/m <sup>3</sup> | 0,72  | [31]   |  |



### 3.6.3. Raw material costs

The raw materials needed for the operation of the plant are FPBO, hydrogen and the catalysts, which are discussed below:

- **Fast Pyrolysis Bio-Oil:** is commercially available, but is still far away from being a commodity. Little is known about the actual price of this product. As mentioned earlier, in Europe there are two commercial pyrolysis plants; Empyro by BTG-BTL in the Netherlands and the plant by Green Fuel Nordic in Finland. The prices of their FPBO were obtained from both parties. According to BTG-BTL the price of one tonne of FPBO ranges around €300 [23]. Green Fuel Nordic gave a production price of €350 per tonne [43]. In this thesis 300 €/tonne is used, additionally a sensitivity analysis is performed on different prices.
- **Hydrogen:** does not exist in a pure form in nature and therefore needs to be produced. Nowadays the most often used method to produce hydrogen is via Steam Methane Reforming (SMR). The methane that is used, can both be from fossil origin as well as renewable (biogas) origin. During the SMR process Carbon Capture and Storage (CCS) can be applied, which reduces the CO<sub>2</sub> emissions. An alternative method to produce hydrogen is via electrolysis. The CO<sub>2</sub> emissions from the grey electricity cannot be captured as this is mostly outside the power of the hydrogen producer. In Table 3.13, the types of hydrogen with their emission factors and prices, based on Dutch electricity and natural gas prices, are presented. SMR-grey is the standard hydrogen that is used in this thesis, however the other types of hydrogen are analysed in the sensitivity analysis.

Table 3.13: Types of hydrogen with Dutch emission factors and costs in 2019 [39].

| Name               | Type of energy used           | Treatment of CO <sub>2</sub>         | Emission Factor<br>[kg CO <sub>2</sub> /kg H <sub>2</sub> ] | Price <sup>a</sup><br>[€/kg H <sub>2</sub> ] |
|--------------------|-------------------------------|--------------------------------------|---|--|
| SMR-grey           | Natural Gas                   | Emitted                              | 9,01  | 2,18   |
| SMR-blue           | Natural Gas                   | CCS (55% capture rate <sup>b</sup> ) | 4,12  | 2,22   |
| SMR-green          | Biogas                        | No net emissions                     | 0,00  | 2,35   |
| Electrolysis-grey  | Electricity (methane turbine) | Emitted <sup>c</sup>                 | 25,00   | 3,50   |
| Electrolysis-green | Renewable electricity         | No emissions                         | 0,00  | 3,65   |

<sup>a</sup> Based on local prices for electricity and natural gas in the Netherlands, see Table 3.12.

<sup>b</sup> Optimal economic CCS value taken from report by Mulder et al. [39]

<sup>c</sup> Based on an emission factor of 189 kg CO<sub>2</sub> per MWh electricity and 0,05 MWh electricity needed per kg H<sub>2</sub> [13, 39].

- **Catalysts:** all information regarding the cost of the catalysts was obtained from BTG and is presented in Table 3.14.

Table 3.14: All assumption related to the cost of the catalysts [23].

| Catalyst      | Unit   | DEMO | Commercial |
|---------------|--------|------|------------|
| <b>Picula</b> |        |      |            |
| Cost          | €/kg   | 100  | 100        |
| Weight        | Tonne  | 1,7  | 33         |
| Lifetime min  | Months | 3    | 12         |
| Lifetime max  | Months | 12   | 24         |
| <b>NiMo</b>   |        |      |            |
| Cost          | €/kg   | 30   | 30         |
| Weight        | Tonne  | 0,7  | 7          |
| Lifetime      | Months | 24   | 24         |

### 3.7. Minimum Fuel Selling Price & lifetime costs

The economic results of the commercial plant will be provided as MFSP. This is relevant as the purpose of this plant is to produce products that are economically viable. In contrast, the purpose the demo plant is not to produce economically viable products, but to prove the technical feasibility of the hydroprocessing design. In reality, it is uncertain whether the technology will work. Therefore, a low capacity and lifetime of the plant was chosen to keep the total investment low, thereby reducing investment risk. Due to this low capacity and lifetime, the costs will be relatively high per output product. However, this is not relevant for the demo plant. It is relevant to know what investment is needed to prove technical feasibility. Therefore, the economic results will be provided as lifetime costs.

The assumptions that are used for the economic calculations are presented in Table 3.15. Chemical plants often show a start-up schedule where the total capital investment and the plant availability scale-up during the first few years. A schedule that is often used for novel technologies is shown in Table 3.16. This schedule is also used to calculate the lifetime costs of the demo plant and the MFSP of the commercial plant.

Table 3.15: Financing and production assumptions.

| Parameter                      | Unit        | Demo          | Commercial    | Source |
|--------------------------------|-------------|---------------|---------------|--------|
| Financing year                 | Year        | 2020          | 2020          | [23]   |
| Equity share of the investment | %           | 20%           | 20%           | [31]   |
| Rate of principal payments     | Years       | 4             | 15            | [31]   |
| Depreciation period            | Years       | 4             | 15            | [31]   |
| Depreciation schedule          |             | Straight line | Straight line | [31]   |
| Interest rate                  | % on debt   | 8%            | 8%            | [31]   |
| Corporate tax rate             | % on profit | 25%           | 25%           | [64]   |
| Discount rate                  | %           | 10%           | 10%           | [31]   |
| Project lifetime               | Years       | 4             | 25            | [23]   |
| Operation hours                | Hr/year     | 6000          | 7500          | [23]   |

Table 3.16: Plant start-up schedule for novel technologies [61].

| Year | TCI schedule                           | Plant availability |
|------|--|--------------------|
| -1   | 30% of fixed capital                   | 0                  |
| 0    | 50% of fixed capital                   | 0                  |
| 1    | 20% of fixed capital + working capital | 30%                |
| 2    |  | 70%                |
| 3    |  | 100%               |

### 3.8. Emission factor analysis

The goal of the emission factor analysis is to provide the average carbon footprint of the end products for the demo and commercial plant. The calculation is based on equation 2.5, but not all parameters from the equation are needed. The report by Spekrijse et al. (2019) has already covered the emissions from extraction and cultivation of raw material, from carbon stock changes caused by land-use change and from savings from soil carbon accumulation via improved agricultural management within the emission factor of the FPBO. As the end products are biofuels, the emissions from the combustion of the fuels may be counted as zero [16]. Also, no carbon capture options are considered. When removing these parameters from the equation, the following equation remains.

$$e = e_{rm} + e_p + e_{td} \quad (3.1)$$

Where:

- $e$  = the emission factor of the fuel
- $e_{rm}$  = the emission factor from the raw materials
- $e_p$  = the emission factor from processing
- $e_{td}$  = the emission factor from transport and distribution

The demo and commercial plants will be located in the Port of Rotterdam. The main reasons for this is that the Port of Rotterdam is located near the developers (BTG), is a major harbour (end users) and offers the possibility to use hydrogen from the grid. The demo and the commercial plants will obtain their FPBO from different suppliers. For the demo the FPBO is supplied by the Empyro pyrolysis plant in Hengelo, the Netherlands. The supply of the commercial plant will come from Scandinavia (Helsinki, Finland <sup>6</sup>). As the feedstock is supplied from other locations, the emissions of the transport of the feedstock differ between both cases.

As a base, the feedstock that is used for both plants is FPBO made from waste sawdust. With the increasing biomass demand it could be that waste sawdust will not be available in the future. Therefore, also other types of wood need to be considered for the production of the FPBO. Chips from top and branch wood from European forest and landscape could be an option. This feedstock has an emission factor of 4,56 gram CO<sub>2</sub> per MJ of wood [32]. With a pyrolysis efficiency of 85% and an energy content of 20 GJ/tonne. The emission factor of the FPBO increases from 376 gram CO<sub>2</sub> to approximately 107 kg CO<sub>2</sub> per tonne of FPBO [23]. Both the emission factors of fuel produced from sawdust FPBO as well as top and branch wood FPBO will be investigated.

The emission factors that are used for the average emission factor calculation of the final products are presented in Table 3.17. Also the emission factor from fossil Marine Gas Oil (MGO) is provided.

Table 3.17: The emission factors of emission-related activities.

| Parameter                                    | Unit                                      | Value          | Source |
|--|---|----------------|--------|
| Fast Pyrolysis Bio-Oil (saw dust)            | kg CO <sub>2</sub> eq / tonne             | 0,376          | [57]   |
| Fast Pyrolysis Bio-Oil (top and branch wood) | kg CO <sub>2</sub> eq / tonne             | 107            | [32]   |
| Hydrogen                                     | kg CO <sub>2</sub> / kg of H <sub>2</sub> | See Table 3.13 | [39]   |
| Green electricity                            | kg CO <sub>2</sub> / kWh                  | 0,0            | [13]   |
| Transportation road                          | kg CO <sub>2</sub> / tonne km             | 0,110          | [13]   |
| Transportation rail                          | kg CO <sub>2</sub> / tonne km             | 0,018          | [13]   |
| Transportation sea                           | kg CO <sub>2</sub> / tonne km             | 0,021          | [13]   |
| MGO  | kg CO <sub>2</sub> / GJ                   | 76,3           | [28]   |

<sup>6</sup>This location was chosen to calculate the transport distance. In the future, possibly the FPBO will be supplied from another location in Scandinavia, but this is not yet known.



# 4

## Results

The results section is based on the three useful output fractions (gas, light and marine) from the hydroprocessing design (Figure 4.1). From the total input weight approximately 17% ends up as gas, 5% as light and 29% as marine fuel. On energy level, this distribution is slightly different. From the total input energy, approximately 27% ends up in gas, 10% in light and 53% in marine fuel. The main product is the marine fraction as it is the largest in mass as well as in energy output. In the first part of the results section, the technical aspects of all streams are discussed. In the second part, the results of the SCENT and MFSP analysis are presented. The results of the economics are based on an energy allocation method<sup>1</sup>. This method was chosen because the end use and therefore the economic value of the gas and light fractions is unknown. In the third part the average emission factor of the output products is presented.

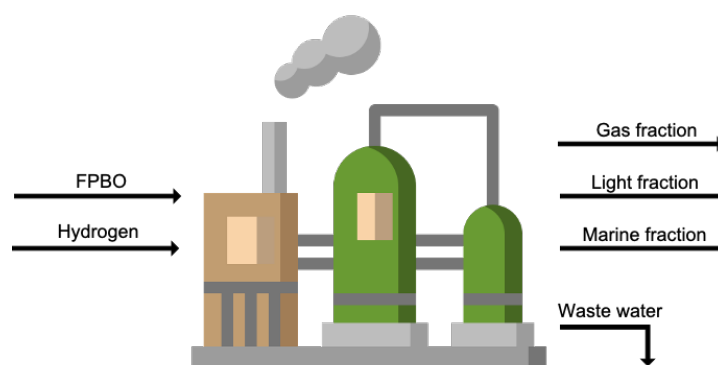


Figure 4.1: Simplified overview of input and output products of the FPBO hydroprocessing design.

### 4.1. Technical results output products

In Table 4.1, the characteristics of the three output streams are shown. The data from the output streams are obtained from the Aspen Plus simulation. Unfortunately, only the fuel characteristics viscosity, density, flash point and lower heating value can be calculated by Aspen Plus<sup>2</sup>. The current simulation is unable to calculate the TAN and Cetane number. However, a TAN of the MTF is approximately 0,01 mg KOH/g, as provided by BTG. This means that the TAN of the light and marine fraction is also around this number, as these fractions are produced from the MTF. The Cetane number can be estimated using the calculation method of the ISO 4264. However, actual combustion tests need to be done to confirm the number from these calculations.

<sup>1</sup>The costs are divided over the streams based on the energy content of the stream. The higher the energy content of the stream, the higher the costs of the stream.

<sup>2</sup>For the gas phase flash point cannot be calculated and the viscosity is irrelevant.

Table 4.1: Characterization of the three output products obtained from Aspen Plus.

| Characteristics     | Unit              | Marine | Light | Gas  |
|---------------------|-------------------|--------|-------|------|
| Density @ 15°C      | Kg/m <sup>3</sup> | 767,5  | 570,9 | 12,3 |
| Viscosity @ 40 °C   | cSt               | 3,1    | 1,1   |      |
| Flash point         | °C                | 66,6   | 9,7   |      |
| Lower Heating Value | MJ/kg             | 45,7   | 50,0  | 38,5 |

#### 4.1.1. Marine fraction

Table 4.2 shows the characteristics of the marine fraction compared to the ISO 8217 DMA marine fuel standard. Based on the characteristics, the marine fraction complies with the standard. The results are evaluated per characteristic, some things should be highlighted. The MTF, from which the light and marine fractions are produced, has a flash point of 43,1 °C according to the Aspen Plus Simulation. By fractionating the MTF into a light (15%) and a marine (85%) fraction, the flashpoint of the marine fraction becomes 66,6 °C. Since the ISO 8217 fuel standard demands the flashpoint to be at least 60 °C (for safety reasons), it would even be possible to fractionate less than 15% and still meet the ISO 8217 requirement. However, because of the consequential density decrease, this is not recommended. Although there is no minimum density specified in the ISO 8217, some engine manufacturers, such as MAN four-stroke, do not allow fuels in their engines with a low density (the limit is typically 820 kg/m<sup>3</sup>) [56]. This limit is not met using the current fractionation ratio, possibly leading to undersupply of energy to the engine. Nevertheless, the density requirements of the synthetic diesels standard, the EN 15940, are met as shown in Table 4.2. Synthetic diesels are used in the shipping sector on a daily basis<sup>3</sup>. In practice, it appears that a low density does not lead to problems as long as the energy content per volume of fuel is high enough (> 35 MJ/kg) [19]. It is recommended to not go lower than 765 kg/m<sup>3</sup>, as the fuel then falls outside the synthetic diesel density range. The EN 15940 requires a Cetane number of 70, while the ISO 8217 DMA only requires 40. The Cetane number of the marine fraction is 75 when using the ISO 4264 method.

Table 4.2: The characteristics of the Marine fraction obtained from Aspen Plus compared to ISO 8217 DMA and EN 15940 Class A.

| Characteristics     | Unit              | limit   | ISO 8217 DMA | EN 15940 Class A | Marine fraction |
|---------------------|-------------------|---------|--------------|------------------|-----------------|
| Density @ 15 °C     | kg/m <sup>3</sup> | Min     | -            | 765,0            | 767,5           |
|                     |                   | Max     | 890,0        | 800              |                 |
| Viscosity @ 40 °C   | cSt               | Min     | 2,0          | 2,0              | 3,1             |
|                     |                   | Max     | 6,0          | 4,5              |                 |
| Flash point         | °C                | Min     | 60,0         | 55,0             | 66,6            |
| Lower Heating Value | MJ/kg             | Typical | 42,0         | 45,0             | 45,7            |
| Cetane number       |                   | Min     | 40           | 70               | 75 <sup>a</sup> |
| TAN                 | mg KOH/g          | 0,5     |              | ≈ 0,01           |                 |

<sup>a</sup> Not obtained from Aspen Plus but calculated using the ISO 4264 method

#### 4.1.2. Light fraction

The end use application of the light fraction is not determined yet. From experimental research it was found that the main components in this fraction are benzene, octane, methyl-cyclohexane, ethyl-cyclohexane and propyl-cyclohexane. The weight shares of these components are unknown. As shown in Table 4.1 the light fraction has a very low density. As a consequence, the light fraction does not meet the EN 228 (gasoline standard), as the minimum density is specified as 720 kg/m<sup>3</sup> [40]. What the future application of this fraction will be is uncertain.

<sup>3</sup>GoodFuels delivers HVO, which is a synthetic diesel, to their shipping customers (mostly to inland and near-shore vessels) [19].

### 4.1.3. Gas fraction

The components of the gas fraction are presented in Table 4.3 and were obtained from experimental research from BTG. The gas fraction has the characteristics of a mixture of biogas and bio-Liquefied Petroleum Gas (LPG). In total, the gas fraction consists of  $\approx 71$  wt% biogas and  $\approx 29$  wt% bio-LPG. Below, some background and potential application of biogas and bio-LPG are provided. Whether it is economically viable to separate this gas fraction into biogas and bio-LPG is not included in this thesis. When the gas fraction is not separated, it may be used for the production of hydrogen.

Biogas mainly contains  $CO_2$  and  $CH_4$  in various ratios, but often also has a fraction of  $C_2H_6$  and  $CO$ . The higher the fraction of  $CO$  and  $CO_2$ , the lower the energy content of the biogas. The biogas produced in this thesis contains 28 % carbon oxides ( $CO$  and  $CO_2$ ) and 72 % hydrocarbons ( $CH_4$  and  $C_2H_6$ ). Biogas typically contains 30-45% of carbon oxides. Therefore the biogas produced in this thesis has a relatively high quality [6]. In the transport sector, fossil gas is mainly used in a compressed or liquefied form, which increases the energy density. Just like fossil gas, biogas can be compressed and liquefied. Biogas can be used as replacement of natural gas, and as transportation fuel in a compressed/liquefied form.

The other component of the gas fraction is the bio-LPG. This bio-LPG has exactly the same composition as fossil derived LPG and consists of  $C_3H_8$  and  $C_4H_{10}$ . In general the ratio between those two components is 40%  $C_3H_8$  and 60%  $C_4H_{10}$ . However, this number may vary. The ratio of the bio-LPG produced in this thesis is 66%  $C_3H_8$  and 34%  $C_4H_{10}$ , meaning it relatively contains more light components. Bio-LPG can be used in transport in modified LPG vehicles. It is also used as a natural gas replacement, in places that have no direct access to a natural gas grid. Contrary to natural gas, which is stored at high pressure ( $\approx 75$  bar), LPG can be stored at low pressure ( $\approx 5$  bar). This is financially beneficial since low pressure storage and transport is less expensive.

Table 4.3: The gas fraction components, weight shares and potential end use.

| Potential end use | Component   | Fraction |
|-------------------|-------------|----------|
| Biogas            | $CO$        | 0.5 wt%  |
|                   | $CO_2$      | 19 wt%   |
|                   | $CH_4$      | 27 wt%   |
|                   | $C_2H_6$    | 24 wt%   |
| Bio-LPG           | $C_3H_8$    | 19 wt%   |
|                   | $C_4H_{10}$ | 10 wt%   |

## 4.2. Economic results

The economic results are obtained from the SCENT and MFSP calculations. The financing and production assumptions vary between the demo and commercial plant, therefore, the economic results cannot be compared. In this thesis, the financing assumptions (Table 3.15) are based on the situation in the Netherlands as this is the geographic location of the plants.

The economic results of the demo and commercial plant are presented as total costs per lifetime and MFSP, respectively. The MFSP presented in €/GJ shows the average MFSP of the plant. The MFSP presented in €/tonne shows the MFSP of each output product separately (marine = 45,7 GJ/tonne, light = 50,0 GJ/tonne, gas = 38,5 GJ/tonne). In Appendix A.4 further details of the calculation are presented.

A sensitivity analysis is performed to test the influence of the input parameters on the economic results of the demo and commercial plant. Also, a sensitivity analysis on the value of the marine fraction compared to the gas and light fraction of the commercial plant is performed.

### 4.2.1. Lifetime costs demo plant

It was found that the total lifetime cost of the demo plant is slightly higher than 22 M€. The main reason for this high price is the short lifetime (4 years) and lower capacity factor of the demo plant. Figure 4.2 illustrates the breakdown of the costs. The costs (including capital recovery-annualised percentage of total capital investment and other fixed cost) are divided in CAPEX, raw materials (FPBO and hydrogen), catalysts (PICULA and NiMo), semi-variable costs (e.g. labour and maintenance, excluding raw materials and catalysts) and interest and taxes (interest on debts and corporate taxes on profit). Most of the costs come from the CAPEX, which is logical as the plant only operates for four years. During these four years, the plant does not run on 100% load (max 6000 hours for demo plant). Due to the start-up schedule shown in Table 3.16, the load in year one is only 1800 hours, year two is 4200 and year three and four is 6000 hours.

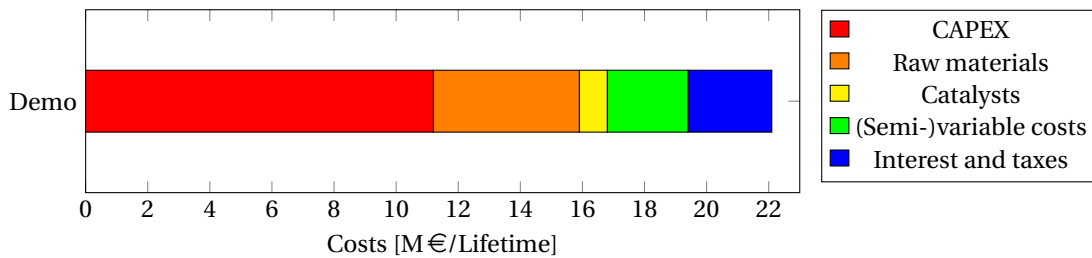


Figure 4.2: Total lifetime cost breakdown of the demo plant (FPBO input = 0.5 tonne/hr input, max load = 6000 hours).

### 4.2.2. MFSP commercial plant

The MFSP results of the commercial plant are presented in Table 4.4. This table shows a plant average MFSP of 29,50 €/GJ, and prices (based on energy allocation) for the three output products ranging from 1.135 to 1.475 €/tonne.

Table 4.4: The MFSP for the three fractions and also the plant average MFSP. The MFSP of the three fractions is based on energy allocation (Marine = 45,7 GJ/tonne, Lights = 50,0 GJ/tonne, Gas = 38,5 GJ/tonne).

| Parameter            | Unit    | Commercial |
|----------------------|---------|------------|
| Marine fraction MFSP | €/tonne | € 1.345    |
| Lights fraction MFSP | €/tonne | € 1.475    |
| Gas fraction MFSP    | €/tonne | € 1.135    |
| Plant average MFSP   | €/GJ    | € 29,50    |

Figure 4.3 illustrates the breakdown of the costs. The raw materials cover most of the cost. The maximum load of this plant is expected to be 7500 hours per year. Just like the demo plant, this plant has a start-up schedule which leads to a load in year one of 2250 hours, in year two of 5250 hours and from year three onward 7500 hours. The assumption was made that the rate of principle payments only takes 15 years while the plant has a lifetime of 25 years. After these 15 years the commercial plant produces 10 more years without paying interest. Jong et al. (2015), also assumed another 10 years of production after the last principle payment.

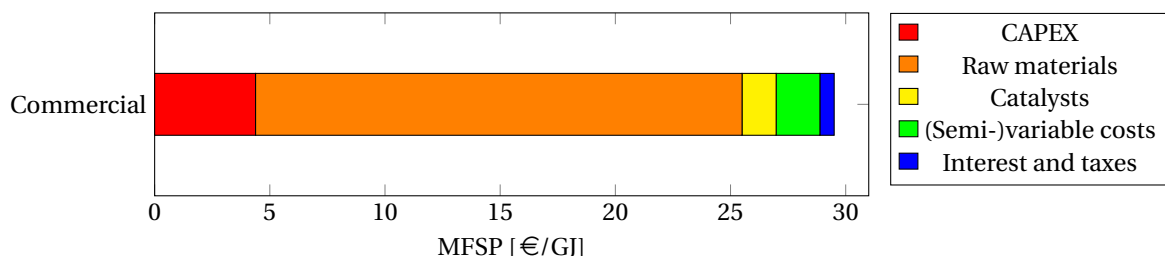


Figure 4.3: Plant average MFSP (based on energy allocation) breakdown of the commercial plant (FPBO input = 10 tonne/hr input, max load = 7500 hours).



### 4.2.3. Sensitivity analysis on the input factors

A sensitivity analysis was performed to examine the impact of the input parameters on the economic results. The sensitivity analysis includes the input parameters FPBO price, hydrogen price, PICULA catalyst lifetime and the equipment costs. The yield of the plant is not taken as an input parameter as the current design has an energy yield of 89%, which is already high. An increase in energy yield is therefore unlikely. The ranges of the input values, used for the sensitivity analysis, are presented in Table 4.5. The lifetime of the PICULA catalyst of the demo plant ranges from 3 to 12 months (base value 7,5 months), while its lifetime for the commercial plant is expected to be between 12 and 24 months (base value 18 months) [23]. However, the lifetime could still be only 3 months, as a longer lifetime has never been demonstrated. For this reason it was investigated what happens with the MFSP of the commercial plant when the PICULA catalyst has a lifetime of only 3 months. As the base values of the demo and commercial plant differ, the sensitivity range of the PICULA catalyst also differ (-60% for the demo and -83% for the commercial). The sensitivity of other input factors like discount rate, labour costs and disposal costs were also tested, but their influence was too small to mention here.

Table 4.5: Ranges used for the sensitivity analysis in Figures 4.4 and 4.5.

| Parameter                    | Unit    | Minimum   | Base      | Maximum   | Reference |
|------------------------------|---------|-----------|-----------|-----------|-----------|
| FPBO price                   | €/tonne | 250       | 300       | 400       | [23, 43]  |
| Hydrogen price               | €/kg    | 1,50      | 2,18      | 3,65      | [26]      |
| PICULA lifetime <sup>a</sup> | Months  | 3/3       | 7,5/18    | 12/24     | [23]      |
| Equipment costs <sup>a</sup> | M€      | 0,79/1,91 | 1,13/2,73 | 1,47/3,55 | [51]      |

<sup>a</sup> Left value = demo plant, and right value = commercial plant

Figure 4.4 illustrates the lifetime costs of the demo plant. The black dotted line represents the accuracy of the SCENT method. Typically such lines are not included in a spider sensitivity plot, as only input factors are analysed. However, it is added here since it provides a good overview of the potential error of the methodology. In the demo, the potential error of all input parameters (assuming only one input parameter changes at the same time) fall within this 30% error of the SCENT methodology. The slope of the line, related to the horizontal line, represents the sensitivity of an input parameter. The figure shows that the lifetime costs of the demo plant are mostly influenced by the equipment costs. This is logical since the CAPEX forms the largest share of the lifetime costs of the demo. The FPBO and hydrogen costs do not play a large role.

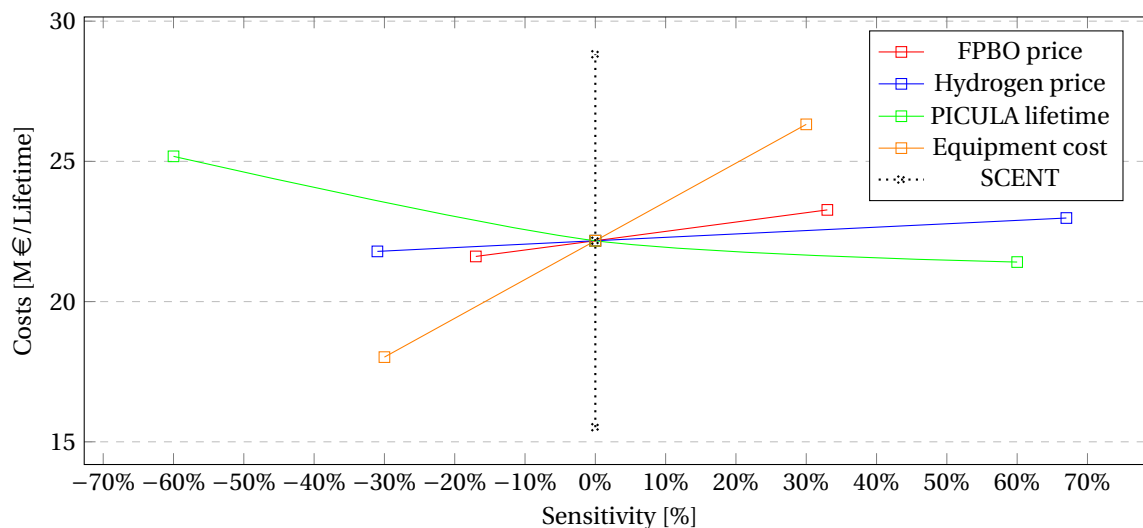


Figure 4.4: The sensitivity analysis of the lifetime cost when the gas, light and marine fractions are weighted equal in price for the **demo** plant.

The sensitivity of the commercial plant, which is presented in Figure 4.5, differs from the sensitivity of the demo plant. Here, the lifetime of the PICULA catalyst plays the largest role. If the lifetime of the catalyst is only 3 months, the MFSP can increase with more than 50%. The second input factor that plays a large role on the MFSP, is the price of FPBO. When the price of FPBO increases to 400 €/tonne, the MFSP increases to 35 €/GJ.

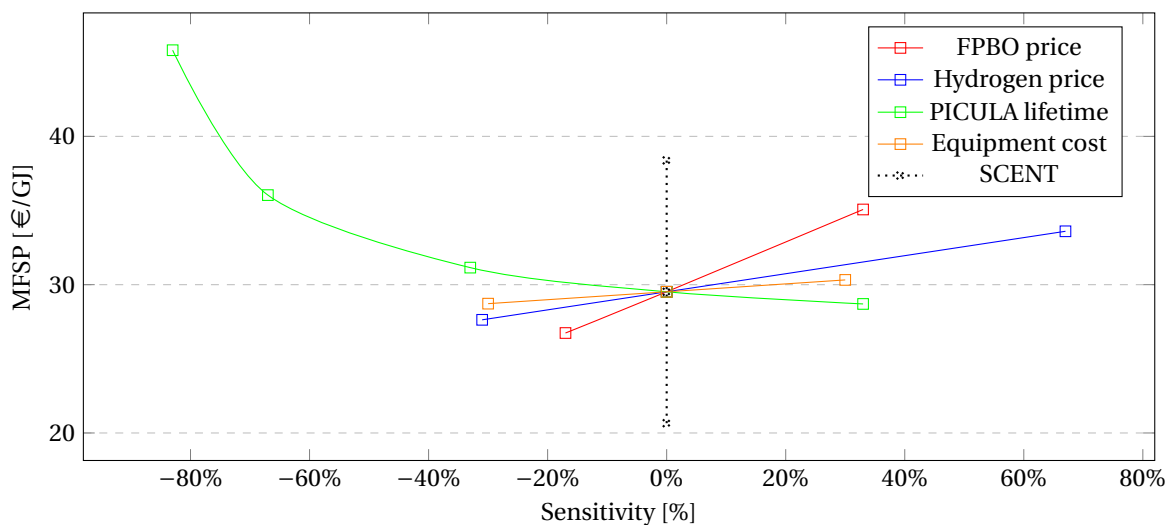


Figure 4.5: The sensitivity analysis of the MFSP when the gas, light and marine fractions are weighted equal in price for the **commercial** plant.

#### 4.2.4. Sensitivity analysis on the value of the output products

The calculation for the MFSP of the commercial plant is based on energy allocation. In reality, there might be price differences between different output products. The actual price of the output is depended on its application. For that reason, it could be be that, despite the higher energy contents of the light fraction compared to the marine fraction, the light fraction is less valuable as a product. Figure 4.6 illustrates the sensitivity of the MFSP of the marine fraction for the commercial plant. The point in the middle of the plot represents the situation where the price per GJ of product is the same for all products. The lines shows the effect on the MFSP of the marine fraction when the MFSP of the other fractions decreases or increases with a value of 25% relative to the marine fraction. For example, when the price of the gas fraction decreases with 25%, it means that 1 GJ of gas fraction would have the same value as 0,75 GJ of marine fraction. The range of 25% was chosen because this is the current price spread between a very high quality (Jet Fuel A-1) and a very low quality (IFO 380, heaviest fuel oil) fossil refinery product [25, 55]. In the plot, the red line represents the change in the value of the gas fraction, the blue line in the light fraction and the green line in the gas and light fractions together. The upper and lower limits of the plot show a minimum value of the marine fraction of 1250 €/tonne and a maximum value of 1520 €/tonne<sup>4</sup>.

<sup>4</sup>When the base input parameters are used for the SCENT and MFSP calculations.

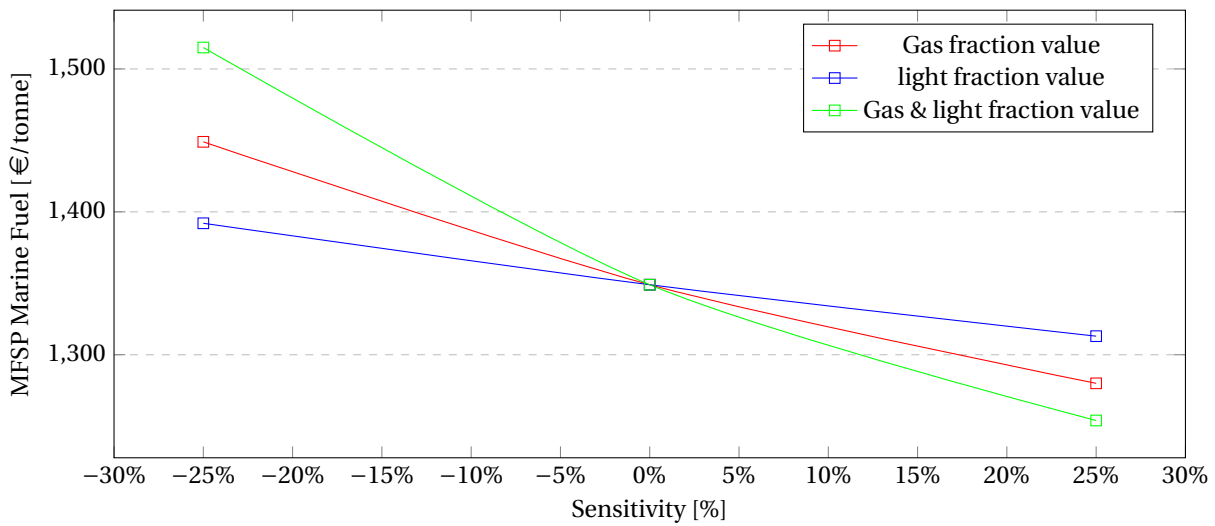


Figure 4.6: The sensitivity analysis of the marine MFSP with respect to variations in the value of the gas and light fraction for the commercial plant.

### 4.3. Emission factor

The average emission factor of both plants is based on the emissions of the FPBO, hydrogen and the transport of the FPBO to the hydroprocessing plant. The plants have no emissions from the utilities as they use green electricity and also use a share of the output gas fraction to produce heat for their heat demand. The average carbon footprints of the demo and commercial plants are presented in Figure 4.7. This figure shows that the emissions of the hydrogen cause the largest share of the average carbon footprint. The emissions from the FPBO made from waste sawdust is only 0,02 kg CO<sub>2</sub>/GJ, while the emissions of FPBO made from top and branch wood is 5,0 kg CO<sub>2</sub>/GJ. The emissions of transport are higher for the commercial plant than the demo plant as the transport distances are much longer. The emission factor of fossil MGO is also presented in Figure 4.7. Biofuel produced from sawdust FPBO has a reduction of 71,2% for the demo and 69,5% for the commercial plant compared to fossil MGO. However, for biofuels produced from top and branch wood FPBO, the reduction is only 64,6% for the demo and 62,9% for the commercial plant.

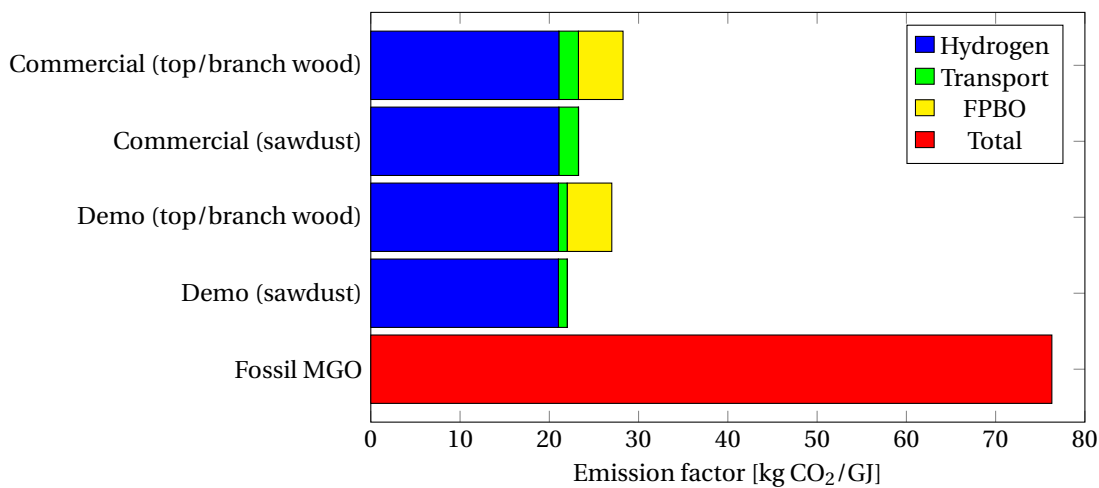


Figure 4.7: The average emission factors of the output products of the demo and commercial plants.

The RED-II has a GHG savings threshold for biofuels produced in plants that start operating from 2021 on-wards. The threshold requires a biofuels to have an GHG emission reduction of at least 65% compared to their fossil fuel comparator [16]. As the fossil fuel comparator of the gas and light fractions is uncertain, only the RED-II threshold of the marine fraction has been taken into account. Considering the emission factor of 76,3 kg CO<sub>2</sub> per GJ fossil MGO, the maximum emission factor of the marine fraction may only be 26.7 kg CO<sub>2</sub> per GJ. The commercial and demo plant which use sawdust FPBO meet the reduction threshold. However, the plants that use top and branch wood FPBO do not meet this threshold. So, the emission factor of the plants that use top and branch wood FPBO needs to be reduced. To achieve this, a different type of hydrogen could be used instead of the grey SMR hydrogen used in the base case.

### 4.3.1. Sensitivity on type of hydrogen

In the base case hydrogen from grey SMR is used as this is the cheapest and most commercially used form of hydrogen. However, it is interesting to investigate how the use of other types of hydrogen will affect the average MFSP and average emission factor of the commercial plant (Figure 4.8). As stated earlier, a plant that uses grey SMR as well as top and branch wood FPBO, does not meet the RED-II threshold. When grey electrolysis hydrogen is used, non of the two types of FPBO meet the threshold. The threshold is met, using the other three types of hydrogen. The figure also shows that the MFSP the prices of blue SMR and green SMR do not increase much compared to grey SMR, while large emission reduction can be achieved. When using hydrogen produced via electrolysis, the MFSP increases a lot.

When switching from grey SMR to blue SMR, the MFSP increases with just 0,11 €/GJ and the emission factor decreases with 11,44 kg CO<sub>2</sub>/GJ. This means that, by switching from grey to blue SMR, the cost for the reduced CO<sub>2</sub> is 0,0096 €/kg. Currently, it is discussed whether the shipping sectors should be included in the European Emission Trading System (ETS). At this moment (July 2020), the value of one tonne of CO<sub>2</sub> emission in the ETS is €23,20. This means that 1 kg CO<sub>2</sub> emission will cost 0,023 €. This is more than the cost per kg CO<sub>2</sub> reduction by switching from grey to blue SMR. Therefore, if the shipping sector would be included in the ETS, it would be financially favorable to pay for the more expensive blue SMR (to reduce CO<sub>2</sub>) instead of paying the ETS costs when using grey SMR. When switching from blue SMR to green SMR, the emission price is 0,0374 €/kg CO<sub>2</sub> and therefore not economically favourable anymore. Blue SMR is with the current carbon price and when the shipping sector is included in the ETS the best economic option. When the sector is not included in the ETS, grey SMR is the best economic option.

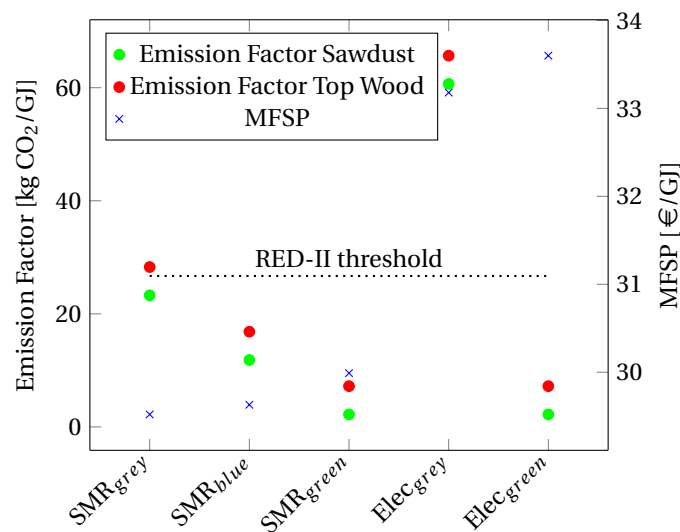


Figure 4.8: The dependency of the emission Factor and MFSP on different type of hydrogen for the Commercial design.

# 5

## Discussion

This thesis analysed the techno-economic potential and carbon footprint of a multi-stage hydroprocessing design which converts FPBO into marine fuel. From a technical point of view, the marine fraction shows high potential as it meets the most important ISO 8217 DMA characteristics. The most uncertain characteristic of the marine fraction is the Cetane number. It is criticised in literature to use the ISO 4264 method for the calculation of the Cetane number of biodiesel (FAME) [21, 34, 62, 69]. The reason for the criticism is the difference in chemical structure between fossil fuels and biodiesel. However, biodiesel is not the same as hydroprocessed FPBO. Biodiesel contains slightly more than 10% oxygen, while hydroprocessed FPBO contains almost no oxygen (just like fossil fuel). Whether the method can be used for hydroprocessed FPBO is unknown. Further research on Cetane number in the form of combustion tests should be done. If the Cetane number turns out to be lower than the required 40, the marine fuel can only be delivered to the market in blends with fuels that have a high Cetane number (such as HVO which typically has a Cetane number of 88).

It is expected that the total lifetime costs of the demo are approximately 22 M€. This is in line with the calculations made by BTG [23]. The commercial plant has a MFSP of around 29,50 €/GJ. This price is almost three times higher compared to MGO as the average price of MGO in 2019 was around 10 €/GJ. However, compared to currently available biofuels (FAME and HVO), the marine fraction MFSP actually falls within the price range. In 2019, the average price of FAME was around 27 €/GJ and the price of HVO was even above 50 €/GJ [19]. The higher price of the biofuels means that they cannot compete with fossil fuel. However, more and more incentive systems are put in place to stimulate the production and consumption of sustainable fuels. For example in the Netherlands, there is an incentive system where biotickets can be made when biofuels are delivered to the shipping sector. The value of a ticket for an advanced fuel like the marine fuel developed in this thesis, has varied during the last few years between 10-25 €/GJ. This means that when the income from the bioticket is subtracted from the MFSP, the marine fraction could be sold for a price between 4,50 - 19,50 €/GJ. In conclusion, because of this incentive, it is possible to compete with fossil marine fuel prices.

The average emission factor of the demo and commercial plant shows that the CO<sub>2</sub> emission can be reduced by 70% when waste sawdust FPBO is used, compared to fossil MGO. When a feedstock like top and branch wood is used the reduction is only 63-65%. The amount of reduction is not only dependent on the emission factor of the produced biofuel but also on the fossil comparator. In the results section the emission factor of 76,3 kg CO<sub>2</sub> per GJ MGO is used as a fossil comparator for the marine fraction [28]. However, in other literature, it is described that the emission factor of MGO could be much higher. A recent study by El-Houjeiri et al. (2019), estimated an emission factor of 222 kg CO<sub>2</sub> per GJ MGO. When such a high emission factor of the fossil comparator is used, the RED-II threshold is met more easily.

## 5.1. Comparison with existing literature

The results of this thesis are compared with existing literature that also converts pyrolysis oil into transportation fuels. There are some differences with the existing literature and this thesis. In most literature, the pyrolysis process is included in the analysis. This means that their input was biomass feedstock (e.g. wood) instead of FPBO. For the economic analysis, this means that the investment costs are higher but the raw material costs are lower. Another difference is that multiple types of feedstock that were used such as red maple, loblolly pine, switchgrass and acacia bark. The feedstock used for the production of FPBO in this thesis was waste sawdust, no specific wood type was specified. The last big difference is the type of fuel produced. In literature, the main focus was on the production of road and aviation fuels, while this thesis focused on the production of marine fuel. An important note to make is that most literature does not focus on the output characteristics, the economics and emission factor of the output products at the same time. Therefore, it is not possible to compare all four research questions with the same literature. Despite all the differences, the previous literature is still relevant for comparison.

### 5.1.1. Output products comparison

When looking at previous literature it is remarkable that the focus of these studies laid on the production of fuels like gasoline, diesel or jet fuel and not on marine fuel. This could be linked to the density of fuel. In Table 5.1, the density of different fuel types and their applications are presented. In general, only fuels with a density higher than  $845 \text{ kg/m}^3$  are used in shipping. According to Elliott et al. (2012), the density of hydroprocessed pyrolysis oil ranges between  $760 - 920 \text{ kg/m}^3$ , based on eleven different FPBO hydroprocessing routes. Six of the eleven routes found a density that exceeds the maximum density ( $845 \text{ kg/m}^3$ ) of non-marine applications. Therefore, it not logical that marine fuel was not investigated in these studies. When comparing the density of the marine fraction from this thesis ( $767,5 \text{ kg/m}^3$ ) to the density range of  $760 - 920 \text{ kg/m}^3$  described by Elliott et al. (2012), it is on the low side of the spectrum. An explanation for this low density could be the extensive hydroprocessing of FPBO executed in this thesis. According to BTG this extensive hydroprocessing was essential to make the marine fraction miscible with existing petroleum derived fuels. It is unclear, whether the aforementioned studies hydroprocessed the FPBO as much as the technology used in this thesis.

Table 5.1: Comparison of the density (@  $15^\circ\text{C}$ ) for different types of fuels.

| Fuel type              | Unit            | Min | Max  | Fuel standard        | Source |
|------------------------|-----------------|-----|------|----------------------|--------|
| Gasoline               | $\text{kg/m}^3$ | 720 | 775  | EN 228               | [40]   |
| Synthetic diesel       | $\text{kg/m}^3$ | 765 | 800  | EN 15940 (Class A)   | [42]   |
| Jet Fuel               | $\text{kg/m}^3$ | 775 | 840  | ASTM D1655 (Jet A-1) | [36]   |
| Road diesel            | $\text{kg/m}^3$ | 820 | 845  | EN 590               | [41]   |
| Distillate marine fuel | $\text{kg/m}^3$ | -   | 900  | ISO 8217 (DMB)       | [46]   |
| Residual marine fuel   | $\text{kg/m}^3$ | -   | 1010 | ISO 8217 (RMK)       | [46]   |

### 5.1.2. MFSP comparison

In Figure 5.1 the MFSP of the commercial plant is compared with prices found in literature. The prices shown in the figure range from  $13,82$  to  $37,05 \text{ €/GJ}$ . The MFSP of  $29,50 \text{ €/GJ}$  falls within this range. Jones et al. (2013) and Brown et al. (2014) found prices below  $20 \text{ €/GJ}$ . In this thesis, where FPBO is used as input, the MFSP of the FPBO costs already  $14,92 \text{ €/GJ}$ <sup>1</sup>. As a consequence, it is almost impossible to achieve a MFSP lower than  $20 \text{ €/GJ}$ . The two studies describing the prices below  $20 \text{ €/GJ}$ , used very cheap feedstocks, which explains the low price.

<sup>1</sup>The energy content of FPBO used in this thesis is  $20,1 \text{ GJ/tonne}$  and has a purchasing price of  $300 \text{ €/tonne}$ . From this the price of  $15 \text{ €/GJ}$  is calculated

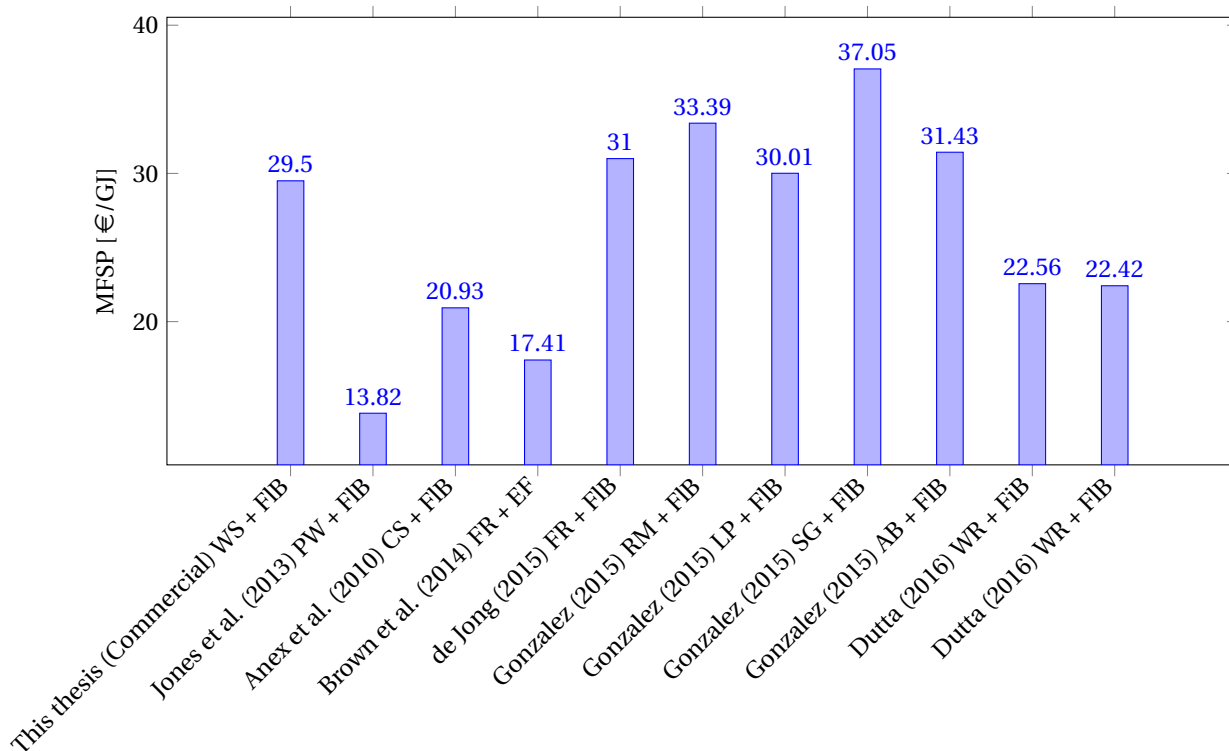


Figure 5.1: A comparison of the MFSP to prices from literature. Most values were presented in \$/gal, this is converted to €/GJ using: density = 0,78 tonne/m<sup>3</sup>, LHV = 45 GJ/tonne and exchange rate 0,9 €/€ [2, 5, 8, 18, 29, 31, 71].

Table 5.2: The types of feedstocks and pyrolysis technologies used in the literature used for the MFSP comparison.

| Author       | Year | Feedstock           | Technology          | Source |
|--------------|------|---------------------|---------------------|--------|
| Jones et al. | 2013 | Pine Wood (PW)      | Fluidised Bed (FIB) | [29]   |
| Anex et al.  | 2010 | Corn Stover (CS)    | Fluidised Bed (FIB) | [2]    |
| Brown et al. | 2014 | Forest Residue (FR) | Entrained Flow (EF) | [5]    |
| Jong et al.  | 2015 | Forest Residue (FR) | Fluidised Bed (FIB) | [31]   |
| Gonzalez     | 2015 | Red Maple (RM)      | Fluidised Bed (FIB) | [18]   |
| Gonzalez     | 2015 | Loblolly Pine (LP)  | Fluidised Bed (FIB) | [18]   |
| Gonzalez     | 2015 | Switchgrass (SG)    | Fluidised Bed (FIB) | [18]   |
| Gonzalez     | 2015 | Acacia Bark (AB)    | Fluidised Bed (FIB) | [18]   |
| Dutta et al. | 2016 | Wood Residues (WR)  | Fixed Bed (FiB)     | [8]    |
| Dutta et al. | 2016 | Wood Residues (WR)  | Fluidised Bed (FIB) | [8]    |
| This thesis  | 2020 | Waste Sawdust (WS)  | Fluidised Bed (FIB) | [23]   |

### 5.1.3. Emission factor comparison

Two of the above mentioned studies, discuss the emission factor of the end products. Jones et al. (2013) calculated an emission factor of 18.9 kg CO<sub>2</sub>-e/GJ using externally purchased hydrogen. The value of Jones et al. (2013) is slightly lower than the value of the commercial plant in this thesis which is 23,3 kg CO<sub>2</sub>/GJ. Jong et al. (2015) calculated an emission factor of 22 and 40 kg CO<sub>2</sub>/GJ for fuels produced from FPBO. The 22 kg CO<sub>2</sub>/GJ is the value when hydrogen is produced from biogenic process gasses. When hydrogen is purchased externally, the emission factor is 40 kg CO<sub>2</sub>/GJ. This is almost two times as high as the emission factor found in thesis, which was also produced from externally purchased hydrogen.

## 5.2. Limitations and future research

This thesis has a number of limitations which reveal several topics for future research. In the early stage of the research the decision was made to focus on the production of heavy marine fuel oil (RMK). It was assumed that just little hydroprocessing was needed to meet the very wide range of the RMK characteristics in the ISO 8217. Later in the research process, it became clear that the FPBO needs a lot of hydroprocessing before it becomes compatible with the marine fuel infrastructure. This level of hydroprocessing led to a very light (low in density) fuel which looks more like a synthetic diesel than a dedicated marine fuel. It is therefore questionable whether the focus should lie on the production of a marine fuel. Maybe, the plant should be considered as a bio-refinery instead of a production plant focused on marine biofuel. More research is needed to investigate the optimal configuration and number of outlet streams of the production plant.

Another limitation is the characterisation of the FPBO. BTG delivered a simplified composition of the FPBO, which is suitable to use for modelling. However, the actual composition of the FPBO consists of hundreds of components. A more detailed analysis of the composition of the FPBO would make the analysis more accurate. Also, the composition of the intermediate streams is unknown. The linear programming model provides potential compositions of the intermediate streams based on model constraints. However, it cannot be confirmed whether the composition of those intermediate streams is realistic. The composition of the intermediate streams is important to determine the energy balance. Also, further research on the characterisation of the intermediate streams is needed.

The geographical location of both plants used in this thesis were directly obtained from BTG. No background research was done to investigate whether this location was optimal from an economic and emission factor point of view. There are arguments for the current location (Port of Rotterdam), as well as for other locations such as the Nordics. When the FPBO is produced in the Nordics, it could be beneficial to build the hydroprocessing there as well, as this would reduce FPBO transportation. However, in a year of low FPBO production (e.g. due to a bad harvest), the FPBO needs to be imported from other places. Also, as there might not be local customers for the end products, leading to more transportation. On the contrary, the Port of Rotterdam is a major chemical hub, where there are plenty of potential customers. Also, feedstocks can be imported and end products can be exported more easily, as it is accessible from all parts of the world. In conclusion the optimal location is not yet known.

Moreover, the scale of the plants was directly obtained from BTG. A plant with a larger capacity, could potentially lower the MFSP since the CAPEX share per output decreases. However, the prices of feedstocks could increase when more feedstock is needed. The reason for this, is that it may be needed to import feedstock from further away or use alternative feedstock, since the amount of cheap and nearby located feedstock is limited. The optimal capacity of the plant is unclear.

Finally, this thesis is short of a full LCA. The basic carbon footprint in this thesis only gives a calculation of the carbon emissions. Therefore, further research should focus on a LCA of the whole production chain. In this LCA the production of hydrogen from the gas or light fraction should also be considered. When the emission from this on-site produced hydrogen is captured and stored, it could potentially lead to a production with negative emissions.



# 6

## Conclusion

In conclusion, the marine fraction, which is the main output product of the process, complies with main technical requirements of marine fuel according to the ISO 8217. The application of the other two output fraction is not yet determined.

The total lifetime costs for the demo plant are estimated to be slightly higher than 22 M€. The largest share of these costs is formed by the CAPEX. The costs were in line with the calculation of BTG.

The average MFSP of the output products of the commercial plant is calculated to be 29,50 €/GJ. For the marine fraction specifically, the MFSP is estimated to be 1.347 €/tonne. This price is comparable to the price of other currently available biofuels. The sensitivity analysis demonstrated that many factors have an influence on this MFSP. Therefore, the above mentioned prices should not be seen as a fixed price, but rather as an estimate. The factors that influence the average MFSP of the commercial plant the most are the lifetime of the PICULA catalyst and the price of the FPBO. The MFSP of the marine fraction is affected most by the value of the other two fractions and could range from 1250 to 1520 €/tonne.

The average emission factor of the end products of the demo and commercial plant is 22,01 kg CO<sub>2</sub>/GJ and 23,28 kg CO<sub>2</sub>/GJ, respectively. These emission factors have a 70% lower carbon emission than fossil MGO. When other types of wood are used for the production of FPBO, the reduction could decrease to below 65% which is RED-II threshold. Hydrogen is the largest contributor to the emission of the output products. The use of other forms of hydrogen could potentially reduce the emissions factor.

Overall, the multi-stage hydroprocessing of FPBO shows potential from the technical, economic and emission factor perspective. The results of this thesis can contribute to the development strategy for the next couple of years. It creates realistic expectations for parties that want to invest in this technology. It is important to acknowledge the limitations of this research and the research gaps that still need to be filled. Once those areas are filled, the marine sector is one step closer towards a more sustainable future.



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# A

## Appendix

### A.1. Components per Reactor of Solver Model

In Table A.1, the molar flow components of the demo plant obtained from the solver model are presented. For the commercial plant these values need to be multiplied by 20 as the size of the commercial plant is 20 times larger than the size of the demo plant.

Table A.1: Molar flow per component per reactor determined by the solver model of the demo design.

| ID           | R1-1 inlet<br>[mol/hr] | R1-1 outlet<br>[mol/hr] | R1-2 outlet<br>[mol/hr] | R1-3 outlet<br>[mol/hr] | R1-4 outlet<br>[mol/hr] | R2-1 outlet<br>[mol/hr] | R2-2 outlet<br>[mol/hr] | R2-3 outlet<br>[mol/hr] | R2-4 outlet<br>[mol/hr] |
|--------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| WATER        | 1,8697                 | 1,8215                  | 2,0070                  | 2,1925                  | 2,3780                  | 0,6367                  | 0,9192                  | 1,2016                  | 1,4841                  |
| FORMA-01     | 0,0000                 | 0,0781                  | 0,0860                  | 0,0940                  | 0,1019                  | 0,0273                  | 0,0394                  | 0,0515                  | 0,0636                  |
| HYDRO-01     | 9,1872                 | 9,1872                  | 9,1872                  | 8,9987                  | 8,7791                  | 8,4860                  | 7,8141                  | 6,8847                  | 5,7420                  |
| CARBO-01     | 0,0000                 | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0045                  |
| CARBO-02     | 0,0000                 | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,1347                  | 0,1931                  | 0,1523                  | 0,1085                  |
| ETHAN-01     | 0,0000                 | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,3819                  | 0,2005                  |
| METHA-01     | 0,0000                 | 0,0000                  | 0,0000                  | 0,0237                  | 0,0513                  | 0,0000                  | 0,2057                  | 0,0000                  | 0,4229                  |
| PROPA-01     | 0,0000                 | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,1083                  |
| N-BUT-01     | 0,0000                 | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0432                  |
| CIS-C-01     | 0,0502                 | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0009                  | 0,0000                  | 0,0000                  | 0,0000                  |
| P-HYD-01     | 0,0292                 | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  |
| PROPI-01     | 0,0676                 | 0,0727                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  |
| VANIL-01     | 0,0420                 | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  |
| ISOEU-01     | 0,0355                 | 0,0051                  | 0,0047                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  |
| LEVOG-01     | 0,0216                 | 0,1056                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0001                  | 0,0000                  | 0,0000                  | 0,0000                  |
| CELLO-01     | 0,1004                 | 0,0418                  | 0,0219                  | 0,0000                  | 0,0000                  | 0,0127                  | 0,0000                  | 0,0000                  | 0,0000                  |
| TRANS-01     | 0,0479                 | 0,0581                  | 0,0394                  | 0,0000                  | 0,0084                  | 0,0185                  | 0,0000                  | 0,0000                  | 0,0000                  |
| DIBENZOF     | 0,0218                 | 0,0152                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  | 0,0000                  |
| DEHYD-01     | 0,0525                 | 0,0351                  | 0,0235                  | 0,0531                  | 0,0764                  | 0,1997                  | 0,2244                  | 0,1118                  | 0,0000                  |
| OLIGOMER     | 0,0244                 | 0,0857                  | 0,1816                  | 0,0512                  | 0,0000                  | 0,0025                  | 0,0000                  | 0,0000                  | 0,0000                  |
| PHENYLCO     | 0,0050                 | 0,0027                  | 0,0026                  | 0,1418                  | 0,1598                  | 0,0343                  | 0,0000                  | 0,0000                  | 0,0000                  |
| MTF          | 0,0000                 | 0,0461                  | 0,0008                  | 0,0000                  | 0,0000                  | 0,0179                  | 0,1753                  | 0,7873                  | 1,3934                  |
| <b>Total</b> | <b>11,5549</b>         | <b>11,5549</b>          | <b>11,5549</b>          | <b>11,5549</b>          | <b>11,5549</b>          | <b>9,5710</b>           | <b>9,5710</b>           | <b>9,5710</b>           | <b>9,5710</b>           |

### A.2. Overall molar balance simulation

In Table A.2, the overall molar balance of the demo plant obtained from the solver model is presented. For the commercial plant these values need to be multiplied by 20 as the size of the commercial plant is 20 times larger than the size of the demo plant.

Table A.2: The overall molar balance of the DEMO plant.

| Phase   | Component Name                  | ID           | Inlet [kmol/s] |                |                |                | Outlet [kmol/s] |                |                |                |                |
|---------|---------------------------------|--------------|----------------|----------------|----------------|----------------|-----------------|----------------|----------------|----------------|----------------|
|         |                                 |              | C              | H              | O              | Total          | C               | H              | O              | Total          |                |
| AQUEOUS | WATER                           | WATER        | 0,00000        | 0,00374        | 0,00187        | 0,00187        | 0,00000         | 0,00702        | 0,00351        | 0,00351        |                |
|         | ACETIC-ACID                     | ACETI-01     | 0,00000        | 0,00000        | 0,00000        | 0,00000        | 0,00030         | 0,00060        | 0,00030        | 0,00015        |                |
| GAS     | HYDROGEN                        | HYDRO-01     | 0,00000        | 0,01837        | 0,00000        | 0,00919        | 0,00000         | 0,01148        | 0,00000        | 0,00574        |                |
|         | CARBON-MONOXIDE                 | CARBO-01     | 0,00000        | 0,00000        | 0,00000        | 0,00000        | 0,00000         | 0,00000        | 0,00000        | 0,00000        |                |
|         | CARBON-DIOXIDE                  | CARBO-02     | 0,00000        | 0,00000        | 0,00000        | 0,00000        | 0,00011         | 0,00000        | 0,00022        | 0,00011        |                |
|         | ETHANE                          | ETHAN-01     | 0,00000        | 0,00000        | 0,00000        | 0,00000        | 0,00040         | 0,00120        | 0,00000        | 0,00020        |                |
|         | METHANE                         | METHA-01     | 0,00000        | 0,00000        | 0,00000        | 0,00000        | 0,00042         | 0,00169        | 0,00000        | 0,00042        |                |
|         | PROPANE                         | PROPA-01     | 0,00000        | 0,00000        | 0,00000        | 0,00000        | 0,00032         | 0,00087        | 0,00000        | 0,00011        |                |
|         | BUTANE                          | N-BUT-01     | 0,00000        | 0,00000        | 0,00000        | 0,00000        | 0,00017         | 0,00043        | 0,00000        | 0,00004        |                |
| OIL     | CROTONIC ACID                   | CIS-C-01     | 0,00020        | 0,00030        | 0,00010        | 0,00005        | 0,00000         | 0,00000        | 0,00000        | 0,00000        |                |
|         | 1,4-BENZENEDIOL                 | P-HYD-01     | 0,00018        | 0,00018        | 0,00006        | 0,00003        | 0,00000         | 0,00000        | 0,00000        | 0,00000        |                |
|         | HYDROXYACETONE                  | PROPI-01     | 0,00020        | 0,00041        | 0,00014        | 0,00007        | 0,00000         | 0,00000        | 0,00000        | 0,00000        |                |
|         | 3-METHOXY-4-HYDROXYBENZALDEHYDE | VANIL-01     | 0,00034        | 0,00034        | 0,00013        | 0,00004        | 0,00000         | 0,00000        | 0,00000        | 0,00000        |                |
|         | ISOEUGENOL                      | ISOEU-01     | 0,00035        | 0,00043        | 0,00007        | 0,00004        | 0,00000         | 0,00000        | 0,00000        | 0,00000        |                |
|         | LEVGLUCOSAN                     | LEVOG-01     | 0,00013        | 0,00022        | 0,00011        | 0,00002        | 0,00000         | 0,00000        | 0,00000        | 0,00000        |                |
|         | CELLOBIOSE                      | CELLO-01     | 0,00120        | 0,00221        | 0,00110        | 0,00010        | 0,00000         | 0,00000        | 0,00000        | 0,00000        |                |
|         | DIMETHOXY STILBENE              | TRANS-01     | 0,00077        | 0,00077        | 0,00010        | 0,00005        | 0,00000         | 0,00000        | 0,00000        | 0,00000        |                |
|         | DIBENZOFURAN                    | DIBENZOF     | 0,00026        | 0,00017        | 0,00002        | 0,00002        | 0,00000         | 0,00000        | 0,00000        | 0,00000        |                |
|         | DEHYDROABIETIC ACID             | DEHYD-01     | 0,00105        | 0,00147        | 0,00011        | 0,00005        | 0,00000         | 0,00000        | 0,00000        | 0,00000        |                |
|         | OLIGOMERIC COMPOUNDS            | OLIGOMER     | 0,00049        | 0,00063        | 0,00019        | 0,00002        | 0,00000         | 0,00000        | 0,00000        | 0,00000        |                |
|         | PHENYLCOUMARAN COMPOUNDS        | PHENYLCO     | 0,00010        | 0,00013        | 0,00004        | 0,00000        | 0,00000         | 0,00000        | 0,00000        | 0,00000        |                |
|         | MTF                             | MTF          | MTF            | 0,00000        | 0,00000        | 0,00000        | 0,00000         | 0,00354        | 0,00606        | 0,00000        | 0,00127        |
|         |                                 | <b>Total</b> |                | <b>0,00527</b> | <b>0,02936</b> | <b>0,00403</b> | <b>0,01155</b>  | <b>0,00527</b> | <b>0,02936</b> | <b>0,00403</b> | <b>0,01155</b> |

### A.3. Pseudo Components in MTF

In Table A.3, the pseudo components of the MTF constructed by Aspen Plus are presented. Those pseudo components are based on the distillation curve of the MTF.

Table A.3: The composition of MTF in pseudo components based on the distillation curve.

| Component | Volume percent of assay | Weight percent of assay | Mole percent of assay |
|-----------|-------------------------|-------------------------|-----------------------|
| PC89C     | 1,13540988              | 1,00372707              | 1,9830465             |
| PC100C    | 2,12542645              | 1,89815026              | 3,53987481            |
| PC114C    | 2,55045091              | 2,30578449              | 3,96249119            |
| PC128C    | 3,64878869              | 3,33807521              | 5,37679894            |
| PC142C    | 4,68189005              | 4,33134901              | 6,55503542            |
| PC156C    | 4,93070991              | 4,61157782              | 6,55955205            |
| PC170C    | 6,28880718              | 5,94416953              | 7,95441671            |
| PC184C    | 5,25498138              | 5,01822677              | 6,32217509            |
| PC198C    | 6,49042402              | 6,26090665              | 7,42627849            |
| PC211C    | 6,7344678               | 6,55725718              | 7,35029488            |
| PC225C    | 4,41912618              | 4,34361607              | 4,59528398            |
| PC239C    | 3,46092936              | 3,43359541              | 3,42862699            |
| PC253C    | 3,37423852              | 3,37792481              | 3,18731203            |
| PC267C    | 3,71892642              | 3,75575721              | 3,35224218            |
| PC281C    | 4,65980532              | 4,74587971              | 4,01301952            |
| PC295C    | 4,52022955              | 4,64140021              | 3,72361209            |
| PC308C    | 4,43405019              | 4,58921195              | 3,49654376            |
| PC322C    | 3,3431074               | 3,48762263              | 2,52301804            |
| PC336C    | 3,33336644              | 3,50445638              | 2,40947815            |
| PC350C    | 3,1533112               | 3,33995642              | 2,18603948            |
| PC364C    | 2,66611341              | 2,84475549              | 1,77332089            |
| PC378C    | 2,4446653               | 2,6273872               | 1,56094295            |
| PC392C    | 2,38271987              | 2,57852662              | 1,46309586            |
| PC405C    | 1,61391805              | 1,75857708              | 0,953144916           |
| PC420C    | 1,17569811              | 1,28987675              | 0,667866664           |
| PC440C    | 1,98540617              | 2,19980038              | 1,06644711            |
| PC468C    | 1,94052324              | 2,17780484              | 0,969434982           |
| PC496C    | 1,87847616              | 2,13417766              | 0,876001269           |
| PC522C    | 1,65403286              | 1,90044921              | 0,724605057           |

## A.4. SCENT calculations

The Tables A.4 and A.6 show the TCI for the demo and commercial plant. This TCI are the cost for the lifetime of the plants. The Tables A.5 and A.7 show the production cost on a 100% load of the demo and commercial plant per year.

Table A.4: Total Capital Investment DEMO plant per year on a 100% load.

| <b>Parameter</b>                      | <b>Base</b> | <b>Factor</b> | <b>Value</b>          |
|---------------------------------------|-------------|---------------|-----------------------|
| TDEC                                  | % of TPEC   | 110%          | € 1.241.795,96        |
| Equipment installation                | % of TPEC   | 28%           | € 316.093,52          |
| Instrumentation and controls          | % of TDEC   | 36%           | € 447.046,55          |
| <b>Total</b>                          |             |               | <b>€ 2.004.936,03</b> |
| <b>Other direct costs</b>             |             |               |                       |
| Building                              | % of TPEC   | 45%           | € 508.007,44          |
| Service facilities                    | % of TDEC   | 70%           | € 869.257,17          |
| Land                                  | % of TDEC   | 6%            | € 74.507,76           |
| Yard improvements                     | % of TDEC   | 10%           | € 124.179,60          |
| <b>Total</b>                          |             |               | <b>€ 1.575.951,97</b> |
| <b>Indirect costs</b>                 |             |               |                       |
| Engineering and supervision           | % of TDEC   | 33%           | € 409.792,67          |
| Construction expenses                 | % of TDEC   | 41%           | € 509.136,34          |
| Contractors fee                       | % of TDEC   | 22%           | € 273.195,11          |
| Legal expenses                        | % of TDEC   | 4%            | € 49.671,84           |
| Start-up capital                      | % of TDIC   | 10%           | € 512.071,50          |
| Contingency                           | % of TDEC   | 44%           | € 546.390,22          |
| <b>Total</b>                          |             |               | <b>€ 2.300.257,69</b> |
| <b>Fixed capital investment (FCI)</b> |             |               | <b>€ 5.881.145,68</b> |
| <b>Working capital</b>                |             |               |                       |
| Working capital                       | % of TCI    | 20%           | € 1.470.286,42        |
| <b>Total Capital Investment (TCI)</b> | €/Lifetime  |               | <b>€ 7.351.432,10</b> |

Table A.5: Production costs DEMO plant.

| Parameter                              | Base  | Factor | Value                 |
|--|---|--------|-----------------------|
| <b>(Semi-) Variable costs</b>          |   |        |                       |
| Raw materials                          |   |        | € 1.509.500,00        |
| Operating labour                       | Wessel's method                             |        | € 190.562,05          |
| Direct supervisory and clerical labour | % of operating labour                       | 15%    | € 28.584,31           |
| Utilities                              |   |        | € 9.574,07            |
| Catalyst                               |   |        | € 282.500,00          |
| Disposal cost                          |   |        | € 1.123,20            |
| Maintenance and repairs                |   | 3,50%  | € 205.840,10          |
| Operating supplies                     | % of maintenance                            | 15%    | € 30.876,01           |
| Laboratory charges                     | % of operating labour                       | 15%    | € 28.584,31           |
| Patents and royalties                  | % of (semi-) variable costs and fixed costs | 3,50%  | € 115.755,82          |
| <b>Total</b>                           |   |        | <b>€ 2.402.899,87</b> |
| <b>Fixed costs</b>                     |   |        |                       |
| Local taxes                            | % of FCI                                    | 3,50%  | € 205.840,10          |
| Insurance                              | % of FCI                                    | 1%     | € 58.811,46           |
| General plant overhead                 | % of labour and maintenance                 | 60%    | € 237.841,29          |
| Administrative costs                   | % of operating labour                       | 20%    | € 38.112,41           |
| Distribution and marketing             | % total production costs                    | 11%    | € 363.804,00          |
| <b>Total</b>                           |   |        | <b>€ 904.409,25</b>   |
| <b>Production cost</b>                 | €/Year                                      |        | <b>€ 3.307.309,12</b> |

Table A.6: Total Capital Investment Commercial plant per year on a 100% load.

| Parameter                             | Base       | Factor | Value                  |
|---------------------------------------|------------|--------|------------------------|
| TDEC                                  | % of TPEC  | 110%   | € 3.003.982,14         |
| Equipment installation                | % of TPEC  | 39%    | € 1.065.048,21         |
| Instrumentation and controls          | % of TDEC  | 36%    | € 1.081.433,57         |
| <b>Total</b>                          |            |        | <b>€ 5.150.463,93</b>  |
| <b>Other direct costs</b>             |            |        |                        |
| Building                              | % of TPEC  | 45%    | € 1.228.901,79         |
| Service facilities                    | % of TDEC  | 70%    | € 2.102.787,50         |
| Land                                  | % of TDEC  | 6%     | € 180.238,93           |
| Yard improvements                     | % of TDEC  | 10%    | € 300.398,21           |
| <b>Total</b>                          |            |        | <b>€ 3.812.326,43</b>  |
| <b>Indirect costs</b>                 |            |        |                        |
| Engineering and supervision           | % of TDEC  | 33%    | € 991.314,11           |
| Construction expenses                 | % of TDEC  | 41%    | € 1.231.632,68         |
| Contractors fee                       | % of TDEC  | 22%    | € 660.876,07           |
| Legal expenses                        | % of TDEC  | 4%     | € 120.159,29           |
| Start-up capital                      | % of TDIC  | 10%    | € 1.268.772,82         |
| Contingency                           | % of TDEC  | 44%    | € 1.321.752,14         |
| <b>Total</b>                          |            |        | <b>€ 5.594.507,11</b>  |
| <b>Fixed Capital Investment (FCI)</b> |            |        | <b>€ 14.557.297,46</b> |
| <b>Working capital</b>                |            |        |                        |
| Working capital                       | % of TCI   | 20%    | € 3.639.324,37         |
| <b>Total Capital Investment (TCI)</b> | €/Lifetime |        | <b>€ 18.196.621,83</b> |

Table A.7: Production costs Commercial plant.

| <b>Parameter</b>                       | <b>Base</b>                                 | <b>Factor</b> | <b>Value</b>           |
|--|---|---------------|------------------------|
| <b>(Semi-) Variable costs</b>          |   |               |                        |
| Raw materials                          |   |               | € 32.980.000,00        |
| Operating labour                       | Wessel's method                             |               | € 306.534,51           |
| Direct supervisory and clerical labour | % of operating labour                       | 15%           | € 45.980,18            |
| Utilities                              |   |               | € 277.145,18           |
| Catalyst                               |   |               | € 2.305.000,00         |
| Disposal cost                          |   |               | € 28.080,00            |
| Maintenance and repairs                | % of FCI                                    | 3%            | € 436.718,92           |
| Operating supplies                     | % of maintenance                            | 15%           | € 65.507,84            |
| Laboratory charges                     | % of operating labour                       | 15%           | € 45.980,18            |
| Patents and royalties                  | % of (semi-) variable costs and fixed costs | 3,50%         | € 1.541.362,51         |
| <b>Total</b>                           |   |               | <b>€ 38.032.309,32</b> |
| <b>Fixed costs</b>                     |   |               |                        |
| Local taxes                            | % of FCI                                    | 3,50%         | € 509.505,41           |
| Insurance                              | % of FCI                                    | 1%            | € 145.572,97           |
| General plant overhead                 | % of labour and maintenance                 | 60%           | € 445.952,06           |
| Administrative costs                   | % of operating labour                       | 20%           | € 61.306,90            |
| Distribution and marketing             | % total production costs                    | 11%           | € 4.844.282,17         |
| <b>Total</b>                           |   |               | <b>€ 6.006.619,52</b>  |
| <b>Production costs</b>                | €/Year                                      |               | <b>€ 44.038.928,84</b> |