Techno-economic analysis of a biorefinery plant in Azores Islands

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Resumo

A biomassa é um material renovável e orgânico, que, tal como os combustíveis fósseis, armazena energia nas ligações químicas. Assim, o desenvolvimento de biorrefinarias para obter energia, combustíveis e químicos torna-se crucial. Este estudo tem como objetivo analisar a viabilidade técnica e económica da instalação de uma biorrefinaria no Arquipélago dos Açores. Estas ilhas possuem uma quantidade significativa de biomassa de *Pittosporum undulatum*, uma espécie invasora sem aplicação comercial. Assim, é proposta uma biorrefinaria baseada na gasificação desta biomassa para a produção de energia, combustíveis e químicos atualmente obtidos através de fontes não renováveis. Os processos analisados neste estudo incluem as sínteses de hidrogénio, metanol e de hidrocarbonetos líquidos (processo de Fischer-Tropsch, FT). É utilizado o software Aspen Plus para modelar as biorrefinarias, estimar as capacidades de produção e determinar as configurações mais adequadas. O processo de FT seria a solução mais viável no contexto açoriano, dado atualmente existir procura para tais produtos combustíveis. Porém, a eventual transição energética nestas ilhas traduzir-se-á em novas exigências energéticas, tornando o hidrogénio e a eletricidade os candidatos preferenciais a produtos da biorrefinaria. Economicamente, a produção de hidrogénio é a solução mais viável, seguida pelo metanol e pela síntese de combustíveis de FT. O custo estimado da produção de hidrogénio na instalação proposta é cerca de 60% do seu valor de mercado previsto para 2025. Quanto aos combustíveis de FT e metanol, as estimativas dos custos de produção seriam duas a três e onze vezes o seu valor de mercado de 2020 respetivamente.

Palavras-chave:

Gasificação de biomassa lenhosa; Biorrefinarias; Processamento termoquímico; Biocombustíveis; Ilhas; Análise tecno-económica

Abstract

Biomass is a renewable and organic carbon-based material, that, similarly to fossil fuels, stores energy in chemical bonds. Hence, the development of biorefineries to process biomass and obtain energy, fuels and chemicals becomes pivotal. The objective of this study is to analyse the technical and economic viability of installing a biorefinery plant in the Archipelago of Azores. These islands have a significant amount of woody biomass, namely *Pittosporum undulatum*, an invasive species with no commercial use. Therefore, a biorefinery plant based on woody biomass gasification is proposed to produce energy, fuels and chemicals which are currently obtained using non-renewable sources. The routes analysed in this study include hydrogen, methanol and Fischer-Tropsch (FT) fuels synthesis. The Aspen Plus software is used to model the biorefinery, estimate its production potential and determine its most viable configuration. The FT-synthesis route seems to be the most viable solution for the Azorean context as there is currently a market for its fuel products. However, the future energy transition in these islands will translate into a new energy demand and, by that, hydrogen and electricity can be the preferred biorefinery outputs. The production of hydrogen is the most economically viable solution, followed by methanol and FT-fuels synthesis. The estimated production cost of hydrogen in the proposed installation in Azores is about 60% of its foreseen market value for 2025. The results for the production costs of FT-fuels and methanol show that these would be two to three and eleven times their market value of 2020, respectively.

Keywords:

Woody biomass gasification; Biorefineries; Thermochemical processing; Biofuels; Islands; Techno-economic analysis

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Nomenclature

Acronyms

1G – First-generation

2G – Second-generation

3G – Third-generation

AEA – Aspen Energy Analyzer

ARA – Autonomous Region of the Azores

ARG – Azores Regional Government

ASF – Anderson-Schulz-Flory

CHP – Combined Heat and Power

CRF – Capital recovery factor

DME – Dimethyl ether

DRRF – Direção Regional de Recursos Florestais

EEZ – Exclusive Economic Zone

EU – European Union

FC – Fuel cell

FT – Fischer-Tropsch

FTS – Fischer-Tropsch synthesis

GDP – Gross Domestic Product

GHG – Greenhouse gas

IEA – International Energy Agency

LCB – Lignocellulosic biomass

LPG – Liquified Petroleum Gas

O/P – Olefin/paraffin

PR-BM – Peng-Robinson with Boston-Mathias function

PSA – Pressure Swing Adsorber

RES – Renewable Energy Sources

Syngas – Synthesis gas

SN – Stoichiometric Number

USA – United States of America

WGS – Water gas shift

Greek characters

β – Correlation factor

ε – Exergy efficiency (%)

η – Energy efficiency (%)

Roman characters

BC – Biomass costs (€)

CAPEX – Capital expenditures (€)

$Cost_{NEW}$ (€) – Investment costs of the equipment (€)

$Cost_{REF}$ (€) – Investment costs available in the literature (€)

Ex – Exergy (kJ/kg)

$\dot{E}$ – Power (W)

EC – Electricity costs (€)

ER – Electricity revenues (€)

FPC – Fuel production cost (€/kg)

LHV – Low Heating Value (J/kg)

m – produced mass (kg)

$\dot{m}$ – flow rate (kg/h)

O&M – Operation and Maintenance costs (€)

OPEX – Operational expenditures (€)

$Scale_{NEW}$ – Scale of the equipment (units depending on the equipment)

$Scale_{REF}$ – Scale of the equipment in the literature (units depending on the equipment)

X – mass fraction (wt.%)

Variables

$CEPCI_{2018}$ – Chemical Engineering Plant Cost Index of 2018

$CEPCI_{REF}$ – Chemical Engineering Plant Cost Indexes available in the literature

f_I – installation factor

f_S – scale factor

i – discount rate

l – lifetime (years)

n – carbon number

1. Introduction

The development of renewable and more sustainable ways of production, storage and usage of energy has been the focus of an increasing amount of research over recent decades. The scarcity of fossil fuels and its inherent price volatility, in addition to the environmental problems related to its use, are some of the core problems that led the research and development of new sources and technologies to process energy.

The continuous global population growth, as well as the technological advancements, have been propelling the energy demand around the world, which consequently drive the pursuit for more renewable and sustainable energy sources. Moreover, these also fostered the consumption reduction and energy waste suppression movements that already take part not only in the industry domain, but also in the daily routine of society itself.

Furthermore, five out of the 17 sustainable development goals adopted by the United Nations member states for 2030 are directly or indirectly related with the above-mentioned information. These goals are the affordable and clean energy (seventh goal), sustainable cities and communities (eleventh goal), responsible production and consumption (twelfth goal), climate action (thirteenth goal) and life on land (fifteenth goal) [1].

1.1. Framing and motivation

The Autonomous Region of Azores (ARA) is known to face some challenges regarding its presently established energy systems, mostly owed to its outermost location. Its geographical characteristics raise obstacles to the supply of energy and its systems efficiency, increasing the energy associated costs. The dependency on external sources of fuels, mostly fossil ones, is a reality for the archipelago energy context, as no electricity connection to continental areas exist.

Nevertheless, the Azorean archipelago exhibits opportunities that can possibly counter these challenges, which grounded this project. Of those, the most relevant are the vast availability of biomass with energetic potential, namely of invasive species that find no commercial use. Additionally, the already significant importance of the biomass related activities on the economy of the islands is also relevant.

The targets by the Azores government for the renewable energy penetration in electricity production (50%) are ambitious since they promote the increase of the already high renewable energy share on electricity produced [2]. As of 2017, the renewable share on electricity consumption represented 36.6% of the demand [3], notably higher than the European goal of 20% for 2020 [4].

Biomass and its residues valorisation have been focus of interest for the energy and chemical industry due to its favourable chemical and structural characteristics. Biomass has been exploited as energy source since the early steps of human life and in 2017 still represented 55.6% of the primary energy produced worldwide [5]. Besides its ease of access and use, biomass is also the only natural carbon-based material, apart from fossil fuels, that can be used for energy purposes. This carbonaceous characteristic turned it into object of study not only for energetic purposes, but also for synthesis of chemical products, conventionally obtained through non-renewable resources.

These facts boost the concept of a bio-based economy, built around the increase of bio-based value-added products that can replace the conventionally obtained ones. It is expected the rise of the biomass resources importance for the upcoming years in the chemical and energy fields, being the biorefineries a crucial part of these forecasts. For the European region, the European Commission [6] sets the targets of 30% of the chemicals to be bio-based and 25% of the fuels to be biofuels in 2030, following the current continuous growth trend.

Within this framework of thought, the sustainable utilization of the Azorean biomass and its residues to produce chemical products and/or energy seems to be an effective measure for the development of the islands in terms of energy, environment and economy. The installation of a biorefinery in the archipelago would meet the environmental goals of greenhouse-gas (GHG) emissions decrease and renewable energy share increase. Additionally, the economic, social and technological development of the region would be expected in regards to the biorefinery activities [6],[7], adding to the decrease of dependency on imported oil-derived products.

Since biomass takes up a large portion of the Azorean archipelago area, its availability has already been studied in terms of its exploitation as energy resource [9]. The sustainable utilization of the Azorean *Pittosporum undulatum* biomass material (Figure 1.1) has already been assessed in former studies due to its invasive behaviour and its presently non-commercial use for any relevant activity [10]. The development of ways to produce energy from this resource is encouraged, as it is seen as an opportunity not only for the landowners but also for the economic development of the islands.

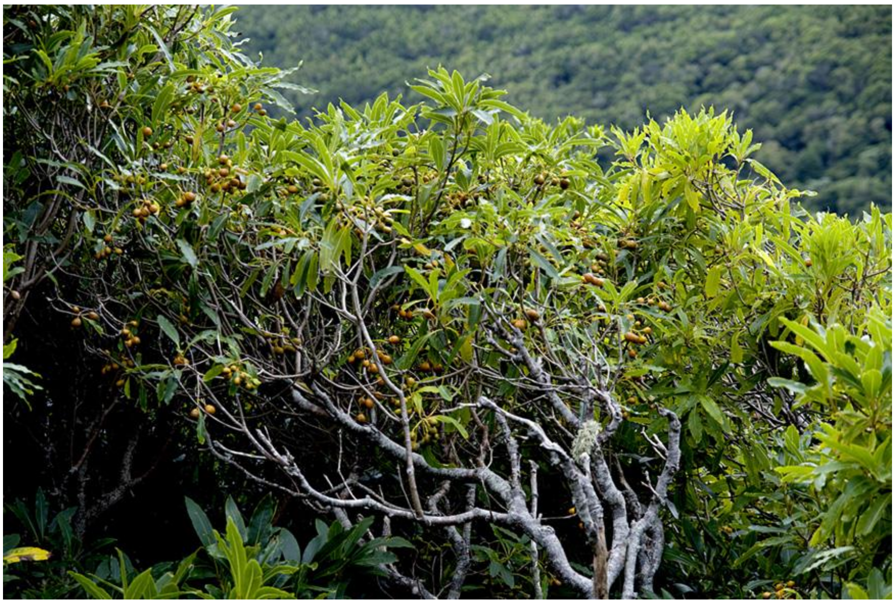

Figure 1.1 – *Pittosporum undulatum* tree [11].

1.2. Objectives of the study

The present thesis comprehends a techno-economic study of the possible installation of a biorefinery plant in the Azorean archipelago, operating through the exploitation of the endogenous available biomass resources. This work aims to estimate the conditions to generate products with significant market importance and with similar production costs to the presently obtained from non-renewable sources. Within this purpose, three plants are modelled using Aspen Plus V9 software to simulate the operations and system performances of a hydrogen, a methanol and a Fischer-Tropsch (FT) fuels synthesis plants. The performed study comprises the process design and analysis, as well as the economic analysis for the plants in terms of investment and operational costs.

In addition, it is crucial to ensure the sustainability of the plants and its feedstock resources exploitation. With respect to the sustainability of the plants and its viability, some objectives are pursued while designing the plants, specifically the energetic self-sustainability and maximization of the synthetized products of each of the plants. The energy efficiency maximization among the processes, besides the reduction of the natural resources' consumption are also vital points in its the design.

The target of higher share of renewable energy sources (RES) and decrease non-renewable products consumption is promoted by the projected implementation of the biorefinery plant in the ARA, going in accordance with the "green economy" ideal.

1.3. Present contribution

This present work comprehends three distinct parts that can be divided as follows:
First, the present ARA geographical, social, economic and endogenous biomass resources characterization is carried out. Particular emphasis is given not only to the biomass availability on the islands, but also to the current power and fuels demand and its supply to the archipelago. A brief explanation of the chemical demand on the islands is also presented.

Second, the simulation of three different biorefinery plants is carried out by means of the Aspen Plus software, considering the utilization of Azorean biomass resources. The modelling of these plants enables the chemical products manufacture and power production estimation and thus assessing its viability for the archipelago current scenario. By means of this analysis, it is also performed an economical study that quantifies the capital and operational expenditures (CAPEX and OPEX) for the designed plants. Then, a sensitivity analysis is carried considering different scenarios involving the operations of the plants.

The final object of discussion addresses the possible measures and initiatives that could enhance the sustainability of the plants and ways to complement the presented work.

1.4. Thesis outline

The present thesis is divided into six different chapters, of which the current represents the introductory one. In this chapter, it is summarized the thesis objectives and highlighted the motivation and framing of the developed work, besides its present contribution. For Chapter 2, an extensive literature review is presented, involving the technological state-of-art regarding the biomass utilization and the existent and considered studies for the modelling of such technologies. Chapter 3 features the ARA characterization in terms of its geography and climate, social-economic context, energy current scenario and its biomass resources availability. Additionally, in this chapter, the same characterization is presented specifically for the S. Miguel Island. Following, in Chapter 4 is provided the methodology of the Aspen Plus simulations performed to estimate the biorefinery plants production capacities. Within this chapter is also presented the economical approach that is implemented to assess the economic viability of the plants. Chapter 5 consists of the results and discussion of the performed simulations in terms of yield capacities and economy of the plants. The results of the sensitivity analyses carried out for the different plants are also presented and discussed in this chapter. Finally, Chapter 6 summarizes the conclusions of the present work and provides suggestions for possible measures and future research.

2. Literature review

The Azorean region has been object of study of an extensive amount of research for the past years in regard of the increase of the RES penetration in the energy systems of the islands. These studies are reviewed in this chapter.

The development of biorefineries has been receiving growing attention over the last three decades as consequence of the already mentioned information concerning energy and chemicals production. Nevertheless, there is still space for progress, so the present state-of-art of the biomass processing technologies and the possibility of biomass use as biorefinery feedstock is also assessed in this chapter.

2.1. Previous studies carried out in ARA

Due to its external energy dependency and its favourable endogenous natural resources availability, the Azorean archipelago has been focus of study over the past years concerning the shift for more RES. Although a large share of renewables is presently found, the 100% RES target is systematically pursued for the region. Here are presented some of the most relevant works performed on this matter.

As reported by Chen et al. [12], the Renewislands project seeked the enhancing of the RES penetration on the market of some European islands energy systems. The steps and activities carried out to achieve this objective for the different islands are presented. The current status of renewable energy share for the studied islands are presented and the most adequate solutions for each are assessed, namely the integration of intermittent renewable energy supply (wind, solar, hydro, etc.…) with fuel cells (FC) and hydrogen (H_2) infrastructures. Moreover, in this work, a techno-economic analysis was performed over the installation of an integrated renewable energy sources/H_2/FC system in island of Porto Santo, Madeira. Applying the methodology introduced by Renewislands, Duic et al. [13] studied the S. Vicente Island, Cape Verde, and the possibility to merge its water and electricity supply systems. This study proved that it would be a successful solution in order to achieve higher RES penetration in the island, by assuming the pumped-storage hydroelectricity as the storage system of the wind power production. As part of the Green Islands Project, the [12] study was elaborated regarding the utilization of the Azorean woody biomass resources for energy production. This work considered the inventory of biomass and its distribution along the islands in 2010. Through field research it was possible to map the territory occupied by the most abundant species, being special attention dedicated to the invasive ones. Hence, it was possible to assess the most important species present in the archipelago, namely *Pittosporum undulatum* (Australian cheesewood), *Cryptomeria japonica* (Japanese cedar) and *Acacia melanoxylon* (Australian blackwood). Moreover, these species were subjected to laboratorial analysis to evaluate their potential and sustainability as energy resources. The reported results show that the studied species exhibit adequate properties for its exploitation as energy resource. Apart from this analysis, this study was also focused on the planning of the invasive species occupied areas reforestation for short life-cycle species, that when harvested found the same energy purposes.

The Azorean *Pittosporum undulatum* biomass potential for energy purposes was evaluated in the work carried by Lourenço et al. [10]. Given its wide forest occupied area, in this work, the amount of this biomass resource availability in the archipelago is estimated, as much as the operational waste resulting from its projected utilization. This estimation is based on the Azorean Forest Inventory [15], obtained from field work performed between 2003 and 2007. Besides this estimation, there were also collected samples to assess the quality of the biomass. The results of the analysis encourage the utilization of this woody material as energy resource, respecting the principles of sustainable forest management. Since it has no important economical use, its gasification or combustion are pointed out as valid alternatives that could generate economical return, stimulating the local economy and increasing the energy security of the islands.

Still on the topic of utilization of the Azorean biomass for energy purposes, the study by Simas et al. [9] assessed the utilization of the forest biomass of the S. Miguel Island as fuel. The current social, economic activities and energy situation of the island was reviewed, as well as its resources availability. After the estimation on the availability of the main biomass resources (*Pittosporum undulatum*, *Cryptomeria japonica* and *Acacia melanoxylon)* and the residues resulting from its processing techniques, different scenarios on the resources utilization for heat and power production were evaluated. Estimations were performed on the capacity of production of heat and power, that were shown to be more than enough to supply its identified potential end users.

Alves et al. [16] also studied the increase of penetration of RES in the archipelago, this time by implementing interconnection of the power systems of Pico and Faial Islands. The main focus of this study was the estimation of the increase on the renewable power share mainly by means of intermittent renewable energy that is currently not used, due to the mismatch between the supply and demand. The power systems and its performances for both the islands are evaluated, and its energy resources identified in order to identify where action may be taken. Moreover, the energy storage technologies are assessed as possible solutions for countering the intermittent performance of some renewable power production. By modelling the islands energy scenario in EnergyPLAN software, it was possible to predict the 2030 energy context status considering the possible interconnection of the islands and implementation of storage systems. The obtained results show that the appliance of these measures, even if only one is chosen, could lead to the decrease on fossil fuels usage and CO_2 emissions on the islands while sustainably taking advantage of its endogenous RES. Although environmentally both measures are encouraged, economically the results show that the best option would be the investment on energy storage technologies for each of the islands rather its interconnection.

Regarding the transportation sector in the islands, Baptista et al. [17] evaluated the impacts of introducing electric powered vehicles in the Flores Island, considering different scenarios upon the replacement of conventional fuelled vehicles by electric ones. This study assessed the power supply status and identified the vehicle fleet of the island, in order to estimate the 2020 and 2050 scenarios. The study outcomes showed that, in 2012, the island was ready for the electric vehicles (EV) implementation in the island, although minor problems were expected, inherent to its arrival. The different scenarios about the introduction of EV exhibited positive indications concerning the CO_2 emissions and the energy loss reductions, and, by that, reported the suitability of EV implementation for the island. As complement of this study, Pina et al. [18] analysed the same EV alternative for the Flores Island, taking into account the recharging strategies of the vehicles. This study concluded that the adoption of EVs in the island alone would not be a very efficient measure, as the electricity supply system would require higher power generation. If not integrated with the investment on renewable power generation capacity, the impact of the substitution would be reduced. Therefore, the adoption of measures to increase the RES share on power produced allied with the EV introduction in the island are suggested as environmental effective measures.

2.2. Biomass and its processing

On account of the vast worldwide availability of biomass resources, its utilization offers an also extensive spectrum of possibilities, namely on the replacement of fossil resources. As an organic material, given its carbonaceous characteristic, biomass finds different uses as fuel as well as chemical precursor for other chemical substances. Furthermore, the mechanical structure of woody biomass extends its utilization also for construction and manufacture of other value-added materials.

As for energy purposes, biomass can be a continuous source for energy supply, not facing the intermittency inherent element to renewable energies such as solar and wind ones. By that, its exploitation can provide a stable renewable energy output. In 2017, biomass already accounted 55.6% of the primary energy produced worldwide [5], and the trend appears to be of continuous exploitation of these resources due to their economic potential [19]. In the same year, 70% of the renewable energy produced worldwide was bioenergy. From this biomass, 92% was used for heating purposes, followed by the transportation sector (5%) and power production (3%) [20]. As of 2017, 86% of the used biomass was used as primary solid fuels (wood, wood chips, wood pellets, etc.), while 7% was used for liquid biofuels [20].

The chemical precursor ability of biomass is already a reality for the industry and its further development is pursued in order to replace the conventional resources. As suggested by [21], the forecasts regarding the global chemical industry point that 22% of the its market will be bio-based by 2025, increasing from the 2% value for 2008.

Presently, biomass resources can be processed in a wide variety of ways to enhance its fuel and other chemicals precursory capability. These processing techniques encompass since the simple mechanical cut and chopping of firewood, up to complex chemical treatments of gaseous mixtures to produce biofuels. In this line of thought, emerges the biorefinery concept as platform to synthetize, in a more or less complex way, a varied product portfolio able to replace the conventionally obtained from non-renewable resources.

2.2.1. Biorefineries

The development of biorefineries has been growing attention over the last three decades as consequence of the above-mentioned information in regard of biomass utilization. As of 2017, the European Commission recognized 803 installed biorefineries in Europe. From these, 507 produce bio-based chemicals, 363 produce liquid biofuels and 141 produce bio-based composites and fibres [22]. Due to the possibility of multi-production in a number of facilities, some are considered two or three times, being 177 classified as integrated biorefineries due to the combined production of bio-based materials and energy. The distribution of operating biorefineries per country in Europe in 2017 can be perceived in Figure 2.1.

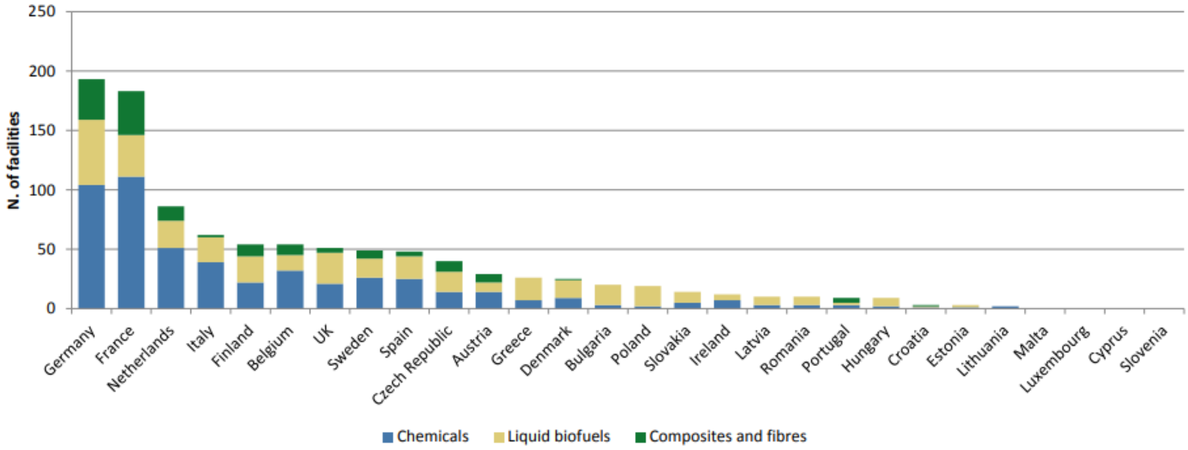

Figure 2.1 – Distribution of operating biorefineries per country in Europe in 2017 [22].

The International Energy Agency (IEA) defines a biorefinery as an integrated production plant using biomass feedstock to produce a range of value-added products', of which bioproducts (chemicals, fuels, etc.) and bioenergy (heat and power) take part. The fundamental driver for these plants is the deconstruction of some of the molecular structures of raw biomass material to obtain simpler molecules that after some chemical processing can generate products with similar characteristics to the ones produced in conventional refineries (fuels, chemicals and/or energy).

Biorefineries can be grouped in three different categories according to its type of feedstock material [23]:
- First-generation (1G) feedstocks, include the edible biomass material, mostly food crops (e.g. vegetable oils, wheat, rice, etc.);
- Second-generation (2G) feedstocks, represent non-edible material, mainly woody biomass (lignocellulosic material, wood waste, forestry and agricultural residues, etc.);
- Third-generation (3G) feedstocks, feature microalgae resources.

One of the main goals of the European Union (EU) directive 2015/1513 is to favour the development of second-generation biorefineries, fuelled by non-edible biomass, over the first-generation, that relies mostly on edible material. This goes towards countering the fuel versus food debate and decreasing the GHG emissions [24]. Although the already wide spread of 1G facilities, namely in USA (corn based) and

Brazil (sugarcane based) for bioethanol production, problems such as the food price increase and land usage are known challenges for the operation of these plants. 2G and 3G are thereby promoted as more sustainable ways to process biomass, even if its further development is required for better economical performances.

Woody biomass belongs to 2G feedstock range of materials and is becoming a key part on the development of more sustainable biorefineries since it is the most abundant organic source on the globe and its potential uses are favourable in spite of other feedstocks [25]. In addition, contrary to 1G feedstocks, woody biomass availability does not suffer from seasonal fluctuations.

Furthermore, the design of plants fed by waste streams and the integration of biorefineries with other industries is desirable as well, since it allows to recover energy otherwise lost from present waste streams [6].

Woody biomass consists of lignocellulosic material, i.e. its generic composition comprises mainly cellulose (35-60%), hemicellulose (10-40%) and lignin (15-30%), being the remaining accounted on extracts (1-20%) and ash (0.1-2%) [26]. Its composition can also be evaluated in terms of moisture, dry matter and the remaining of ash, the first depend two not only on the type of biomass but also on ambient conditions. Moisture values can range from 8 to 60% of the biomass weight, depending on the processing and ambient conditions of the resources [26]. Figure 2.2 presents the generic woody biomass composition and some examples in terms the moisture content.

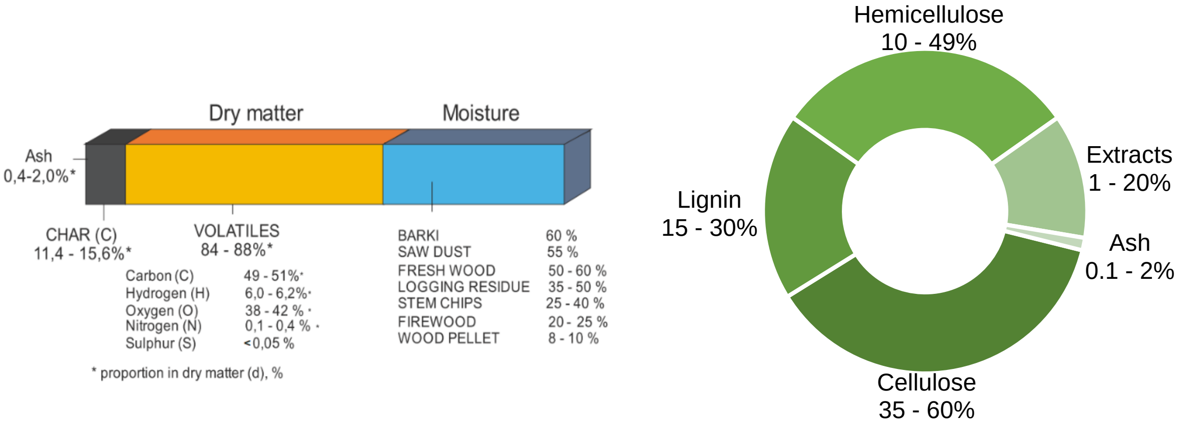

Figure 2.2 – Woody biomass generic composition [26].

Moreover, biorefineries can also be split into two divergent routes concerning the type of material processing techniques applied. These are the biochemical and thermochemical routes.

The main biochemical paths comprehend the enzymatic or chemical hydrolysis of the feedstock prior to its transformation into other chemical materials. Therewith, the depolymerization of polysaccharides to monosaccharides (e.g.: arabinose, fructose, glucose and xylose) and their consequent conversion to analogous petroleum platform molecules occurs, through fermentation or chemical synthesis. Below are presented the most important possibilities regarding the biochemical routes for woody biomass, based on [27], Figure 2.3.

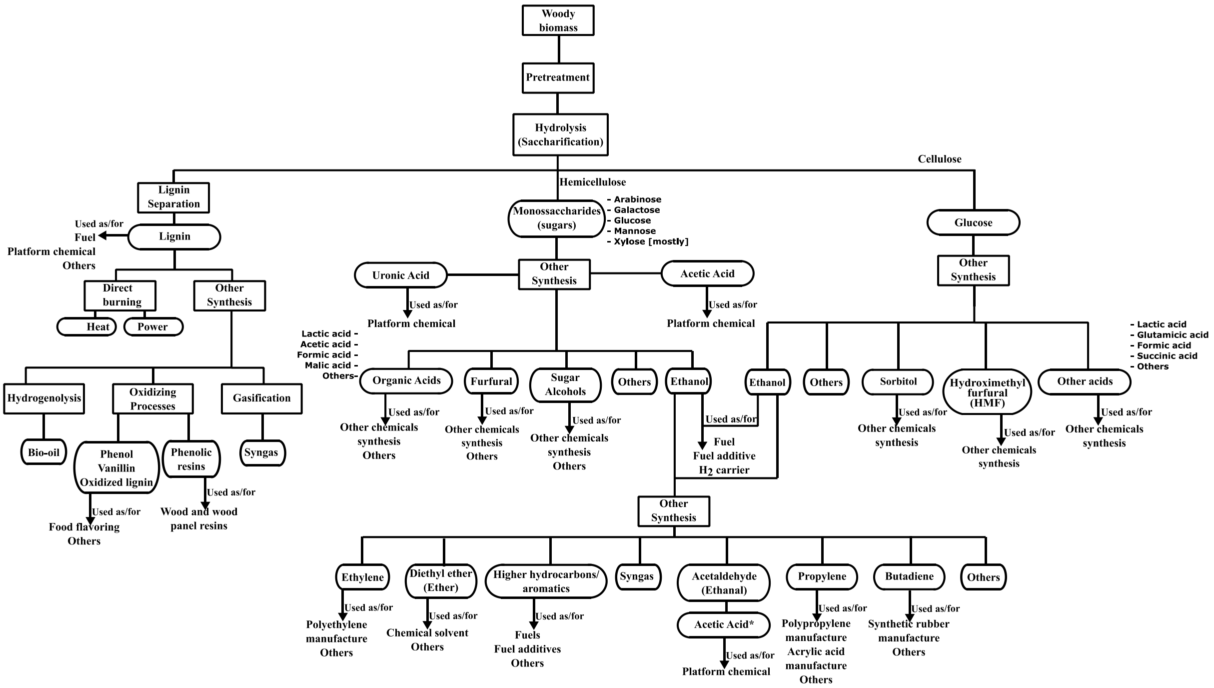

Figure 2.3 - Main biochemical routes for biorefineries for woody biomass [27].

The appliance of pre-treatments is recurrent on biochemical plants to ease the breakdown of molecules due to the lignocellulosic characteristic of the feedstock. After this, the hydrolysis step is promoted to convert the carbohydrates material into soluble sugars (usually enzymatically stimulated) [28]. Cellulose is converted to glucose while the hemicellulose can be transformed into other sugars (monosaccharides). At the same time, lignin separation techniques are applied.

The produced sugars serve, in most of the cases, as fermentable material to produce alcohols or acids that, further on, find use as fuels or as chemical precursors. Ethanol is the most notable option as it possesses fuel characteristics that in part match the gasoline and diesel ones, being utilized as a fuel additive. Besides its fuel ability, ethanol is also a valuable chemical platform chemical, due to the capacity of its conversion into other important chemical products. As assessed by Werpy and Petersen [27], besides ethanol, the synthesis of acids (acetic, uronic and organic acids) and other alcohols must also be pursued, due to its relative easiness of conception and its market value, namely for the food, construction and pharmaceutical industries.

As for the separated lignin portion, lignin can be used as fuel material, although its chemical precursor ability is also recognized and viable. Although lignin's purpose in operating biorefineries is in most cases for power production, it also possesses other utilization opportunities such as synthesis of macromolecules or aromatics and monomers, as detailed by Holladay et al. [29].

Biodiesel is currently the second most synthetized liquid biofuel in the world [28]. However, its synthesis from lignocellulosic biomass (LCB) is challenging. Due to the complex chemical structure of LCB, it is required to submit the material to an also complex set of processes to enable the synthesis of lipid products and, consequently, biodiesel. These challenges increase the economic costs associated with the plants, promoting the current financial unviability of these plants [30]. Like ethanol, if intended to be used as fuel, biodiesel must be blended with the conventional fuel, diesel in its case, or used in engines designed to run on it.

These routes are currently more exploited than the thermochemical ones, mostly due to its already mature technology status, which can be noticed by the high number of operating plants at commercial scale [22].

The thermochemical biorefineries, however, are becoming more important. These routes also present a wide range of possibilities. The most important consist of gasification, pyrolysis and direct burning of biomass and its further processing, as presented next, Figures 2.4 and 2.5. These thermochemical paths require a number of material treatments primarily controlled by heat and pressure that promote the breakdown of molecules and later the synthesis of other chemical products. Although matured technology is not yet fully available, there already exist plants running at commercial scale [6], [7], [31], [32] and a significant number of projects are being developed.

Figures 2.4 and 2.5 present the main thermochemical routes involving woody biomass. Figure 2.4 presents the pyrolysis-based routes, while Figure 2.5 presents the routes based on the gasification of biomass and the biomass burning option.

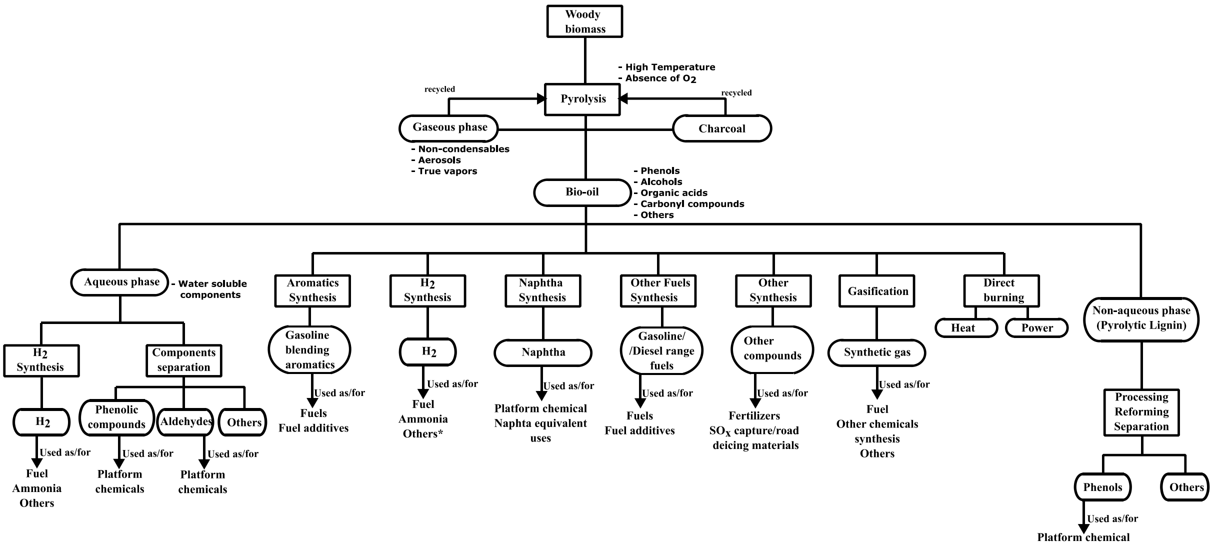

Figure 2.4 - Main thermochemical routes for biorefineries fed with woody biomass (pyrolysis).

Pyrolysis is recognized as the thermal decomposition of organic molecules in the absence of air (i.e. oxygen) at moderate temperatures conditions, ranging from 300 to 600ºC [33]. From this process result various products, grouped in three different phases: gas, liquid (condensed vapours) and char. From these phases streams out four main products:

- Bio-oil, accounting up to 65% of the mixture weight. Resulting from the condensation of the pyrolysis vapours, bio-oil consists of a complex mixture of oxygenated hydrocarbons, moisture and fragments of biomass. Chemically, its composition relies on phenols, alcohols, organic acids and carbonyl compounds (ketones, aldehydes and esters) [34]. This liquid product divides itself in two phases: an aqueous high-density phase and a low-density organic phase (pyrolytic lignin). The first cannot be used directly as substitute of conventional fuels but can be catalytically reformed to produce hydrogen. This phase possesses some water-soluble components such as acetic acid, hydroxyl, acetone and phenol. The second possesses higher heating values and can be used as fuel for specifically designed engines;
- Gaseous phase, that amounts up to 13% of the mixture. It is composed by aerosols, true vapours and non-condensable gases (mainly CO, CO_2 and CH_4). The non-condensable gases can be recycled to the reactor for better fluidization or combusted for heat purposes. The remaining can be used for hydrogen molecules production to be reused in the pyrolysis process or just for heat purposes;
- Biochar, in quantities up to 12% of the mixture content. This product consists of fractions of inorganic materials, unconverted solids and carbonaceous residues. This char is a carbon rich material and, consequently, possesses value not only as combustible but also as soil improvement material [34];
- Water, which represents up to 10% of the mixture. The remaining amount of the mixture is set to be composed of ash and flue gas.

The possibility to synthetize a liquid fuel (bio-oil) directly from the raw biomass without need of further processing phases to liquify the product is the most relevant feature of this technology. The resulting bio-oil contains almost 70% of the initial biomass energy and possesses less nitrogen and sulphur than conventional diesel and gasoline fuels. However, this liquid fuel still possesses some drawbacks in its utilization. Its high-water content (15-35%) due to the initial biomass moisture and the dehydration reactions that occur during pyrolysis are a setback. Besides this, high oxygen content makes it immiscible and with heating values no more than 40-45% of current fuels ones [34]. Its acid characteristic is also a problem, mainly due the presence of phenols, that can be corrosive to the systems. Finally, the fact that it consists of a complex mixture of more than 300 chemical compounds in the liquid phase, turns it into an unstable product.

Although the production of bio-oil as a liquid fuel is one of the most promising paths after pyrolysis, as shown in Figure 2.4 there are other relevant possibilities. Regarding energy purposes, paths like gasification, hydrogen or naphtha synthesis through bio-oil are achievable and seem promising paths. Nevertheless, these processes did not yet achieved cost-competitive technology levels [35], mainly due to the bio-oil inherent components separation constraints.

Concerning other products synthesis, bio-oil is a potential chemical precursor for the most varied fields. Its utilization for fertilization materials production achievable by simple mixing with ammonia (NH_3) is known. Also, without much processing, due to the presence of phenolic compounds, bio-oil can be used as wood adhesive [33]. Its capacity ranges also to the food industry, for the manufacture of flavouring products [36]. As for the energy purposes, the production of specific chemicals does not seem very promising due to the components' separation difficulties.

Compared to gasification technology, pyrolysis technology is known to be less costly in terms of equipment (less equipment needed) if working on 50-100 tons of feedstock per day. These systems minimize char formation comparing with gasification and its products are more favourable in terms of transport and storage.

Figure 2.5 presents the routes based on the gasification of biomass and the biomass burning option.

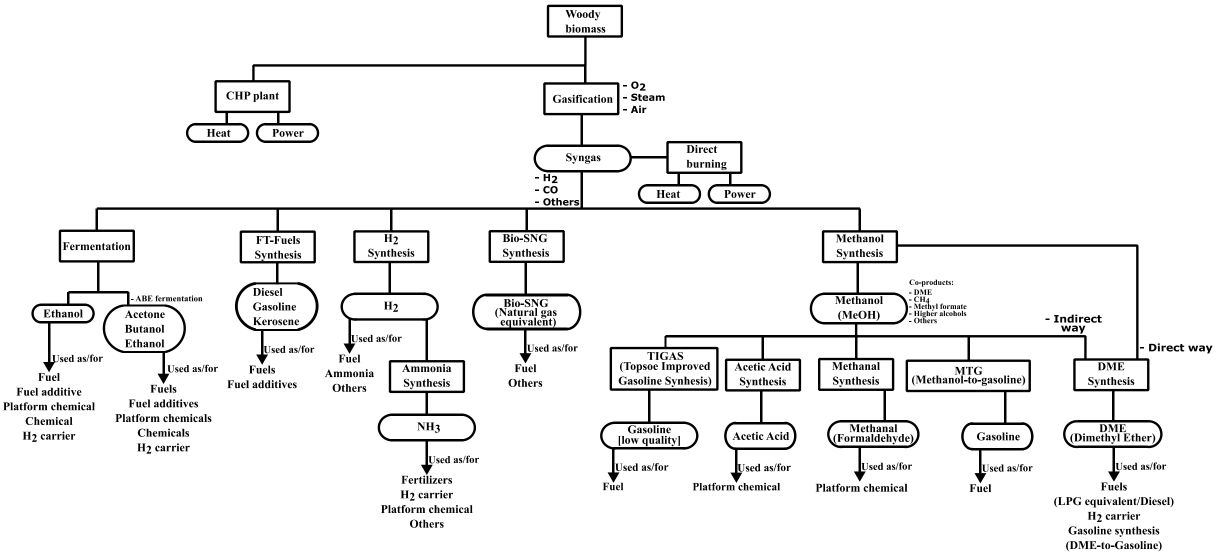

Figure 2.5 - Main thermochemical routes for biorefineries fed with woody biomass (gasification and burning).

Gasification process can be divided in four main stages: Drying, where the moisture content of the material is reduced by means of the vaporization of the water content. This step is set to occur in the 100-200ºC range of temperatures; Devolatilization (or pyrolysis), which consists on the thermal decomposition of the material in the absence of oxygen or air and the consequent reduction of its volatile matter. In this stage, the biomass is reduced to solid charcoal by means of the hydrocarbon gases release from the biomass. Oxidation, in which the oxygen and hydrogen react with the solid carbonized biomass material, forming carbon dioxide and water, respectively, in a pair of exothermic reactions. Still in this stage, if in sub-stoichiometric quantities, the oxygen can react with the carbon and produce carbon monoxide; Reduction, in the 800-1000ºC range of temperatures, where several reduction reactions occur, mostly endothermic. From these results a gaseous combustible mixture, consisting mostly of hydrogen, carbon monoxide, carbon dioxide and methane.

Gasification differs from the pyrolysis mainly on the higher residence time and the temperature of the process (>700ºC) [33], at the same time that it produces a gaseous mixture rather than a liquid one. By comparison with pyrolysis, biomass gasification comes with the following advantages:

- The synthesis gas (syngas) is recognized to hold not only higher energy but also higher hydrogen content [37];
- Higher recovery of the feedstock material as useful material for chemical synthesis [37];
- Its low-oxidation conditions enable a more environmental friendly behaviour, producing less NOx and SOx, comparing to other processes [38];
- Chemical structure similarities between syngas and natural gas enable the possibility of following some already mature processes used for natural gas processing to synthetize other chemical structures.

The gasification process occurs in the presence of a gasification medium, such as air, steam or oxygen. Air gasification is the most used option as it is cheaper and presents high efficiencies. However, the resulting gas presents the lowest heating value (4-6 MJ/Nm^3) due to the entrainment of nitrogen (up to 60%) present in the air [39]. Oxygen gasification yields the better-quality gas with heating values up to 10-15 MJ/Nm^3. The heating value, however, is decreased by the presence of oxygen, as it consumes some of the combustible gases (H_2, CO, CH_4, etc.). However, this solution is more costly and can represent safety problems related to the oxygen storage and usage [39]. Steam gasification seems to be the best solution as it produces more combustible gases (H_2, CO, etc.) besides the fact that steam production is considerably economical when compared to air or oxygen as gasifying agent. Some of the possible problems associated with this technology are related with corrosion, poisoning of catalysts and the production of tars [39]. Nevertheless, the major challenge of the gasification technology is the equipment costs that can become prohibitive for the projects.

The combustion of biomass is another process considered. The operation of a combined heat and power system (CHP) allows the cogeneration of heat and power by the direct burning of woody biomass. Its process complexity is relatively low, although a lot of different designs exist for these plants. This technology generic operation consists of a biomass boiler that produces heat which then drives a steam or gas-turbine to produce power. The residual heat that results from this process is then used for heating purposes. In terms of energy efficiency, this technology is acknowledged to be considerably high, as it is designed to recover all the possible amount of energy from the feedstock. Nevertheless, its application is usually preferable for local production of power and heat since these resources storage and transmission are challenging. Additionally, for the Azores islands case, if no interconnection exists between its power grids, the power produced would only be consumed in the island where it is generated.

2.2.2. Gasification technologies

There exists a broad range of gasification technologies, being the most relevant reactor designs evaluated by Puig-Arnavat et al. [40]. In [40] the existing biomass gasification models are reviewed and the performance of gasification technologies are evaluated in terms of efficiency and produced gas.

Besides the review on the models, the performed analysis classified the gasification reactors in terms of gasification agent, heat source, gasifier pressure and reactor design. This work considers three of the most recurrent reactor designs: fixed bed, fluidised bed and entrained flow. In Figure 2.6 are schematically represented some of the fixed bed, fluidised bed and entrained flow gasification reactors designs.

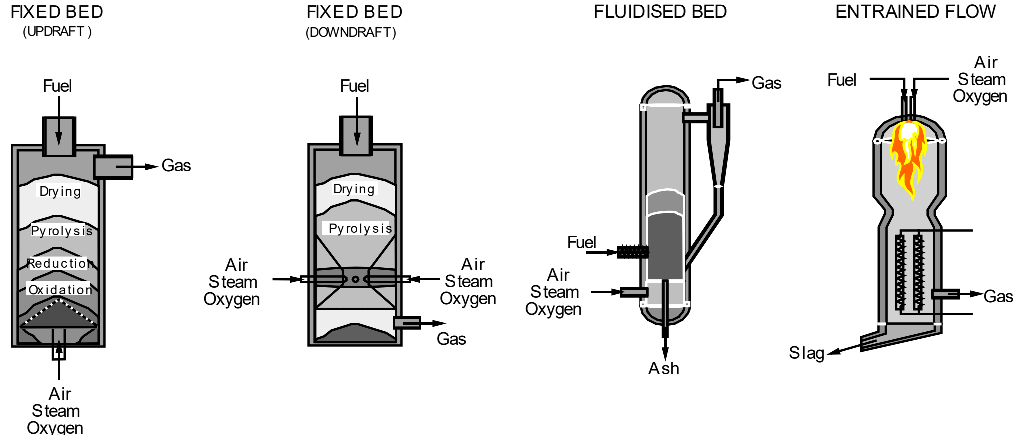

Figure 2.6 – Schematic representation of the fixed bed, fluidised bed and entrained flow gasifiers [41].

Fixed bed gasifiers represent the simplest design and operation principle. These gasifiers can be sub-classified as updraft, downdraft or cross-draft gasifiers, depending on the direction of the biomass and air flows. Its operation principle consists of a bed of solid fuel particles, in this case the biomass, through which the gasifying agent and air is passed. This operation is acknowledged to occur with high conversion of carbon, long solid residence time and low gas velocity [40].

Fluidised bed gasifiers' importance comes mostly due to its high flexibility and efficiency of operation [31],[32]. These gasifiers are sub-classified as bubbling or circulating, according to the type of performed fluidization. Its operation comprises the blowing of the gasifying agent (water, steam or oxygen) through a bed of solid granular material, usually sand, at speeds that promote the state of suspension of the particles. At the same time, fuel (i.e. biomass), is injected in the reactor, mixing with the bed material, reaching the temperature of the bed material almost instantaneously. Consequently, the drying and devolatilization phases occur very quickly, producing a large quantity of gaseous materials [40]. This technology typically operates at the 800-1000ºC temperature range and by this avoiding ash agglomeration [40].

Entrained flow gasifiers have been demonstrated to be unsuitable for biomass due to its restrictions regarding the particle size of the fed material, which is not easily attainable for biomass [41]. Therefore, these gasifiers are mostly used for coal gasification and are proved to be economically favourable for this purpose. Its operation is based on the injection along with the gasifying media of a powdered fuel and is set to occur usually above ash slagging temperatures (1400ºC) and under considerable pressure conditions (20-70 bar) [40]. For feeding purposes within its operation, usually the particulate matter is mixed with water to make a slurry.

Although the fixed bed reactor usually represents a valid option, some of its features, such as its limited capacity and its unsuitability for medium to high moisture biomasses, turn it into an unviable option.

In this regard, the fluidised bed reactors seem to be more suitable for this study, rather than the entrained flow or fixed bed gasifiers reactors. In this sense, the most important features of the fluidised bed gasification reactor, as assessed by Puig-Arnavat et al. [40], are as follows:
- High carbon conversion efficiency;
- Flexibility and ease of operation;
- High fuel flexibility in terms of size and type;
- Possibility of large-scale capacity;
- Very good scale-up potential;
- Good temperature control and high reaction rates.

Motta et al. [44] reviewed the influence of the moisture content of biomass and the operating pressure of fluidised bed biomass gasifiers in the products and efficiency of the gasification process. In this review it was possible do assess that the increase on the pressure conditions of the reactors, in most of the evaluated cases, decrease the syngas H_2 and CO content, although it is recognized that higher yields of the gaseous mixtures are synthetized. Furthermore, there is also pointed that the pressurization of the gasification reactor can create operation difficulties which discourage this practice in this type of reactors.

The synthetized gaseous mixture (syngas) is a relatively known platform chemical as a lot of processes are known in regard of its conversion into other chemical products. The syngas composition resembles the natural gas one, making both processing technologies identical, despite minor adjustments are required.

Hence, for the present study, atmospheric biomass gasification was the chosen technology to be the basis of the synthesis of different chemical products (liquid fuels and materials) and energy, since this is the most appropriate technology for woody biomass.

2.2.3. Syngas processing products

Syngas resulting from gasification possesses a wide range of applications, being the most viable presented in Figure 2.4. Syngas can be used as a fuel itself since it possesses adequate properties to do so, but it can also be reformed to Bio-SNG (bio-synthetic natural gas) to match the characteristics of natural gas and be used as so as chemical platform for other compounds. The production of hydrogen and methanol are established to be the most viable solutions, considering its ease of manufacture and the actual and future market demands, as assessed by the National Renewable Energy Laboratory (NREL) in [45]. In recent years, developments have been occurring concerning the production of liquid fuels, equivalent to conventional diesel, gasoline and kerosene, from biomass. In this sense, the Fischer-

Tropsch (FT) synthesis process has been gaining ground, as it allows the production of hydrocarbon mixtures equivalent to the conventional ones.

As of 2003, methanol was one of the top ten chemicals produced worldwide [45]. Its largest use remains as feedstock for the plastic industry, namely by producing formaldehyde (methanal), polyesters, poly (methyl 2-methylpropenoate), poly(ethene) and poly(propene). Additionally, methanol finds use as a fuel itself (to substitute natural gas or some liquid fuels) as it possesses similar properties to liquified petroleum gas (LPG) or fuel additive to use in conventional engines, by blending with oil-derived fuels. It possesses also the capacity to be a precursor of other fuels and fuel additives, such as gasoline, diesel, dimethyl ether (DME) and other oxygenates (methyl t-butyl ether (MTBE, no longer used for pollution reasons) and t-amyl methyl ether (TAME)). Methanol is also recognized as potential H_2 carrier for future fuel-cell vehicles. Its usage in 2015 is shown in Figure 2.7.

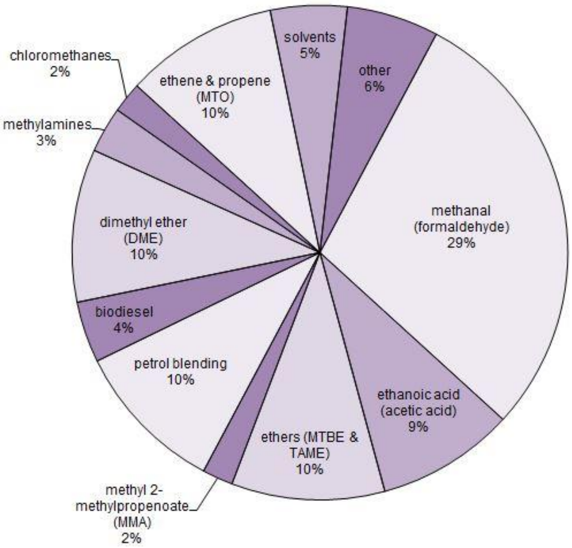

Figure 2.7 – Uses of methanol in 2015 [46].

Methanol manufacture synthesis from natural gas is an already well-established process worldwide, therefore methanol production cost is relatively low, 0.273 € per kilogram [47].

Hydrogen is seen as the fuel of the future as it is a non-toxic “clean fuel” and can be obtained in many ways to fuel internal combustion or fuel-cell vehicles or even turbines designed to run on it. Hydrogen is both a product and by-product as it is currently used on the manufacture of other important chemical materials, such as ammonia and methanol, or even in the processing of other fuels. Hydrogen utilization as fuel comes with various advantages, being the most significant: its high heating value (in a mass basis), its non-toxicity and the fact that its combustion products are mostly water and heat [45].

As of 2016, the 53% of the hydrogen produced was used for the production of ammonia, 20% for refinery processes and 7% for methanol production, while the remaining 20% had other ends [48], as represented in Figure 2.8.

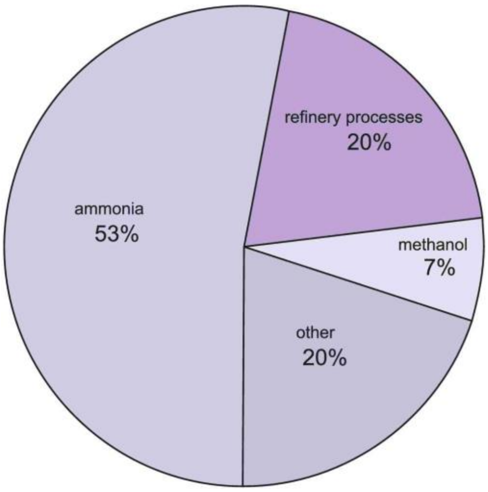

Figure 2.8 – Uses of hydrogen in 2016 [48].

Due to its properties, the production and utilization of hydrogen as a vehicle fuel is not yet economically viable. Some of its drawbacks rely on the way of its transportation and storage. Concerning this, various ways to transport hydrogen in a safer and more controlled way are being studied, being one of the solutions the use of other chemicals as carriers, such as: ethanol, ammonia, etc.

The conversion of hydrogen into ammonia is easily achievable after the hydrogen synthesis. For that is only takes the compression and a few catalytical conversion steps (usually using iron as catalyst). Ammonia is a well-known fertilizer component with global utilization. As of 2016, ammonia was used mostly as fertilizers (85%) in the urea, ammonium salts and ammonium solutions forms. The other 15% are approximately equally divided into three other product streams: nitric acid (5%), polyamides (5%) and other uses [48].

Fischer-Tropsch synthesis (FTS) is a catalytically governed process in which purified syngas is catalytically transformed into a range of hydrocarbons and other products that are lately upgraded and separated. The gas must be fed with a specific H_2/CO ratio that depends on the projected syngas use. The usual recommended values for the H_2/CO syngas ratio for FTS are in the 1.7-2.15 range, but the one resulting from lignocellulosic biomass (LCB) is usually 0.5 (due to large oxygen fraction in the biomass). Therefore, syngas adjustment is usually performed, through water gas shift reaction to promote its increase to suitable values [49].

The products types and yields of the FTS are dependent on the catalysts used (iron or cobalt), as on the reactor's temperature and pressure conditions. The synthetized hydrocarbons are grouped in ranges as come: light hydrocarbons (C_1-C_4); Naphtha (C_5-C_{12}); Kerosene-diesel range fuels (C_{13}-C_{22}); Low-molecular weight waxes (C_{23}-C_{32}); High-molecular weight waxes (C_{33+}).

Besides this, FTS process always, and unavoidably, produces other oxygenated compounds rather than gasoline and/or diesel equivalent liquids. In the case of the diesel equivalent, besides the desired fuel, other compounds, mostly waxes, are produced. In the gasoline case, compounds such as olefins are always produced besides.

After separation, these mixtures of hydrocarbons can be used in the actual infrastructures designed for fossil-derived fuels, without need for modifications, without significant losses of performance. Its utilization is environmentally advantageous not only on the source of the materials but also in its combustion resultant emissions. Due to its chemical composition, these biofuels burning do not produce significant nitrogen or sulphur oxides (NOx or Sox) quantities or even polycyclic aromatic hydrocarbons (PAHs) [50].

Ethanol production is already achievable through syngas fermentation. This, contrary to the fermentation of the LCB sugars, enables to use the whole biomass feedstock, without separation of lignin. However, this process in not yet economically viable [51].

2.3. Gasification and syngas processing modelling

This study is only focused on three of the before mentioned process paths: hydrogen, methanol and Fischer-Tropsch (FT) fuels synthesis. The choice over these products takes into account not only the present and future Azores market demands, but also the remarks on [45], where hydrogen and methanol were named as the most promising paths for future biorefineries.

The proposed plants are modelled using Aspen Plus and the estimation of the production cost of each synthetized product is carried out considering the capital and operational expenditures (CAPEX and OPEX). Thereby, in order to model the different plants, some models found in the reviewed literature were followed.

The model presented in Pala et al. [52] describes biomass steam gasification in a fluidised bed gasifier through six phases in order to replicate the real gasification occurring processes. Different process conditions are tested (steam to biomass ratio, temperature and pressure) and the model results are compared with experimental data obtained from the gasification of different biomass species. The comparisons show that the model data agree reasonably well with the experimental data in terms of quantities and trends. Small deviations (6 to 10%) were observed in the prediction of the production of hydrogen and methane, being the hydrogen yield overestimated and the methane underestimated [52].

Marcantonio et al. [53] studied the gasification of hazelnut shells in a circulating bubbling fluidised bed gasifier using a quasi-equilibrium approach developed in Aspen Plus. The unit integrated with a water-gas shift (WGS) reactor to increase the hydrogen content in the outlet stream and a pressure swing adsorption (PSA) unit for hydrogen separation. The authors simulated the WGS reactor using two WGS reactors, one at higher temperature and another at lower temperature, because this reaction is moderately exothermic and tends to shift to the reactants side at high temperature. The authors concluded that the mole fraction of hydrogen increased about 50% with the integration of the WGS reactor and that the model developed was in good agreement with experimental data report in the literature [53].

Ortiz et al. [54] modelled a methanol production plant based on the syngas resulting from the reforming of glycerol. The objective was to maximize the overall process efficiency in terms of total net power and methanol production, under the constraint of making the overall process energy self-sufficient. The obtained model results could reproduce well the experimental data and model results from the literature in terms of methanol yields (deviations from 2 to 12%) [54].

Pondini and Ebert [55] modelled the FT-fuels synthesis using Aspen Plus, with different plant configurations and correlations obtained from experimental data. The focus of this work was to evaluate the production capacity in terms of products' quality and quantity as a function of the process operating conditions. Despite the substantial amount of assumptions considered on the development of the plant model, the results obtained could predict satisfactory the reality. Nevertheless, deviations from 2 to 20% were found to occur on the estimation of some of the hydrocarbons yields comparing with the experiments [55].

3. Case Study – Autonomous Region of the Azores and S. Miguel Island

Within this chapter it is performed an analysis on the archipelago and the potential island to develop the project, S. Miguel Island. For this purpose, first, the archipelago is evaluated in terms of geography and climate, followed by the current social and economic status assessment. After this, the energy production and demand in the ARA is object of study. Further on, the biomass resources and its exploitation activities in the archipelago are evaluated. Finally, the S. Miguel island status is evaluated, focusing on its current energy scenario, since this island represents the most developed centre so as the second highest availability of biomass resources in the archipelago. This way, this seems to be the preferable location for the projected biorefineries.

3.1. Geography and climate

Azores archipelago, Figure 3.1, is composed of nine volcanic islands and some islets, located in the northeast Atlantic Ocean, in the Macaronesia region. The archipelago is geographically divided in three regions: Occidental (Corvo and Flores Islands), Central (Faial, Graciosa, Pico, S. Jorge and Terceira Islands) and Oriental (Santa Maria and S. Miguel Islands). The Azores archipelago is located in the region delimited by 39°43`34" N (northern point) and 36°55`39" N (southern point). In terms of longitude, the extreme points are -25°00`47" W and -31°16`07" W.

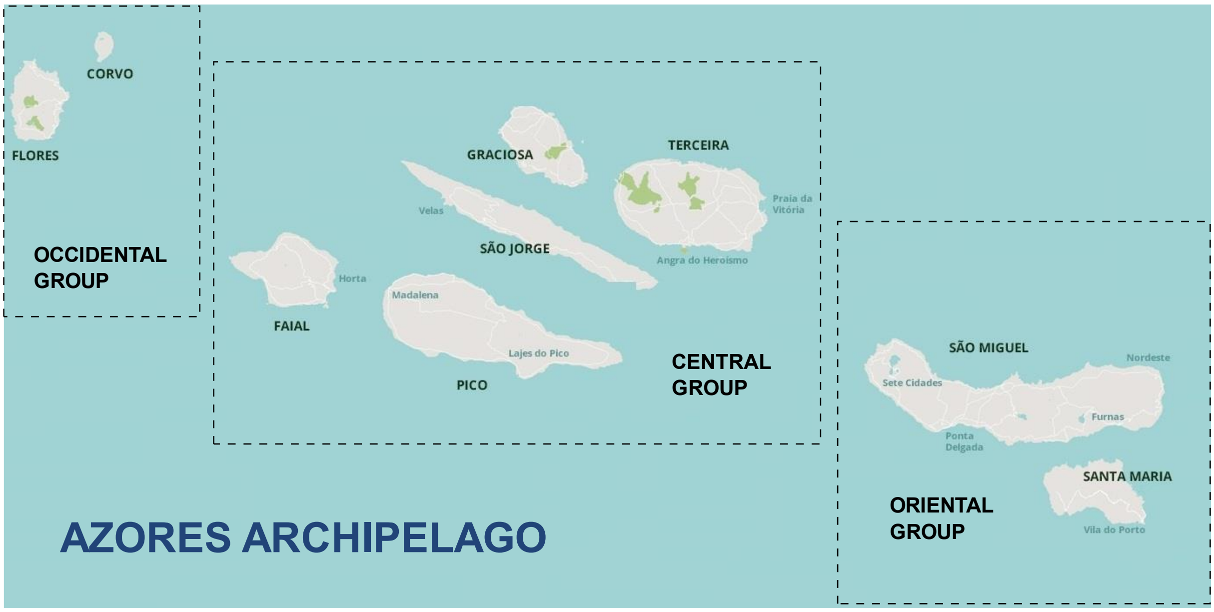

Figure 3.1 – ARA map (distances between groups not at real scale), adapted from [56].

Being an autonomous region of the Portuguese Republic, ARA is an integrated member of the European Union. Due to its relative distance to the continental land (1500 km distance to Europe), Azorean region is recognized as outermost region of the EU. Its distance to North America is more than twice the distance to the European Continent (3900 km).

The total ARA area sums 2322 km^2 being 32% of this area accounted on S. Miguel Island, followed by Pico (19%), Terceira (17%) and S. Jorge (11%) islands [57]. The remaining five islands amount up to 21% of the ARA area.

Distributed along 650 km of length, the nine islands present varied terrain shapes and heights, reaching up to 2351 meters of height in the Pico Island. Due to its volcanic origin, the landscape is very hilly, being the landform coincident with the fault line observed in the region, due to the meeting point of the African and European tectonic plates.

Related to the climate conditions, Azores presents an oceanic climate. For the 2019 period, the mean temperature in all the ARA was 13.8ºC, reaching a maximum 29ºC in August and minimum value of 3ºC in January [58]. The relative humidity of the air is observed to reach mean values close to 80%. Rarely, are observed days where the value is below 50%. In concern of the rainfall, the mean value varies between 700 and 900 mm per year, varying among the islands [59]. The presence of such climate conditions enables the existence of a valuable and unique fauna and flora around the archipelago

3.2. Social and economic context

Apart from its distinct terrain characteristics, the economic and social development among the nine islands also enclosure large discrepancies. As of 2017, there was a total of 243,862 inhabitants [57], over 19 municipalities, divided into 156 parishes. Faial, S. Miguel and Terceira Islands represent the most developed centres, having respectively 14,640, 137,519 and 55,519 inhabitants, comprising 85% (208,265 inhabitants) of the total archipelago population in 2017 [57].

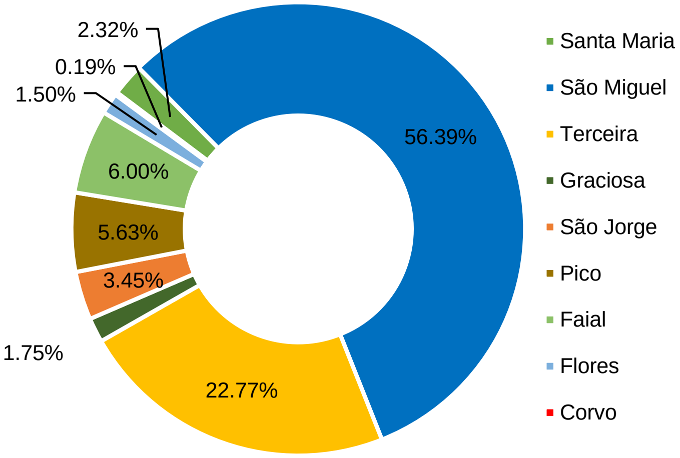

Figure 3.2 – ARA population distribution by island [57].

In the employment sector, as of 2019, from the 113,663 working population, approximately 10% pertain to primary, 17% to secondary and the remaining 73% to tertiary sector activities [60]. The region economy is dominated by services activities, namely the public administration, commerce, transports, and the hospitality sector.

In regard of the remaining economic activities, the islands' main activities are owed to the agriculture and cattle breeding. Cattle and milk production play a large role in the economy of the islands. Indeed, the most exported materials are products from the milk transformation industry. The fishery industry and its conservation, followed by other industries, also play an important role on the economy. Due to its vast Exclusive Economic Zone (EEZ), 984,300 km^2, the Azorean islands present a considerable economical potential on the fishing activities. Hence, it is recognized the current economic growth of this industry [61].

Tourism is also continuously growing and already represents a large share on the economy of the islands. This activity promotes the people and goods flow between islands, besides the development of new services and infrastructures. Hence, in 2017 there were registered approximately 2 million overnight stays in the archipelago [62].

Still in regard of the economy, as of 2016, the gross domestic product (GDP) *per capita* of the archipelago reached 16,136 euros, 89% of the GDP per capita found for the Continental Portugal region. For the same year, the total Azores GDP, 4,128 million euros, only accounted for 2.1% of the total Portugal area GDP (194,613 million euros) [57]. Table 3.1 presents the GDP share distribution per island.

Table 3.1 – Distribution of the archipelago total GDP per island [57].

Santa Maria	S. Miguel	Terceira	Graciosa	S. Jorge	Pico	Faial	Flores	Corvo	Total
2.8%	58.2%	21.5%	1.5%	3.3%	5%	6.2%	1.3%	0.2%	100%

As for chemical industry and related activities, apart from small projects and retail commerce, no relevant activities are known for the archipelago. Nevertheless, the agriculture and forestry sectors are important consumers of chemical products, such as fertilizers or pesticides that presently are mostly imported.

3.3. Energy sector

On account of its vast and varied natural resources availability, the archipelago already presented a large share on renewable electricity consumed (36.6%) in 2017 [2]. Although this value is already above the UE target of 20% for 2020 [4], there is still space for improvement. Presently, the islands still rely much on the importation of fuels to comply with the remaining of the power generation and fuel all the transportation sector.

In regard of the power production, throughout the archipelago a lot of different sources exist. EDA (Electricidade dos Açores) reports that for the 2017 period the electrical production in the region reached 802 944 MWh, whilst the final consumption achieved a total of almost 734 584 MWh [63]. The distribution of the annual accumulated production sources is presented in Figure 3.3.

Apart from the thermal electrical power production via conventional fuels (diesel and fuel oil), a significant portion of renewable wind, solar, hydro and geothermal power is produced, amounting almost 37% of the total annual produced electricity. Related to existence of a triple tectonic plate junction in the region, the geothermal power production becomes a meaningful part of the electricity generation in the islands as shown in the figure above. Currently, only two islands produce electricity by this means, S. Miguel and Terceira.

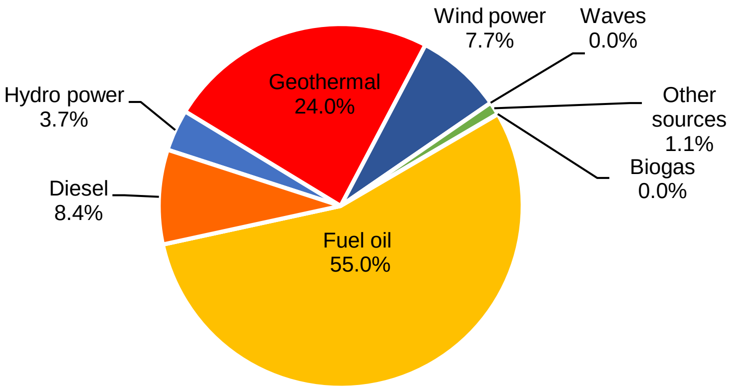

Figure 3.3 – Accumulated production of electricity in ARA in 2017 [63].

Concerning the consumption of electricity, the distribution of end-users is also vast. Following are presented the sectors responsible for the accumulated consumption in 2017, Figure 3.4.

From the chart it is observable that the major consumption sector is the commerce and services one, followed by the domestic sector. Although industry sector share on the total archipelago electricity consumption is reduced when compared with the domestic and commerce and services ones, only 17.7%, it already accounts a significant share on the consumption of some islands [64].

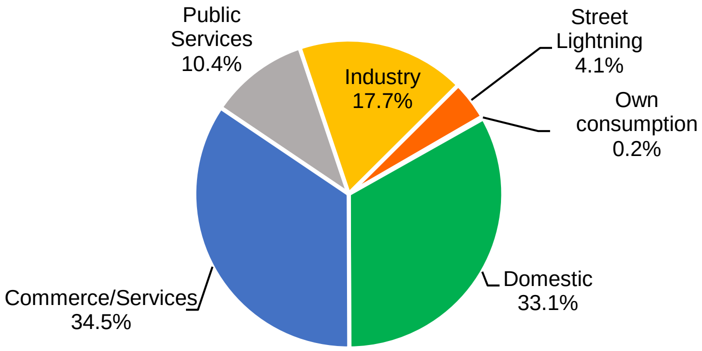

Figure 3.4 – Accumulated consumption of electricity in ARA in 2017, by sector [61].

In Figure 3.5 is presented the distribution of the electricity consumption along the islands. As consequence of the high number of inhabitants and its more developed economies, S. Miguel and Terceira Islands are responsible for 79% of the archipelago consumption as seen above. S. Miguel ensures 55% of the archipelago total consumption, more than two times the value for the Terceira Island, 24%.

Out of the nine islands, only S. Miguel ensures more than half of the electricity production from renewable sources, with a 51% renewable share. The remaining islands burn fuel oil and diesel to produce at least 50% of its electricity demand, being Corvo and Graciosa 100% fossil electricity producers [3].

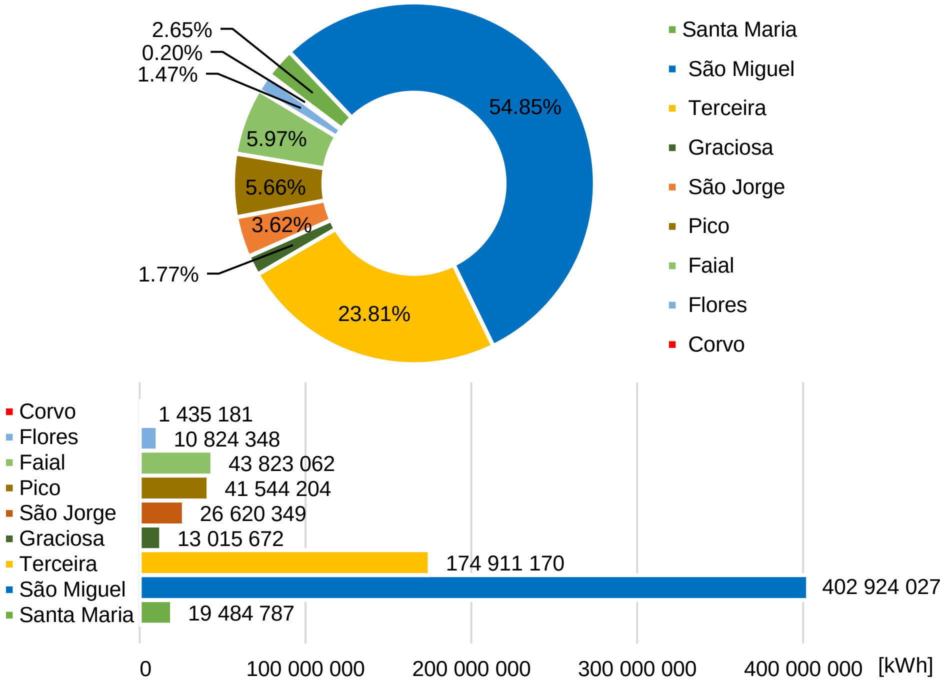

Figure 3.5 – Accumulated consumption of electricity distribution in ARA in 2017 by island [64].

Currently, no natural gas supply is present in the Azores islands, neither do any district heating systems. As consequence, electricity and diesel, fuel-oil and butane fossil fuels play a large role in terms of heating of buildings.

In concern of the oil-derived energy products utilization in the islands, in 2017, the most used was fuel oil, which purposes are mostly electricity production and heating of buildings. For that year, its utilization ascended to 93,362 tons. In the same time period, 16,702 tons of diesel were consumed for the same purposes. In this matter, greases were also used, although in considerably reduced values, 556 tons, as shown in Figure 3.6 [65].

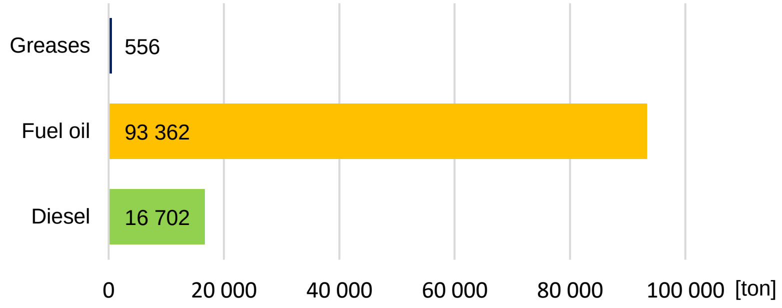

Figure 3.6 – Fuel sales for electricity production and heating of buildings in ARA in 2017 [65].

Following is presented the distribution of fossil fuels in the archipelago (by weight) for the 2017 period [65], Figure 3.7. From the figure is possible to perceive the importance of diesel for the region, not only due to its utilization for transportation, but also for other purposes such as heating and electricity production. Butane also presents an important role in terms of the islands' energy systems, namely for the residential sector.

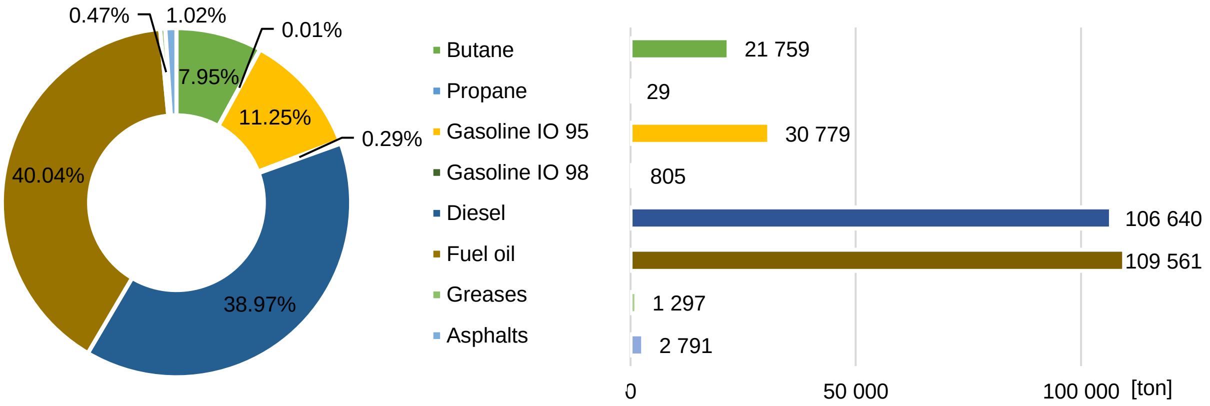

Figure 3.7 – Sales of fuels in ARA (2017) [65].

The islands transportation sector is still totally dependent on fossil fuels. The actual vehicle fleet consists of diesel and gasoline cars. Although more environmentally friendly solutions, like electric vehicles (EV), are completely suitable for the roads and current islands consumers habits, the investment cost is seen as the bottleneck for the transition to occur [17].

The fuel sales for road vehicles for the archipelago for the 2017 period are presented in Figure 3.8. Diesel represents the highest share on the road transportation fuels sales while gasoline numbers are approximately half of the diesel ones, in weight. In regard of ships, boats and other watercrafts, diesel is the predominant fuel. For aircrafts and airplanes, Jet A1 is the preferred option. In this sense, as of 2017, 135 tonnes of Jet A1 were sold [65].

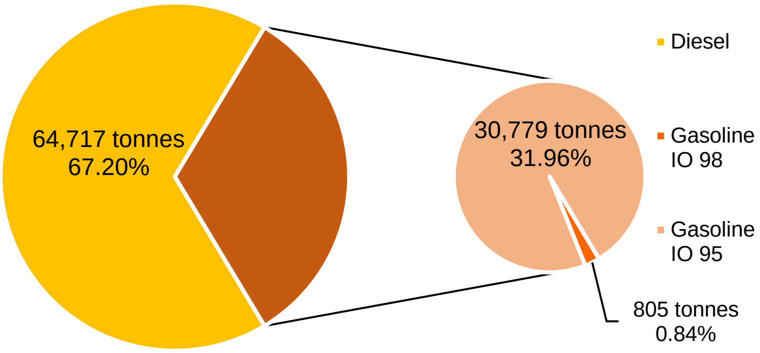

Figure 3.8 – Fuel sales for road transportation vehicles in ARA in 2017 [65].

Since no oil refinery is present in the Azores region, all the fuels are imported from other regions (namely Continental Portugal region), distributed and sold to end-users.

3.4. Biomass resources

The wood industry is a known source of economic revenues for the islands, while responsible for the employment of more than 1400 people. Currently, around the archipelago exist 216 companies of woodwork and 30 of wood exploitation/sawmill. From the first, 40% and 29% of the companies are present in S. Miguel (86) and Terceira Islands (62), respectively. For the second, S. Miguel comprehends 13, while Pico and Terceira each comprehend 8 and 4, respectively, of the total 30 companies around the archipelago. Such wood-related activities are responsible for a 1.8 million euro business volume by the direct wood sales and 10.9 million euro volume of business relative to the transformation sector [66].

The Forest Inventory provided by DRRF (Direção Reginal de Recursos Florestais) [66] shows that 22% of the ARA total area is occupied by forest, corresponding to 493.4 km^2. The region is dominated by five species, that together comprise 96% of its forest area. These five are *Pittosporum undulatum* (48.51%), *Cryptomeria japonica* (26.06%), *Acacia melanoxylon* (8.82%), *Eucalyptus globulus* (7.67%) and *Morella faya* (4.95%).

S. Miguel, Pico and Terceira Islands, are, by far, the islands with largest area occupied by forest spaces with 159.5, 149.2 and 56.9 km^2 each. In percentage, each of them occupies respectively 33%, 31% and 12%, amounting 76% of the total ARA forest area.

In Table 3.2 are summarized the occupied areas by the five most important species in the archipelago. In annex A, Figure A.1, are represented the forest plans for all the islands, considering the dominant species and the domination of land use.

Table 3.2 - Areas occupied by the dominant species in the archipelago by island [66].

Island		Dominant species				
		Acacia melanoxylon	***Cryptomeria japonica***	***Morella Faya***	***Pinus pinaster***	***Pittosporum undulatum***
Corvo	Occupied area (km^2)	-	0.016	0.006	-	0.29
Faial	Occupied area (km^2)	0.001	8.675	1.409	0.044	17.57
Flores	Occupied area (km^2)	0.749	5.479	0.439	-	18.12
Graciosa	Occupied area (km^2)	0.091	0.629	-	0.025	3.42
Pico	Occupied area (km^2)	5.077	8.4	9.562	6.576	117.05
Santa Maria	Occupied area (km^2)	3.078	2.037	-	0.827	11.75
S. Jorge	Occupied area (km^2)	3.248	1.823	10.352	0.203	20.21
S. Miguel	Occupied area (km^2)	29.557	85.405	2.358	0.02	37.50
Terceira	Occupied area (km^2)	1.742	16.099	0.294	1.043	13.48
Total	Occupied area (km^2)	43.543	128.564	24.42	8.738	239.39

As illustrated in Table 3.2, from the five outlined species, three occupy significant higher areas. These three more dominant species (*Pittosporum undulatum*, *Cryptomeria japonica* and *Acacia melanoxylon*) also differ in terms of utilization and commercial value. The most abundant, *Pittosporum undulatum*, is an invasive species that has spread around all the islands, since the 19th century, due to the favourable climate to its proliferation. Its invasive properties make it a problem in terms of infestation and propagation, encouraging its utilization as feedstock for industries. Although its high share on the forest area, its exploitation as wood or fuel is not developed and, derived to that, its use is channelled to other industries, mostly as fertilizer, animal feed and fencing for other cultures.

Cryptomeria japonica, the second most abundant species in the archipelago, is one of the brand images of the region, although its Japanese origin. Its material composition turns it into a preferable raw material for the construction sector and by that its commercial value is considerably high. Its utilization as fuel is not common, but the remaining of its physical processing (sawmill, saw dust, saw shavings, etc.) are seen as a good opportunity. Another issue considering its utilization is the fact that its growth rate is relatively low and approximately 30 years are needed to achieve a choppable tree.

The third, *Acacia melanoxylon*, is mostly used in carpentry and wood industries derived to its chemical and physical favourable properties. Despite its high construction market value, this species possesses an invasive character as the *Pittosporum undulatum* that must be managed. Nevertheless, its occupied area is considerably low compared to the other two species.

In this sense, DRRF regulates the exploitation and utilization of these species to promote their sustainability and prevent the proliferation of some less-desirable species.

Energetic valorisation of these species it not yet a fully implemented reality in the islands. Nevertheless, some of the biomass sub-products are already used to feed boilers in the facilities of some of the plants that process biomass. Other known valorisation process is the production of pellets, that are further sent to Portugal to be sold.

Residue production on island territories is a well-known problem as the isolation and smallness of the islands hinder the residues disposal and/or their potential valorisation. Current policies in the archipelago do not take into consideration the energy potential of organic residues. The current implemented strategy for these residues consists of its collection and further unloading into centres, spread all around the islands, where they are composted by aerobic biodegradation for future use with agricultural purposes [67]. The exception goes for the biogas plant located in S. Miguel that produces not only fertilizer materials, but also biogas which is burned to produce power. This plant makes use of waste streams coming from canned fish and dairy products industries, as from fruits and vegetables that are no longer viable to be sold. Some vegetable oils and animal fats are used too [68].

Hence, the woody biomass represents the most suitable choice from the archipelago resources for energy and chemicals production. Since the acquisition costs of *Cryptomeria japonica* and *Acacia melanoxylon* are prohibitive for its exploitation, as consequence of its potential for other industries, *Pittosporum undulatum* comes as the most viable option. Nevertheless, this species also represents the largest occupied forest area in the archipelago.

In terms of resources availability, the estimates on *Pittosporum undutalum* annual production for the ARA are presented in Table 3.3. These estimates are based on [69] that only accounts 65% of the species occupied area in the territory, considering its sustainable exploitation. The operational waste is considered to be 20% of the available biomass. Also, this approximation only contemplates the islands' areas where *Pittosporum undulatum* was found in pure stands or as the dominant tree.

Table 3.3 – Distribution of the *Pittosporum undulatum* annual wood production by island [69].

Island	Annual wood production (ton dry weight)	Annual operational waste (ton dry weight)	Total annual biomass (ton dry weight)
Santa Maria	5,551	832	6383
S. Miguel	17,513	2,627	20,140
Terceira	6,374	956	7,330
Graciosa	1,618	243	1,861
S. Jorge	9,563	1,434	10,998
Faial	8,314	1,247	9,561
Pico	55,388	8,308	63,696
Flores	8,574	1,286	9,861
Corvo	137	21	158
Total	113,032	16,954	129,986

As shown above, the estimated *Pittosporum undulatum* availability in the archipelago, considering a sustainable utilization, sums up to 130 kilotons per year. This value takes into account the wood and its handling associated waste.

3.5. S. Miguel Island

Projecting the installation of the biorefinery plant in the S. Miguel Island, becomes essential to assess the current scenario in terms of its energy system, apart from its social and economic status. Thereby, following are evaluated the S. Miguel Island energy sector, besides the economic activities inherent to the island.

Figure 3.9 shows the map of S. Miguel Island. S. Miguel is located in the southeast of the archipelago, pertaining to the Oriental group of islands. Its area (747 km^2) is by far the highest in the region and is divided in six counties: Ponta Delgada, Lagoa, Ribeira Grande, Vila Franca do Campo, Povoação and Nordeste. From this area, 159.5 km^2 is occupied by forest, which is the largest forest area over all the archipelago [70].

Figure 3.9 – Map of S. Miguel Island [71].

As above-mentioned, besides the largest area, S. Miguel is also the most populous in the ARA (137,828 of the total 208,265 inhabitants) [57]. The island constitutes one of the most dynamic politico-administrative centres and, by that, currently comprehends the headquarters of the Azorean Regional Government (ARG) [72]. Due to its unique natural landscapes and resources, the island, as much as the archipelago itself, is a tourist attraction that attracts visitors from all the globe. Therefore, the tourism related activities already represent an important portion of the island's activities. Nevertheless, primary sector activities related to agriculture and cattle farming still represent a considerable share on the economic activities of the island.

In 2017, S. Miguel produced almost 434 GWh of electricity, comprising more than 50% of the archipelago produced electricity. Even so, S. Miguel is the only island in the archipelago with a renewable share of electricity production higher than 50%. This is achieved mostly on account of the geothermal power produced in the island, that ascends to 42% of the produced power. The remaining renewable power is produced by wind (3%) and hydro power (6%), while other renewable sources account for 0.15% (such as the biogas facility in the island and photovoltaic panels). The thermal electricity produced is 99,97% based on fuel oil burning, being the remaining 0,03% based on the burning of diesel [63]. In Figure 3.10 is represented the energy production distribution in the island for the 2017 period.

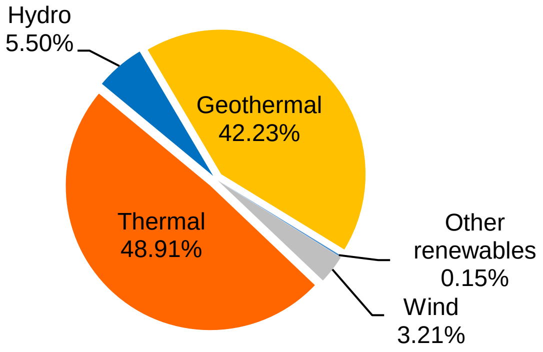

Figure 3.10 – Electricity production sources in 2017 for the S. Miguel Island [63].

As for the consumption of electricity, in 2017, almost 403 GWh were consumed in the island, corresponding to 54% of the archipelago total consumption [3].

Since no significant power storage units exist in the island, there is recognized the existence of periods of overproduction of power in S. Miguel. Moreover, the non-existence of interconnection of energy systems between the Azores islands isolates the islands' power grids. This fact makes it impossible to share some of the surplus produced power.

The handling of residues in the island has been gaining relative importance over the last years. The known challenges around the disposal and treatment of urban and other kind of wastes led to the implementation of numerous measures to assure its valorisation. Reports on the island's residue treatment and disposal suggest that even though the residue production per capita has been increasing in the 2012 to 2018 period, the increase on the valorisation instead of disposal in landfills of such residues is recognized [73].

4. Methods

The present study comprehends the assessment of the available feedstock to feed the installation and the estimates on the production capacities of the plants and the costs of such activities. Hence, the implemented methods to generate estimates on the production capacity and the synthetized materials production costs are presented in this chapter.

First the production capacity is estimated by means of the Aspen Plus V9 simulation tool. After evaluated the yield capacities of the plants, its associated operational and capital expenditures (OPEX and CAPEX) are estimated based on accessed literature and some of the Aspen Plus economical results.

4.1. Aspen Plus modelling

Aspen Plus V9 was chosen to model the operation of the three proposed plants (hydrogen, methanol and FT-fuels. This software is a powerful tool to design and predict real performances of chemical plants in most industry fields, being already highly implemented in the petrochemical industry.

To model each plant, all the components that are involved in the process must be defined. This is achieved by specifying the components from the Aspen Plus database, that are set to figure in the systems, and set which of those are conventional or non-conventional. Due to its non-existence in the database, it is necessary to define the biomass used in the simulation as a non-conventional component and input its chemical composition data in order to fully define its physico-chemical properties. Ash is also considered as a non-conventional component and its ultimate and proximate analysis are set to be 100% ash.

After this, the property method, which produces the properties and equilibrium calculations, is selected. The fluid dynamic package chosen in this study is the Peng-Robinson with Boston-Mathias function (PR-BM), since it is indicated for applications such as gas processing, refinery or petrochemical plants [52], [74], [75].

Finally, the plant is designed using a flowsheet with operation blocks and material and energy streams. At this point, the properties of the feed streams (flow rate, composition and thermodynamic conditions) are entered based on the available biomass resources.

For modelling purposes, the following assumptions are made:

- Processes are in steady state;
- Pressure and temperature conditions uniform inside reactor units;
- Gasification and water-gas shift reactions occur at atmospheric pressure;
- Tar formation is not considered;
- No unconverted carbon is present in the gasification products;
- Char only contains carbon and ash;

- Drying, pyrolysis, partial oxidation and gasification are instantaneous processes;
- Gasification products consist of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), nitrogen (N_2), water (H_2O), ammonia (NH_3) and hydrogen sulphide (H_2S) only;
- The reactors are not adiabatic, but the heat lost to the environment is neglected.

Although tar formation is not considered, it is recognized its formation in the real operation of the gasifier. Nevertheless, its production is projected to be marginal when compared with the syngas. Similarly, the gasification phases are also not instantaneous in the real operation of the reactor. However, the residence time in the reactor is expected to be long enough so that the duration of such phases become almost instantaneous.

Figure 4.1 shows the three different paths and the common processes between them. The three plant configurations analysed comprise four distinct stages: gasification, syngas adjustment, product upgrading and its recovery and energy recovery. From these, the gasification, syngas H_2/CO adjustment and energy recovery are quite similar processes over the three plants, differing only in the process conditions (temperature, pressure and stream flows).

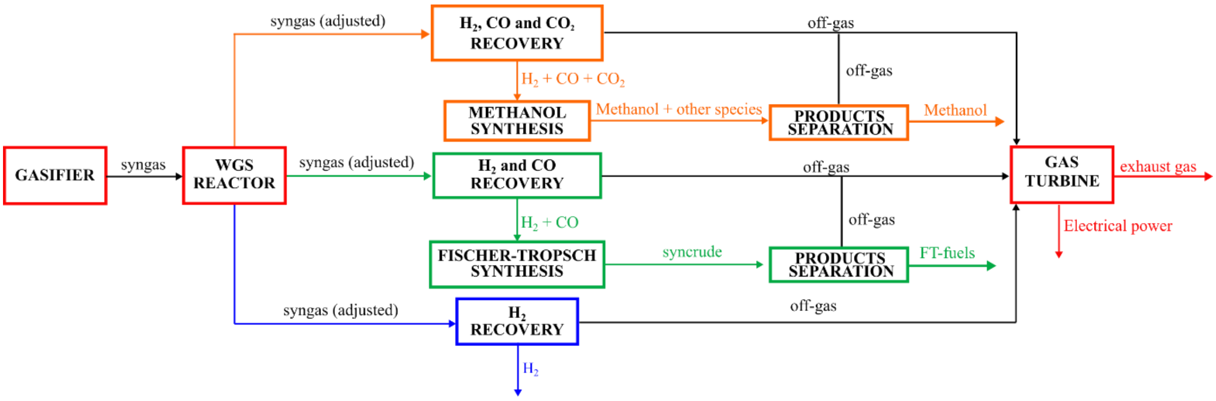

Figure 4.1 – Simplified block diagram of the three plant configurations.

4.1.1. Gasification, water-gas shift reactor, products separation and energy recovery modelling

The modelling of the steam gasification unit followed essentially the work of Pala et al. [52]. Although usual designs ensure the drying of the biomass prior gasification this is not considered in this model. Here, the drying of the biomass occurs through the vaporization of its moisture in the reactors. This way, the energy consumed in the water vaporization is the one that would be consumed in the drying of the fed biomass. Since the vaporized water remains in mixture, it already accounts for some of the steam that would be injected in the real gasifier.

Figure 4.2 presents the flowsheet section of the gasification modelling in Aspen Plus. The biomass stream is directed to the RYIELD block, where the raw biomass is decomposed into the simpler carbon (C), hydrogen (H_2), nitrogen (N_2), oxygen (O_2), sulphur (S), water (H_2O) components and ash.

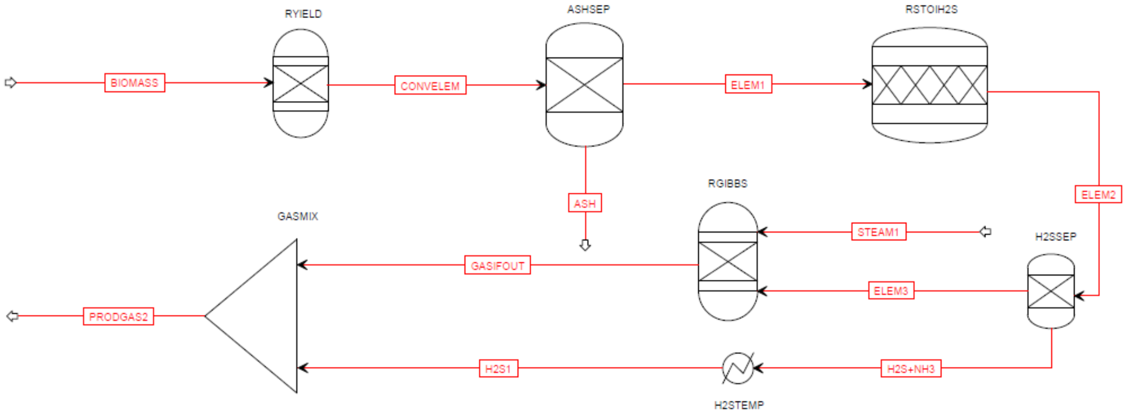

Figure 4.2 – Flowsheet section of the gasification modelling in Aspen Plus.

The products stream from this reactor is determined according to the ultimate analysis of the biomass fed as follows:

$$m_C = (1 - X_{moisture}) \times X_C \times m_{feed} \quad (1)$$

$$m_{H_2} = (1 - X_{moisture}) \times X_H \times m_{feed} \quad (2)$$

$$m_{N_2} = (1 - X_{moisture}) \times X_N \times m_{feed} \quad (3)$$

$$m_{O_2} = (1 - X_{moisture}) \times X_O \times m_{feed} \quad (4)$$

$$m_S = (1 - X_{moisture}) \times X_S \times m_{feed} \quad (5)$$

$$m_{H_2O} = X_{moisture} \times m_{feed} \quad (6)$$

$$m_{ash} = (1 - X_{moisture}) \times X_{ash} \times m_{feed} \quad (7)$$

m_C, m_{H_2}, m_{N_2}, m_{O_2}, m_S, m_{H_2O} and m_{ash} are the produced mass of carbon, hydrogen, nitrogen, oxygen, sulphur, water and ash, respectively, while X is the mass fraction of each component in the fed material. $X_{moisture}$ is the mass fraction of moisture in the raw biomass, and m_{feed} is the mass of the raw biomass.

Subsequently, the ash is separated from the products stream through a simple separator (ASHSEP), that simulates an ash separator, originating an ash-free stream which is directed to RSTOIH2S block. This stoichiometric reactor is responsible for the conversion of all the sulphur into hydrogen sulphide (H_2S) through reaction R9 and half of the nitrogen into ammonia through R10 [76]. The resultant stream, ELEM2, is then directed to a separator where the flow splits into two streams, one with the H_2S and NH_3, and the other with the remaining components (ELEM3). These components are then supplied to the RGIBBS block, where the final gasification step takes place by specifying the most important reactions that occur (R1-R8), at 900ºC. In Table 4.1 are presented the chemical reactions that are set to occur during the gasification process.

Table 4.1 – Chemical reactions inherent to the gasification process.

Reaction	Chemical equation	Reaction name
R1	$C + O_2 \rightarrow CO_2$	Carbon combustion
R2	$C + 0.5O_2 \rightarrow CO$	Carbon partial combustion
R3	$C + CO_2 \rightarrow 2CO$	Boudouard reaction
R4	$C + H_2O \rightarrow CO + H_2$	Water gas reaction
R5	$CO + H_2O \rightarrow CO_2 + H_2$	Water gas shift reaction
R6	$C + 2H_2 \rightarrow CH_4$	Methanation of carbon
R7	$H_2 + 0.5O_2 \rightarrow H_2O$	Hydrogen partial combustion
R8	$CH_4 + H_2O \rightarrow CO + 3H_2$	Steam reforming of methane
R9	$H_2 + S \rightarrow H_2S$	H_2S formation
R10	$1.5H_2 + 0.5N_2 \rightarrow NH_3$	Ammonia formation

As the gasification is assumed to occur in the presence of steam (gasifying agent choice), steam might be injected at this point in the RGIBBS reactor. Next, the resultant gas is mixed with the previously separated H_2S and NH_3 mixture that was heated through the H2STEMP block to reach the same temperature as the GASIFOUT mixture. The resultant stream PRODGAS comes as the final product of the gasification process.

The adjustment of the syngas H_2/CO ratio to its most convenient value, for each of the three processes, is performed in a WGS reactor. To this end, in the Aspen Plus flowsheet, two equilibrium reactors are used (LTWGSR and HTWGSR), as carried out by Marcantonio et al. [53]. These reactors operate at different temperatures, the LTWGSR at 200ºC and HTWGSR at 400ºC, to comply with the results of a real WGS reactor. The residence time in these reactors is assumed to be long enough to allow for the establishment of thermodynamic equilibrium. Similar to the gasification stage, steam is injected in the reactor in order to obtain higher yields of hydrogen, by promoting the WGS reaction (R5). Figure 4.3 presents the flowsheet section of the WGS reactor in Aspen Plus.

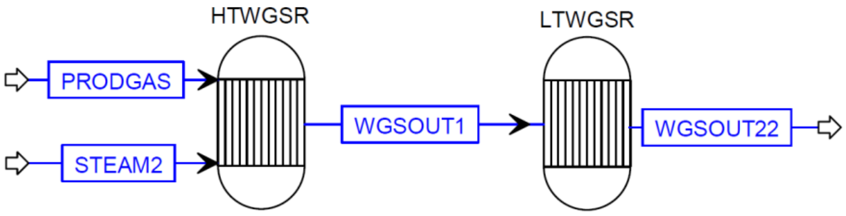

Figure 4.3 – Flowsheet of the WGS reactor in Aspen Plus.

Since the Aspen Plus software does not have a separation unit that operates as a PSA reactor, to recover the desired components, its implementation in the flowsheet requires the simplified use of a simplified separator. To this purpose, the separator recovery capability is set to be similar to a real context PSA reactor (Figure 4.4). The capacities of the PSA for H_2 recovery were based on the values indicated by Sentis et al. [77], while for the CO and CO_2 capture were based on the values specified by

Ortiz et al. [54]. Since the separator block used do not represent the real operation (high- and low-pressure conditions variation), the energy analysis requires an estimation of the power consumption based on the study of Ishibashi et al. [78], who considered that a PSA unit for CO_2 recovery consumes 0.62 kW per kilogram of recovered CO_2. The same approach is used in this study for the three PSA units in the three plants. For these PSA units, the consumption of power is considered to be of 0.62 kW per kilogram of recovered species (H_2, CO and CO_2).

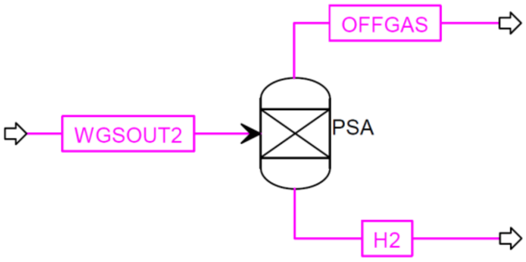

Figure 4.4 – Flowsheet section of the PSA reactor modelling in Aspen Plus.

In order to allow for the recovery of the heat released from the hot streams of each plant, the Aspen energy analyzer (AEA) is used. This tool provides the most suitable ways to recover and direct heat from the different streams and estimate the available energy savings (heating and cooling needs).

Besides the AEA, steam turbine and gas turbine systems are also considered to recover power from the hot streams. The produced power is intended to cover the power needs of the system and, if exceeded, be sold to the power grid to be a source of revenue. The steam used for power production is the produced steam that is not injected into the system. The turbines and compressors were modelled as isentropic, assuming isentropic and mechanical efficiencies of 0.85 and 1 [79], respectively.

Other Aspen Model Analysis Tools are used in design phase, namely the Optimization tool. The three plant configurations are established to attain the best results according to the settled goals. The settled goals are as follows:

- To maximize the products yields (H_2, methanol and FT-fuels) in each plant;
- To attains maximum energy efficiency for all processes;
- To reduce the water consumption and, if possible, not to consume more than the produced one;
- To promote the self-sustainability of the plant regarding energy consumption;
- To maximize the power production.

Through this, the input streams conditions as the settings of some of the reactors are shifted in ranges of values that promote the best results for the plant operations.

4.1.2. H_2 synthesis

Hydrogen can be synthetized through different processes, being the most recurrent the water hydrolysis and the fossil fuels reforming. These processes comprehend the hydrogen separation from other chemical elements, which is not always economically viable. That way, biomass-derived syngas might represent an effective alternative to these processes.

Figure B.1, in annex B, represents the designed flowsheet in Aspen Plus for the hydrogen synthesis plant. As shown, this plant requires a unique PSA unit for the hydrogen recovery and separation after the WGS reactor, which is simulated by the pair of LTWGSR and HTWGSR blocks. A simplified separator block (PSA) is used with the recovery capacity according to Sentis et al. [77]. The remaining syngas is then compressed and directed to a gas-turbine to produce power. Prior to combustion of the syngas, water is removed from the off-gas stream, through a flash separator (WATSEP), to achieve higher combustion efficiency. Some of the recovered water is then redirected to the system being injected as steam in the prior process steps, namely the gasification step and WGS reactor. Figure 4.5 represents a simplified block diagram of the designed system.

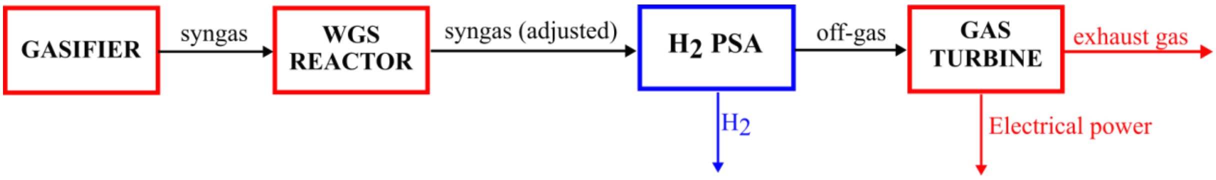

Figure 4.5 – H_2 synthesis plant block diagram.

4.1.3. Methanol synthesis

The most recurrent methanol synthesis from syngas process occurs through a Cu-based catalyst. It is usually used for reformed natural gas, but it might be applied to the biomass-derived syngas. From this process are co-produced DME, methane, methyl formate, higher alcohols, acetone and other in even small quantities.

The designed Aspen Plus flowsheet concerning the methanol synthesis is presented in Figure B.2, annex B. As illustrated, to produce methanol (CH_3OH), after the syngas adjustment, the stream leaving the WGS reactor (LTWGSR and HTWGSR system) goes into a series of three PSA reactors, promoting the recovery of H_2, CO and CO_2 (PSA1, PSA2 and PSA3, respectively).

To maximize the methanol yield a stoichiometric number (SN) of the gaseous mixture $\left(\frac{[H_2]-[CO_2]}{[CO]+[CO_2]}\right)$ has to be equal to 2-2.1 [54], which implies that some of the produced CO_2 must be removed through a flow splitter (CO2SPLIT). The resulting mixture (MIXGAS1, containing mostly H_2,CO and CO_2) is then compressed and fed to a stoichiometric block reactor (METHSYNT) where the reactions in Table 4.2 take place in decreasing order of magnitude, from reaction R11 to reaction R17, according to Trop et al.

[80]. Table 4.2 presents the reactions that occur in the reactor METHSYNT and the CO and CO_2 fractional conversion set for each of the occurring reactions.

Table 4.2 – Chemical reactions occurring in the METHSYNT reactor.

Reaction	Chemical equation	Fractional conversion
R11	$CO + H_2 \rightarrow CH_3OH$	0.355 (CO)
R12	$CO + H_2O \rightarrow CO_2 + H_2$	0.018 (CO)
R13	$C + CO_2 \rightarrow 2CO$	0.178 (CO_2)
R14	$2CO + 4H_2 \rightarrow CH_3CH_2OH + H_2O$	0.0009 (CO)
R15	$CO + 3H_2 \rightarrow CH_4 + H_2O$	0.0005 (CO)
R16	$3CO + 6H_2 \rightarrow CH_3CH_2CH_2OH + 2H_2O$	0.0004 (CO)
R17	$2CO + 3H_2 \rightarrow CH_4 + H_2O$	0.00007 (CO)

Although other species are known to be synthetized during this process, those are not considered due to their marginal quantities.

Although CO_2 does not take part in most of the above-mentioned reactions, CO_2 acts as promoter of other reactions through R13. In addition, the presence of CO_2 in the reactor ensures the catalyst longevity by not allowing carbon deposition by means of the R13 in the inverse direction [54].

The resulting stream from the methanol synthesis block (METHNOL1) consists of new formed species (methanol, ethanol, dimethyl ether and water) and unconverted species (CO, CO_2 and H_2). The separation of methanol from the stream occurs via distillation, which is simulated in the flowsheet through a distillation column (DISTILL1) and a flash separator (FLASHSEP). The remaining off-gas (PURGEGAS) is then mixed with the unabsorbed syngas (OFF-GAS4) and subsequently burned in air to produce power in a gas turbine. The developed plant block diagram is presented in Figure 4.6.

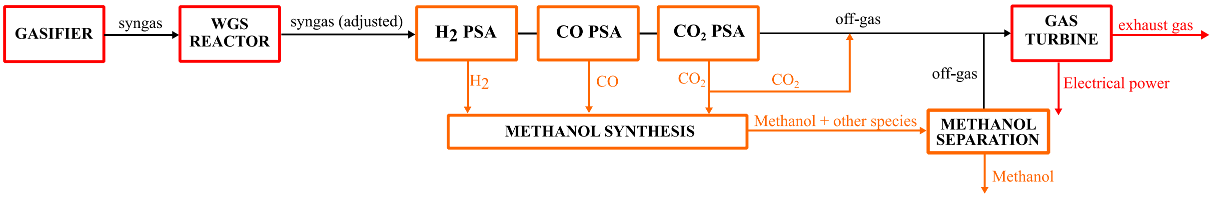

Figure 4.6 – Methanol synthesis plant block diagram.

4.1.4. FT-Fuels synthesis

The FTS process is a catalytically governed and highly exothermal process in which purified syngas is fed to a reactor where it is transformed into a range of fuel products that are lately upgraded and separated. The major reactions that occur in the FTS are the methanation and synthesis of paraffins, olefins and alcohols. The type of products and its yields depend on the utilized catalysts (most used are iron- or cobalt-based), as on the reactor's temperature. High temperatures (300-350ºC) are mostly used for production of C_3-C_{11} olefins (with low molecular weight), in the presence of an iron (Fe) catalyst, which are further on reformed (oligomerization, isomerization or hydrogenation) to a gasoline equivalent mixture. Low temperatures conditions (200-240ºC) are known to maximize C_{20+} waxes yield (with cobalt or iron catalysts), that after hydrotreated are transformed into a diesel equivalent fuel [81].

In annex B, Figures B.3 and B.4, are represented the two flowsheets designed for the FT fuels synthesis regarding the two scenarios considered. As demonstrated in both flowsheets, after the syngas adjustment in the WGS reactor, two PSA reactors are designed to recover H_2 and CO separately (PSA1 and PSA2) and then mixed (SYNGAS1). This mixture H_2/CO molar ratio must be close to 2.15, as indicated by van Steen and Claeys [82], in order to maximize the hydrocarbons yield. The resulting stream is then compressed and directed to a reactor block (FTREACT) where the FT fuels synthesis is set to occur, by setting the products distribution.

To model the complex hydrocarbons synthesis that occurs in the FT reactor the following additional assumptions are considered:

- The Anderson-Schulz-Flory (ASF) ideal product distribution model [83], the alpha parameter correlation [84] for a cobalt-based catalyst, and the O/P distribution [85] are used;
- FT products are only paraffins, olefins, water and unconverted syngas;
- Only linear hydrocarbons are formed;
- No oxygenates or other products are produced besides hydrocarbons and water;
- Highest hydrocarbon carbon number is thirty (C_{30});
- Oxygen only participates in reactions that form H_2O;
- Recirculation of syngas occurs to increase the CO conversion.

To estimate the FT reactor composition of the stream leaving the FT reactor (SYNCRUDE), a CALCULATOR block was designed in an Excel spreadsheet. This spreadsheet calculates the reactor outlet stream conditions by inputting the temperature and pressure of the reactor and the molar composition of the incoming stream. The calculations follow the ASF distribution, the alpha correlation method and the O/P distribution. CO conversion is set to be 0.93 according to [86].

Then, the Aspen Plus model variables are exported to the Excel flowsheet and, after doing the calculations, the results are imported to the Aspen Plus environment by means of the reactor products distribution. The used Excel flowsheet is presented in annex B, Figure B.5.

Since diesel range hydrocarbons are preferable in this study, given the higher market demand of diesel in the region and its less pollutant behaviour as fuel [50], the FT synthesis process conditions must be adjusted. In this sense, low temperatures (200-230ºC), along with the utilization of a cobalt-based catalyst in the process, are the major features of the process to consider.

After synthetized, the syncrude stream (SYNCRUDE) is directed to a three-outlet flash separator to separate the water from the liquid hydrocarbons stream (FTL) and the unconverted syngas (plus some of the C1-C4 gases). Following this, three distillation columns (DEST1, DEST2 and DEST3) are settled to promote the separation and recovery of the desired hydrocarbons. This combination of distillation columns allows to separate the hydrocarbons in gasoline (C_5-C_{10}), kerosene (C_{10}-C_{13}), diesel (C_{14}-C_{20}) and waxes (C_{21}-C_{30}), as considered in Pondini and Ebert [55].

The unavoidably produced waxes are conducted to a hydrotreatment unit, simulated by a RStoic block (HYDCRACK), where its hydrocracking is performed to increase the desired higher diesel yields. This hydrotreatment occurs through the injection of H_2, separated from the PSA outlet stream. The needed amount of hydrogen is considered to be 0.06 kg per kg of wax [87] ,while the hydrocracking reactions set to occur are based on the work of Jiang et al. [88], through a Pt/ZSM-5/SSMF catalyst. Following [88], the hydrocracking is set to catalytically convert 60% the long-chain paraffins (C_{20+} waxes) into hydrocarbons with half of the carbon atoms, as shown in R18 and R19. R18 occurs for hydrocarbons with even carbon number, $n,$ while R19 is set for odd n numbers.

$$C_nH_{2n+2} + H_2 \rightarrow 2C_{n/2}H_{n+1} \qquad \text{(R18)}$$

$$C_nH_{2n+2} + H_2 \rightarrow C_{(n+1)/2}H_{n+1} + C_{(n-1)/2}H_{n+1} \qquad \text{(R19)}$$

The resultant stream (HC14-30) is recirculated, while some of the wax (10%) is purged. The off-gas stream, consisting of C_1-C_4 gases, unconverted syngas and some remaining water is then fed to a gas turbine for power production. The resultant hot combustion gases then allow heat recovery through a heat exchanger, producing steam to be directed to steam turbine. For this plant, the simplified block diagram is presented in Figure 4.7.

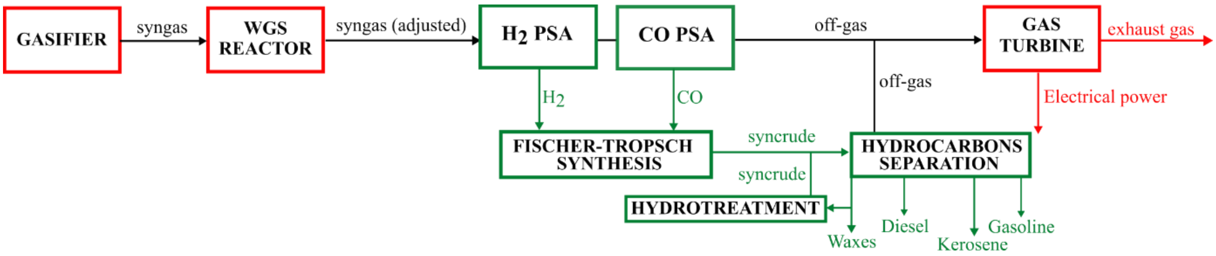

Figure 4.7 - FT fuels synthesis plant block diagram.

This plant is designed to produce the maximum amount of fuels possible with the available biomass, but since it produces three different liquid fuels and one of them (kerosene) has a quite low demand in Azores (about 135.3 ton/year), two different scenarios are considered. The first scenario considers the use of the excess kerosene produced in relation to the demand for power production within the plant, while the second scenario considers the exportation of this excess kerosene. As illustrated in Figures B.3 and B.4, the only difference between the two plants in the flowsheets' designs is the implementation of a flow splitter (KERSPLIT) that separates the kerosene set for the Azores demand (KEROSEN2) and channels the remaining (KEROSEN3) to be mixed with the off-gas for further burning.

4.2. Energy and exergy efficiency analysis

The energy and exergy efficiencies of the three different plants are also estimated in this study. Energy efficiency is defined as:

$$\eta = \frac{\dot{E}_{output}}{\dot{E}_{input}} \times 100\% \qquad (8)$$

where $\dot{E}_{output}$ is the sum of the power produced and the synthetized products heating value ($\dot{m}_{chemical} \times LHV_{chemical}$) and $\dot{E}_{input}$ is the sum of the consumed power and the heating value of the fed biomass ($\dot{m}_{biomass} \times LHV_{biomass}$). LHV is the lower heating value and its values for the synthetized chemicals are taken from [89]. To estimate the LHV of the biomass Eq. 9 is used [90].

$$LHV_{biomass} = (0.3393\, X_C) + \left[1.443\left(X_H - \frac{X_O}{8}\right)\right] + (0.01494\, X_N) - 21.97\, X_H \quad (9)$$

where X_C, X_H, X_O, X_N are the mass fractions of carbon, hydrogen, oxygen and nitrogen of the biomass, as in Equations 1 to 7.

The exergy efficiency, in turn, is defined as:

$$\varepsilon = \frac{\dot{Ex}_{\text{products}}}{\dot{Ex}_{\text{biomass}}} \times 100\% \qquad (10)$$

where $\dot{Ex}_{\text{products}}$ is the sum of the exergy rate of the products, each calculated by multiplying their specific exergy (kJ/kg), taken from the Aspen Plus results, by their mass flow rate (kg/h), and $\dot{Ex}_{\text{biomass}}$ is the (chemical) exergy rate of the input biomass given by:

$$\dot{Ex}_{\text{biomass}} = \beta \times LHV_{\text{biomass}} \times \dot{m}_{biomass} \qquad (11)$$

where [90]:

$$\beta = \frac{1.044 + 0.016\frac{X_H}{X_C} - 0.3493\frac{X_O}{X_C}\left(1 + 0.0531\frac{X_O}{X_C}\right) + 0.0493\frac{X_N}{X_C}}{(1 - 0.4124)\frac{X_O}{X_C}} \qquad (12)$$

4.3. Cost analysis

The total investment cost of each equipment ($Cost_{NEW}$) is estimated using the following equation [71],[79]:

$$Cost_{NEW} = Cost_{REF} \times \left(\frac{Scale_{NEW}}{Scale_{REF}}\right)^{fs} \times \frac{CEPCI_{2018}}{CEPCI_{REF}} \qquad (13)$$

This value is based on the cost of the equipment available in the literature, $Cost_{REF}$. In order to take into account the difference in scales of the equipment used in this work ($Scale_{NEW}$) and that in the literature ($Scale_{REF}$), a scaling factor (f_S) is considered. Finally, to adjust the estimation of the costs, the Chemical Engineering Plant Cost Indexes (CEPCI) from the case considered in the literature ($CEPCI_{REF}$) and the most recent value ($CEPCI_{2018}$) are considered [93]. These average annual values consider the developments in the chemical industry and the evolution of the inflation rate.

The total investment cost of each equipment is multiplied by the installation factor (f_I) to obtain the CAPEX, i.e.:

$$CAPEX = Cost_{NEW} \times f_I \qquad (14)$$

which considers the costs associated with the site installation of the equipment, including piping and electrical setups.

For the equipment that Aspen Plus provides real cost estimates, the installation factor is already accounted for and there is no need for further adjustments, and thus the installation factor is 1.

The gasifier investment cost already takes into account the start-up of the system, namely the gasifier start-up by external means, consequently, its installation factor is 1.

The scales, scale factors, investment costs, installation factors and CEPCI available in the literature of the different equipment are presented in Table B.1, in Annex B. The value for $CEPCI_{2018}$ is 603.1 [93].

The OPEX is estimated using the following equation:

$$OPEX = O\&M + BC + EC \qquad (15)$$

where O&M are the operation and management costs, considered as 4% of the equipment's investment cost, BC are the biomass costs, including its acquisition and its transportation (maritime and terrestrial transportation), and EC are the costs related to the electricity demand of the plant.

The fuel production cost (FPC) in each plant is calculated through:

$$FPC = \frac{CAPEX \ . \ CRF \ + OPEX - ER}{FP} \qquad (16)$$

where ER are the electricity revenues from the selling of the excess electricity to the power grid, FP is the yearly fuel production, and CRF is the capital recovery factor used to annualize the investment costs, i.e.:

$$CRF = \frac{i \times (1+i)^l}{(1+i)^l - 1} \qquad (17)$$

where i is the discount rate and l is the equipment lifetime - these values are assumed 10% [91] and 20 years [94], respectively. Table 4.3 presents the values necessary to estimate the OPEX and the ER. For the EC, the power tariffs of Azores are considered, for ER, the tariff of Continental Portugal for the selling of power produced from biomass to the grid is considered.

Table 4.3 **-** Tariffs considered to estimate OPEX and ER.

Cost category	Tariff	Source
Raw biomass + delivery (by land)	20 €/ton	[30]
Biomass maritime transportation	58.24 €/ton	[95]
Power purchased from the grid	0.0941 €/kWh	[32]
Power sold to the grid	0.0855 €/kWh	[96], [97]

In regard to the biomass costs, the biomass maritime transportation is only considered when the biomass is collected in islands other than the one where the plant is located.

Although three different fuels are synthetized in the FT-fuels plant, the same approach is used. In this way the resulting FPC is the minimum selling price for the three synthesized fuels, which would make the plant economically viable if all were sold at the same price.

4.4. Sensitivity analysis

Since the tariffs for the purchase of biomass and its transportation can vary significantly, a sensitivity analysis is carried out with these variables. In this analysis, the variables range from 50% to 150% of the reference values. Furthermore, the possibility of the implementation of the biorefinery facility in other island of the archipelago is also assessed, since it promotes different costs regarding the maritime transportation of biomass. For the analysis on the implementation in other islands, apart from the production cost, also the viability of the plants' operations is evaluated, comparing such operations with the current energy scenario in the islands.

In addition, a sensitive analysis is performed for some of the PSA technology variables that affect the production and consequently the costs of the synthetized products. Between these, were evaluated the influences of the PSA hydrogen recovery, ranging from the reference value (70%) to the value referred by Gutierrez Ortiz et al. [54] (95%), and the PSA reactors power consumption, ranging from 50% to 150% of the considered reference value. Besides the production costs, the sensitivity analyses carried out also comprises the analysis on the influence of such shifts on the energy and exergy efficiencies of the plants.

4.5. Scenarios considered

This work considers the synthesis of different chemical products that have different uses and purposes, projecting the synthetized materials to the Azores market.

In regard of the hydrogen production, the estimated synthetized hydrogen is set to be used as fuel for the future scenario where hydrogen-fuelled vehicles replace the conventional fuelled ones, or at least part of them. In this sense, the hydrogen plant is desirable for a near future, where hydrogen can play an important role in the transportation sector of the islands.

Concerning the methanol production, methanol finds its use as a fuel itself, but mostly as a chemical precursor. Although yet not a very developed process, methanol is also recognized as a possible future hydrogen carrier for fuel-cell vehicles. Methanol fuel properties are similar to the liquified petroleum gas (LPG), having half the heating value of gasoline [45]. Also, its possibly of use as a fuel additive is known. Methanol utilization for the synthesis of other chemical products is by far its most relevant feature. The synthesis of chemicals for the plastic industry is currently the most chosen option, although the synthesis of fuels such as gasoline and dimethyl ether (DME) are also recognized as valid options [45]. Since currently no methanol is known to be consumed in the islands, the produced methanol will be exported. Nevertheless, the potential implementation of such industries in the archipelago might legitimate future projects, contributing for the economic development of the territory and reduction of the external materials dependency. In addition, this would be achieved while taking advantage of a natural resource that currently does not have a relevant use.

Finally, FT-fuels such as diesel, gasoline and kerosene are vital in the current energy context of the archipelago. Hence, these will be consumed internally, in the archipelago, replacing fossil fuels. Since the FT-fuels plant produces simultaneously diesel, gasoline and kerosene, and this last fuel has a rather small demand in Azores, two scenarios are considered that differ in the way the excess kerosene produced is handled, as mentioned earlier. In this first scenario, the excess kerosene is used for power production within the plant, and in the second scenario, the excess kerosene is exported.

On the possibility of producing surplus electricity in the plants, since there is no interconnection between the islands' power systems, this electricity will be used only in the island where the biorefinery is installed.

The outputs of each biorefinery plant and their possible applications in the archipelago context are summarized in Table 4.4.

Table 4.4 **-** Outputs of each biorefinery plant considered and their possible applications.

Output	Potential application	Azores context
Hydrogen	• Transportation fuel • Fertilizers synthesis	• Conventional fuels replacing in a near future • Production of fertilizers for local consumption
Methanol	• Intermediate for potential chemical industry • Production of fuels	• Production of currently imported chemical products • Potential synthesis of fuels for the region (DME, gasoline, others) • Exportation to other areas with known consumption
FT-fuels	• Transportation fuels	• Oil-derived fuels substitution (gasoline, diesel and kerosene) • Surplus kerosene to power production (Scenario 1) or exportation (Scenario 2)
Surplus power	• Electricity production	• Renewable energy production

5. Results and discussion

This chapter presents and discusses the results for this study. Initially, there are presented the results for the reference case scenario for each of the modelled plants. The viability of each of the plants are then evaluated in terms of its products market value and demand in the Azores archipelago, considering the results of its production capacities and production costs, following the methodology introduced in Chapter 4. Subsequently, the results of the inherent power production or consumption of each of the plants are also evaluated by comparing with the current power production and consumption in the ARA. Following, the sensitivity analysis results are presented, addressing variables that concern the operational costs and the systems' performances, such as: the biomass cost; biomass transportation (terrestrial and maritime) cost; installation of the biorefinery in other Azorean island; PSA reactors performance (hydrogen recovery and power consumption). The results are then compared to reference scenario ones, performing a comprehensive analysis on the results for the energy and exergy efficiencies, the production capacities, the power consumption or production capacities and the FPC. Finally, the results of the reference case scenario and the sensitivity analysis are discussed.

As mentioned earlier, the woody biomass used to feed the system is *Pittosporum undulatum*, an invasive species with no commercial use. Table 5.1 shows the chemical properties of this specie.

Table 5.1 - *Pittosporum undulatum* chemical characterization [98].

Ultimate Analysis (wt.%, db*)		Proximate Analysis (wt.%, db*)		Heating Value (MJ/kg, db*)
Carbon	49 - 68	Ash content	0.9 - 1.1	19.6 - 20.4
Hydrogen	2	Volatile matter	81.1	
Nitrogen	0.9	Fixed carbon	18	
Oxygen	34 - 43.2			
Sulphur	4	Moisture	46 - 47	
Ash	0.9 - 1.1			

*db – dry basis

The mass flow rate for the biorefinery plants is approximately 16.25 ton/h. This value corresponds to the utilization of 130 kton per year, which obeys to a sustainable exploitation approach [26] of the *Pittosporum undulatum* biomass available in the archipelago (Table 3.3). The estimation of mass flow rate considers an annual load of 8000 hours, being the remaining hours of the year for the plant maintenance. Consequently, the biomass yearly costs amount to 9 M€ per year.

5.1. Biomass gasification and handling processes

Since the same amount of biomass is utilized for the three different biorefinery plants, the biomass handling and processing prior the gasification and the gasification itself are similar processes for all the plants. This way, the scale of the equipments for the processing of the raw biomass is identical for all the evaluated plants. Table 5.2 presents the scale of the equipments for the biomass processing and gasification.

Table 5.2 – Equipment's scale for the raw biomass processing and gasification.

Equipment	$Scale_{NEW}$
Biomass reception and unloading	16.25 wet ton/h
Biomass storage, preparation and feeding	16.25 wet ton/h
GTI gasifier, gas cooling and gas cleaning, including scrubber	88.46 MW

5.2. Hydrogen synthesis plant

The hydrogen synthesis plant does not require heating or cooling through external sources, being self-sufficient, according with the AEA tool. The total water injected into the system is equal to the recovered one, avoiding thereby the need for external sources of water. Table 5.3 shows the modelling results for this plant. It is observed that this plant is able to produce more electricity than it needs, allowing for the selling of the surplus electricity to the power grid.

The surplus electricity (Table 5.2) can cover 23.9% of S. Miguel's yearly fossil fuel thermal power production. This value is about 11.68% of the total yearly power production of this island.

Table 5.3 **-** Modelling results of the hydrogen plant.

Hydrogen plant	Modelling annual results
Hydrogen production (ton)	5,485.3
CO_2 emissions (ton)	126,027
Electricity consumed (MWh)	23,178
Electricity produced (MWh)	73,823
Surplus electricity (MWh)	50,645
Energy efficiency (%)	59
Exergy efficiency (%)	14

In Table 5.4 and Figure 5.1 the distributions of the electricity consumption and production in each equipment of the hydrogen biorefinery plant for a one-year period of operation are presented. The higher share of electricity consumption is due to the compressing of the off gas, while the higher electricity production comes from the gas turbine operation.

Table 5.4 – Yearly electricity consumption and production in the hydrogen plant.

Hydrogen plant equipment	**Annual electricity consumption (MWh)**
H_2 PSA	3,401
Off-gas compressor	19,727
Water pumps	49.9
Hydrogen plant equipment	**Annual electricity production (MWh)**
Steam turbine	11,266
Gas turbine	62,558

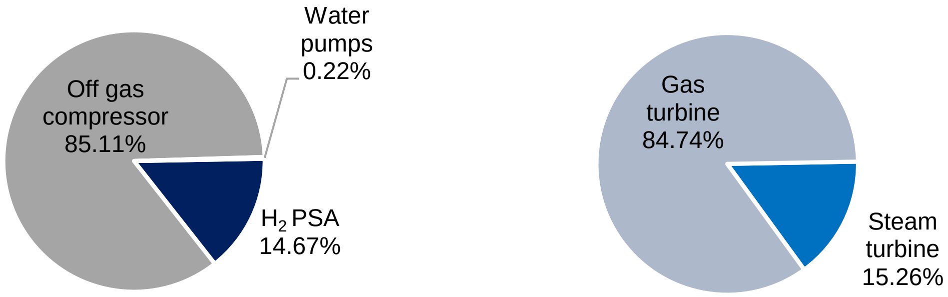

Figure 5.1 – Yearly electricity consumption and production shares in the hydrogen plant.

In order to assess the impact on the transport sector of the yearly hydrogen production of the plant, bearing in mind that hydrogen fuelled vehicles are not yet a reality in any of the islands, an evaluation is carried out considering the travelled distance by all the existing light-duty vehicles. For this, the current yearly distance travelled by the light-duty vehicles in Azores is estimated. For this estimation, data from 2017 is used and the following assumptions are made:

- The heavy-duty, industrial and agricultural vehicles in the archipelago [99] are diesel fuelled and are not considered in this study;
- The gasoline and diesel running vehicles shares in Azores are assumed equal to those in Continental Portuguese region [100], considering that there are no LPG running vehicles in the islands;
- The travelled distance/vehicle.year is taken from of Baptista et al. [17].

As result, the mean daily distance travelled by the light-duty vehicles is 63 km/vehicle.day. From these, the gasoline-fuelled vehicles travel 42 km/vehicle.day and the diesel ones 74 km/vehicle.day. The islands’ gasoline light-duty vehicle fleet is estimated to be of 39 340 vehicles, while the diesel fleet amount 82 285 vehicles.

The travelled distance per kg of hydrogen is considered 82 km, based on estimates of NREL [101]. Hence, considering the yearly hydrogen produced in the proposed plant, 16% of the current travelled distance by all light-duty vehicles would be covered. If only diesel vehicles are replaced with hydrogen, it would be possible to cover 20.3% of the distance, while for the gasoline case it would cover 74.8%.

Table 5.5 shows the scale of the equipment for the hydrogen plant used to estimate the CAPEX, and Table 5.6 shows the energy and water recovery equipment costs estimated by the Aspen Plus. The CAPEX of the proposed hydrogen plant amounts to 129 M€, and the yearly OPEX amounts to 13 M€ (being 9 M€ due to the biomass). The revenues of the surplus power selling to the grid amounts to 4.3 M€ per year.

Table 5.5 - Equipment's scale for the hydrogen plant.

Equipment	$Scale_{NEW}$
Biomass reception and unloading	16.25 wet ton/h
Biomass storage, preparation and feeding	16.25 wet ton/h
GTI gasifier, gas cooling and gas cleaning, including scrubber	88.46 MW
WGS reactor	550.79 kmol/h*
H2 PSA	340.14 kmol/h*
Steam turbine	1.66 MW
Gas turbine	7.82 MW

*Output stream.

Table 5.6 - Energy and water recovery equipment costs estimated by Aspen Plus.

Equipment	CAPEX (€)
Heat Exchangers, Coolers and Heaters	685,929
Pumps	87,178
Water recovery - Flash vessel	164,619

The FPC obtained for the hydrogen synthesis is 4.36€/kg. This value is 48% to 60% of the United States hydrogen retail price (7.28 to 9.10 €/kg) foreseen for the 2020-2025 period [102]. This FPC for hydrogen results in a cost of 0.053 € per travelled km, considering the assumptions made for the hydrogen fuel economy. Comparing to the current Azorean context, this represents 53% of the current cost for the light-duty gasoline vehicles (0.10 €/km).

The specifications of the main units used in the simulation of this plant are presented in Table C.1, Annex C.

5.3. Methanol synthesis plant

The methanol synthesis plant can be self-sustainable in terms of cooling and heating needs according with the AEA tool. Table 5.7 shows the modelling results for this plant. In contrast with the hydrogen plant, this plant requires power from the grid.

Also contrary to the hydrogen plant, the methanol synthesis plant does not need steam injection due to the high moisture content of the raw biomass. This allows for enough hydrogen recovery, without further steam injection in the gasification or WGS reactors. A gas turbine and a steam turbine are used to produce power that is able to cover 97% of the plant's power demand. The remaining electricity (5,550 MWh per year) is acquired from the grid and it is estimated to amount 1% of the current annual produced electricity in the S. Miguel Island [63].

Table 5.7 - Modelling results of the methanol plant.

Methanol plant	Modelling annual results
Methanol production (ton)	11,201
CO_2 emissions (ton)	110,599
Electricity consumed (MWh)	159,736
Electricity produced (MWh)	154,186
Electricity from the grid (MWh)	5,550
Energy efficiency (%)	38
Exergy efficiency (%)	26

In Table 5.8 and Figure 5.2 the distributions of the electricity consumption and production in each equipment of the methanol biorefinery plant for a one-year period of operation are presented. The higher share of the electricity consumption is relative to the PSA equipment, while the higher electricity production comes from the gas turbine operation. Nevertheless, the electricity consumption regarding the syngas compression covers a high share on the total consumption of the plant as well.

Table 5.8 – Yearly electricity consumption and production in the methanol plant.

Methanol plant equipment	Annual electricity consumption (MWh)
H_2 PSA	3,957
CO PSA	14,638
CO_2 PSA	45,352
Syngas compressor	36,203
Off gas compressor	59,507
Water pumps	71.2
Methanol plant equipment	**Annual electricity production (MWh)**
Steam turbine	29,106
Gas turbine	125,080

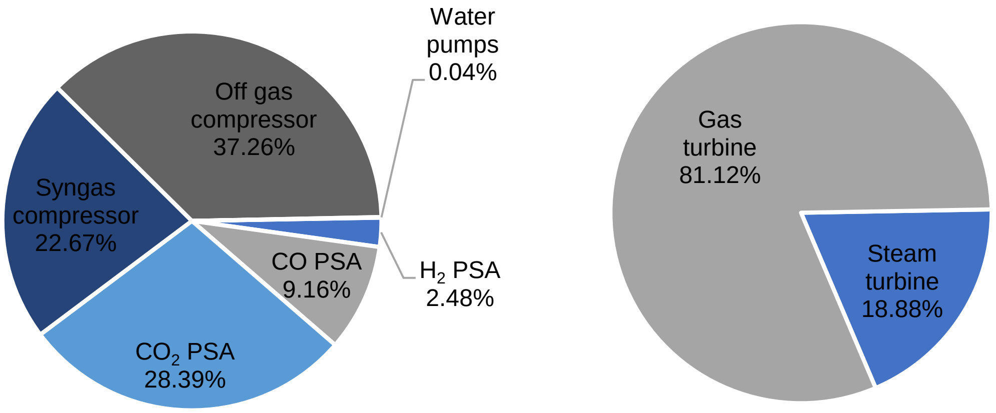

Figure 5.2 – Yearly electricity consumption and production shares in the methanol plant.

Table 5.9 shows the scale of the equipment for the methanol plant used to estimate the CAPEX. Note that the equipment related with the biomass handling and gasification is the same for the three plants – see Table 5.2. Table 5.10 shows the energy, water and methanol recovery equipment costs estimated by the Aspen Plus.

The CAPEX of the proposed methanol plant amounts to 157 M€, and the yearly OPEX amounts to 14.49 M€ (being 9 M€ due to the biomass).

The FPC obtained for the methanol synthesis is 2.90 €/kg. This value is eleven times higher than the market price (0.273 €/kg) for the European region in 2020 [103].

Table 5.9 - Equipment's scale for the methanol plant.

Equipment	$Scale_{NEW}$
WGS reactor	550.74 kmol/h*
H_2 PSA	306.43 kmol/h*
CO PSA	110.71 kmol/h*
CO_2 PSA	192.06 kmol/h*
MeOH Synthesis	1.4 ton/h*
Syngas compressor	4.52 MW
Recycle compressor	3.64 MW
Steam turbine	15.63 MW
Gas turbine	550.74 kmol/h*

*Output stream.

Table 5.10 - Energy, water and methanol recovery equipment' costs estimated by Aspen Plus.

Unit	CAPEX (€)
Heat Exchangers, coolers and heaters	1,927,771
Pumps	138,138
Water recovery - flash vessel	88,270
Methanol separator - flash vessel	125,398
Distillation column	271,544

The specifications of the main units used in the simulation of this plant are presented in Table C.2, Annex C.

5.4. FT-Fuels synthesis plant

According with the AEA tool, the FT-fuel synthesis plant is self-sustainable in terms of heating needs but not in terms of cooling needs. It requires 8.65 MW of cooling. Table 5.11 shows the modelling results for this plant. It is seen that the first scenario's plant is able to produce more electricity than it needs, while the second scenario one requires power from the grid. The surplus electricity (Table 5.11), in the first scenario, can cover 11.2% of S. Miguel's yearly fossil fuel thermal power production. This value is about 5.5% of the total yearly power production of this island. The electricity consumption in the second scenario corresponds to 0.3% of the current electricity production in the island [63].

The diesel and gasoline annual production covers 6.6% and 10.5% of the current Azores fuels' demand, respectively [104]. The first scenario allows for the complete replacement of the current kerosene demand in the islands, while the second scenario allows to exceed this demand and to produce a surplus of 4152.7 ton of kerosene to export.

Table 5.11 - Annual production capacities estimates for the both scenarios of FT-fuels plants.

Modelling annual results	First scenario	Second scenario
Gasoline produced [ton]	3,320	
Diesel produced [ton]	4,184	
Kerosene recovered [ton]	135.3	4,288
CO_2 emissions [ton]	101,854	88,968
Electricity consumed [MWh]	75,796	74,431
Electricity produced [MWh]	99,634	72,953
Electricity from the grid [MWh]	-	1,478
Surplus electricity [MWh]	23,838	-
Energy efficiency (%)	44	39
Exergy efficiency (%)	34	35

In Table 5.12 and Figures 5.3 and 5.4 the distributions of the electricity consumption and production in each equipment of the FT-fuels biorefinery plants for a one-year period of operation are presented. For both scenarios, the higher share of the electricity consumption is relative to the compression of the off gas, while the higher electricity production comes from the gas turbine operation. Nevertheless, the electricity consumption regarding the PSA reactors operation covers a high share on the total consumption of the plant as well.

Table 5.12 – Yearly electricity consumption and production in the methanol plant.

FT-fuels plant equipment	Annual electricity consumption (MWh)	
	First scenario	Second scenario
H_2 PSA	2,908	
CO PSA	19,994	
Syngas compressor	17,450	
Off gas compressor	27,665	36,384
Water pumps	56.4	76.3
FT-fuels plant equipment	**Annual electricity production (MWh)**	
	First scenario	**Second scenario**
Steam turbine	11,416	13,571
Gas turbine	60,286	86,064

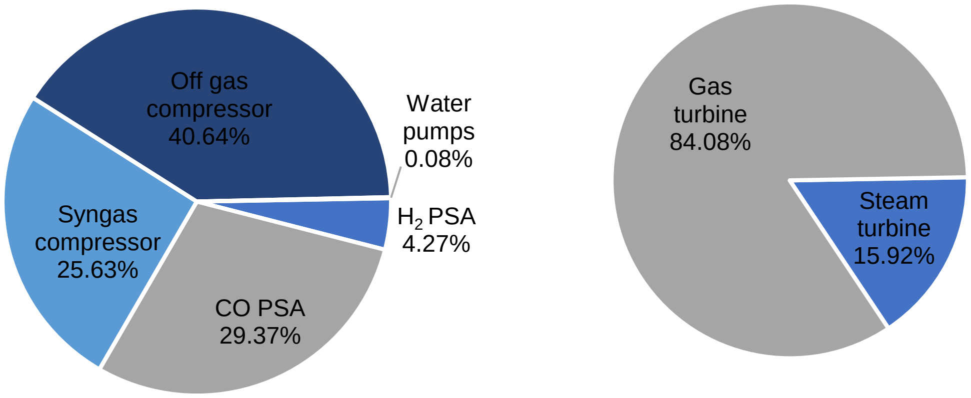

Figure 5.3 – Yearly electricity consumption and production shares in the FT-fuels plant (first scenario).

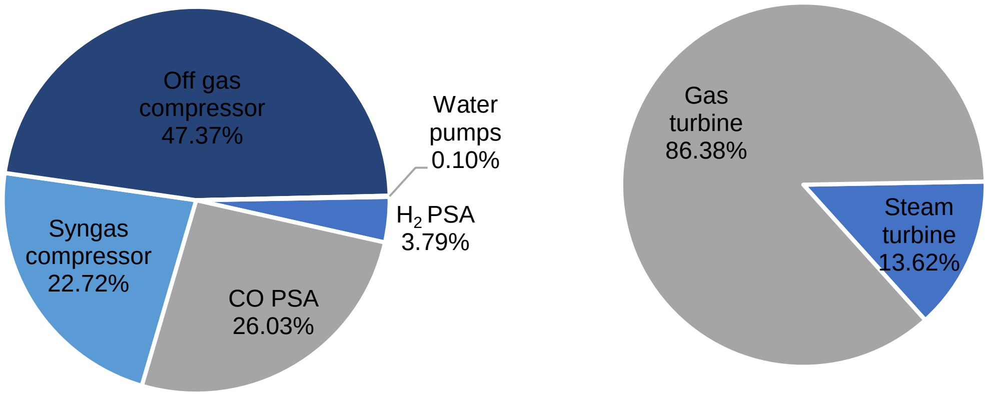

Figure 5.4 – Yearly electricity consumption and production shares in the FT-fuels plant (second scenario).

Table 5.13 shows the scale of the equipment for the FT-fuels plant used to estimate the *CAPEX*, and Table 5.14 shows the energy, water and hydrocarbons' mixtures recovery equipment costs estimated by the Aspen Plus.

The *CAPEX* of the proposed FT-fuels plant amounts to 201 M€ in the first scenario and to 203 M€ in the second scenario. The yearly *OPEX* amounts to 16.1 M€ in the first scenario and to 16.4 M€ in the second scenario. For the first scenario, the revenues of the surplus power selling to the grid amounts to 2 M€ per year.

The *FPC* obtained for the FT-fuels synthesis is 4.91 €/kg in the first scenario and 3.39 €/kg in the second scenario. Both values are significantly higher than the Azores retail fuel prices (1.92 €/kg for gasoline, 1.55€/kg for diesel [55] and 0.53 €/kg for kerosene [56]).

Table 5.13 - Equipment' scale for the FT-fuels plant.

Unit	$Scale_{NEW}$	
WGS reactor	550.03 kmol/h*	
H_2 PSA	290.87 kmol/h*	
CO PSA	136.71 kmol/h*	
Selexol unit (acid gas removal)	9.61 tonCO_2/h	
FT synthesis	11.26 MW	
Initial fill of FT catalyst	11.26 MW	
Syngas compressor	3.65 MW	
Recycle compressor	3.65 MW	
Scenario	First scenario	First scenario
Steam turbine	2 MW	1.7 MW
Gas turbine	10.76 MW	7.7 MW

*Output stream.

Table 5.14 - Energy, water and hydrocarbons' mixtures recovery equipment' costs estimated by Aspen Plus.

Equipment	Investment costs (€)
Heat Exchangers, Coolers and Heaters	1,610,136
Pumps	108,472
Water recovery - Flash vessel	128,900
Distillation column (1)	501,300
Distillation column (2)	748,100
Distillation column (3)	748,100
C1-C4 hydrocarbons recovery – Flash vessel	107,600

The specifications of the main units used in the simulation of both plants are presented in Table C.3, Annex C.

5.5. Sensitivity analysis

In this section are presented the results of the performed sensitivity analysis. These results comprise the evaluation on the biomass and its transportation costs effects on the FPC for each of the plants, the evaluation of the possibility of implementation of the biorefinery in other island of the archipelago and the analysis on different operation performances of the PSA reactors in each of the plants.

5.5.1. Hydrogen biorefinery sensitivity analysis

The results of the sensitivity analyses carried out for the biomass and its transportation costs are shown in Tables 5.15 and 5.16. Table 5.17 concerns the sensitivity analysis regarding the price of purchasing biomass and its maritime transportation, and its impact on the hydrogen FPC. It is observed that all values considered give hydrogen production costs below its foreseen market value.

All the considered values for the biomass transport costs result in a hydrogen production cost below its market value, varying between 3.54 and 5.18 €/kg.

Table 5.15 - Sensitivity analysis of the biomass and its transportation costs for the hydrogen production plant.

Price of biomass (€/ton)	Maritime transportation costs (€/ton)	FPC (€/kg)	FPC variation (%)
10	29.12	3.54	-19
	58.24	4.12	-5
	87.36	4.71	8
20	29.12	3.78	-13
	58.24	4.36	-
	87.36	4.94	13
30	29.12	4.01	-8
	58.24	4.60	5
	87.36	5.18	19

Table 5.16 shows the results of the possible implementation of the biorefinery in different islands of the archipelago. The implementation of the biorefinery in Terceira or S. Miguel Islands would allow to cover 35% or 23.9% of the current thermal electricity production, while for the remaining Azores islands would be possible to reach a 100% RES in terms of electricity production, completely replacing the current thermal electricity production. From these, the Pico island is the only one where the FPC would be lower than for the S. Miguel island case. For this case, the FPC value would be 4.15 €/kg. Although economically viable for all the islands, for seven of them surplus power would be produced, that finds no way to be distributed to other islands, and consequently is lost. In this regard, the Pico Island results are shown to be the most promising, since it would allow to decrease the FPC while completely replacing the thermal electricity production. Nevertheless, 19% of the annual produced electricity in the plant would not find use.

Table 5.16 – Sensitivity analysis of the implementation of the hydrogen synthesis plant in different islands.

Island	Electricity production / Island's thermal electricity production	FPC (€/kg)	FPC variation (%)
Santa Maria	263%	5.00	12
S. Miguel	23.9%	4.44	-
Terceira	35%	4.58	3
Graciosa	355%	5.12	15
S. Jorge	199%	4.85	9
Faial	114%	4.57	3
Pico	124%	4.05	-9
Flores	835%	5.16	16
Corvo	3089%	5.34	20

Table 5.17 presents the results concerning the sensitivity analysis on the hydrogen recovery and electricity consumption of the PSA technology for the hydrogen synthesis plant.

The results show that by considering a higher hydrogen recovery (95%) than for the reference case (70%) it would be possible to obtain 36% more hydrogen per year, being able to cover 28% of the actual distance travelled by diesel-fuelled vehicles, or 102% of the gasoline-fuelled ones, while producing 11.42 of the actual thermal produced electricity. Furthermore, the range of FPC values for hydrogen would be from 3.41 to 3.47 €/kg and the exergy efficiency would increase to 19%.

By considering higher electricity consumption by the PSA, the revenues from the selling of electricity to the grid would decrease, which would promote the increase of the FPC and the decrease of the energy efficiency of the plant.

Table 5.17 – Sensitivity analysis of the performance of the PSA reactor of the hydrogen plant.

PSA hydrogen recovery	PSA electricity consumption (kW/kg)	Synthetized product (ton/year)	Electricity production / Island's thermal electricity production	FPC (€/kg)	Energy efficiency (%)	Exergy efficiency (%)
70%	0.31	5,485	24.7%	4.33	60	14
	0.62		23.9%	4.36	59	
	0.93		23.1%	4.39	59	
95%	0.31	7,444	12.4%	3.41	68	19
	0.62		11.3%	3.44	68	

	0.93		10.2%	3.47	68	

Therefore, all the assessed cases result in production costs for the hydrogen synthesis plant that are considerably lower than foreseen market value for the 2020-2025 period. Hence, the plant is proven to be economically viable even for the least favourable case, where its FPC reaches 5.34 €/kg.

5.5.2. Methanol biorefinery sensitivity analysis

Table 5.18 shows the results of the sensitivity analysis carried out on the price of purchasing biomass and its maritime transportation, and its impact on FPC. It is seen that all values considered originate methanol production costs that range from 1.69 to 2.17 €/kg, which are higher than its market value.

Table 5.18 - Sensitivity analysis of the biomass and its transportation costs for the methanol plant.

Price of biomass (€/ton)	Maritime transportation costs (€/ton)	FPC (€/kg)	FPC variation (%)
10	29.12	2.50	-14
	58.24	2.78	-4
	87.36	3.07	6
20	29.12	2.61	-10
	58.24	2.90	-
	87.36	3.18	10
30	29.12	2.73	-6
	58.24	3.01	4
	87.36	3.30	14

In Table 5.19 is presented the sensitivity analysis of the possibility of installation of the biorefinery for methanol synthesis in other islands of the archipelago. The results show that the production costs would only decrease if the plant was installed in the Pico Island, although this would result in a FPC of 2.67 €/kg, still higher than its market price. Furthermore, the implementation of such plant in the Pico Island would require up to 12% of the current total electricity produced in the island which might become prohibitive for the project.

Table 5.19 – Sensitivity analysis of the implementation of the methanol synthesis plant in different islands.

Island	Electricity consumption / Island's total electricity consumption	FPC (€/kg)	FPC variation (%)
Santa Maria	26%	2.97	2
S. Miguel	1.3%	2.90	-
Terceira	3%	2.96	2
Graciosa	39%	2.99	3
S. Jorge	19%	2.94	2
Faial	11%	2.95	2
Pico	12%	2.67	-8
Flores	46%	2.95	2
Corvo	338%	3.00	4

Table 5.20 shows the sensitivity analysis on the hydrogen recovery and electricity consumption of PSA technology for hydrogen recovery of the methanol synthesis plant. Considering a higher recovery of hydrogen (95%), the methanol yield would increase 14% and the electricity consumption of the plant would decrease, although not considerably. The results show that the decrease on the electricity consumption of the PSA reactors to a 0.31 kW per kg of recovered species could lead to the plant self-sustainability in terms of electricity consumption. This way the plant would produce surplus electricity that would be sold to the grid. By that, the FPC would decrease to 2.65 and 2.29 €/kg and the energy efficiency would increase to 46% and 41%, for the 70% and the 90% recovery of hydrogen cases, respectively. By increasing the electricity demand of the PSA reactors, the electricity demand of the plant would increase and by that represent up to 9% of the S. Miguel Island electricity produced, which can be challenging and potentially unviable for the operation of the plant. Moreover, the FPC would increase to 3.17 and 2,76 €/kg and the energy efficiency decrease to 41% and 37%.

Table 5.20 - Sensitivity analysis of the performance of the PSA reactors of the methanol synthesis plant.

PSA hydrogen recovery	PSA electricity consumption (kW/kg)	Synthetized product (ton/year)	Electricity consumption / Island's total electricity production	Electricity production / Island's thermal electricity production	FPC (€/kg)	Energy efficiency (%)	Exergy efficiency (%)
70%	0.31	11,201	-	12.5%	2.65	46	26
	0.62		1.3%	-	2.90	44	
	0.93		8.7%	-	3.17	41	
95%	0.31	12,789	-	14.3%	2.29	41	29
	0.62		0.8%	-	2.52	39	
	0.93		8.5%	-	2.76	37	

Nevertheless, for all the evaluated cases, the FPC values for methanol are still considerably high when comparing with its market price. Consequently, the plant is proven to be economically unviable.

5.5.3. FT-Fuels biorefinery sensitivity analysis

Table 5.21 presents the results of the sensitivity analysis carried out on the price of purchasing biomass and its maritime transportation, and its impact on FPC. For both scenarios, it is seen that all values considered give fuels production costs substantially higher than its market values, ranging from 4.32 to 5.50 €/kg and 3.00 to 3.76 €/kg, for each of both scenarios.

Table 5.21 - Sensitivity analysis of the biomass and its transportation costs for the FT-fuels plant.

Price of biomass (€/ton)	Maritime transportation costs (€/ton)	First scenario		Second scenario	
		FPC (€/kg)	FPC variation (%)	FPC (€/kg)	FPC variation (%)
10	29.12	4.32	-12%	3.00	-12%
	58.24	4.74	-3%	3.27	-4%
	87.36	5.16	5%	3.54	5%
20	29.12	4.49	-9%	3.11	-9%
	58.24	4.91	0%	3.39	-
	87.36	5.33	9%	3.65	8%
30	29.12	4.66	-5%	3.22	-5%
	58.24	5.08	3%	3.49	3%
	87.36	5.50	12%	3.76	11%

In Table 5.22 are presented the sensitivity analyses considering the possible installation of the biorefinery for FT-fuels synthesis in other islands of the archipelago. As the results show, the only island where its implementation would decrease the FPC would be the Pico Island, reducing by 7 and 76 the FPC for the first and second scenarios, respectively. Regardless, for the first scenario, the plant would allow to replace different shares of each of the islands' current thermal electricity demand, replacing 100% in four of these islands. For the second scenario, the implementation of such plant in the Pico island would require 3% of the island's current electricity production.

Table 5.22 – Sensitivity analysis of the implementation of the FT-fuels synthesis plant in different islands.

Island	First Scenario			Second Scenario		
	Electricity production / Island total electricity production	FPC (€/kg)	FPC variation (%)	Electricity consumption / Island thermal electricity production	FPC (€/kg)	FPC variation (%)
Santa Maria	124%	5.07	3%	7%	3.46	2%
S. Miguel	11%	4.91	-	0%	3.39	-
Terceira	16%	5.01	2%	1%	3.46	2%
Graciosa	167%	5.16	5%	10%	3.48	3%
S. Jorge	94%	4.98	1%	5%	3.44	1%
Faial	53%	4.99	2%	3%	3.44	2%
Pico	58%	4.58	-7%	3%	3.18	-6%
Flores	393%	5.19	6%	12%	3.44	1%
Corvo	1454%	5.31	8%	90%	3.49	3%

Table 5.23 presents the sensitivity analysis on the hydrogen recovery and electricity consumption of the PSA for hydrogen recovery technology for the FT-fuels synthesis plant for both the scenarios evaluated. The increase of the recovery of hydrogen by the PSA would increase the gasoline, diesel and kerosene yields for the same biomass input. Nevertheless, the recovered kerosene would be set to match the Azores consumption. In this sense, for a 95% recovery of hydrogen, the produced diesel would cover 8% of the current diesel demand in the archipelago and the produced gasoline cover 13% of the current gasoline demand [104]. For the first scenario, although the plant would consume higher electricity, the FPC would decrease, ranging from 4.05 to 4.29 €/kg. Consequently, the energy would increase to values ranging from 39% to 42%, while the exergy efficiency would increase to 42%. The increase on the electricity consumption of the PSA reactors would translate into lower electricity productions and even, for the cases of 0.93 kW/kg (considering a 95% of hydrogen recovery), promote the need to acquire electricity from the grid for its operations.

For the second scenario, even though the plant would consume higher electricity by recovering more hydrogen in the PSA (95%), the FPC would decrease, ranging from 2.80 to 2.98 €/kg. Consequently, the energy would increase to values ranging from 45% to 48%, while the exergy efficiency would increase to 44%. The increase on the electricity consumption of the PSA reactors would translate into lower electricity productions and even, for the cases of 0.31 kW/kg (considering a 95% of hydrogen recovery), promote the need to acquire electricity from the grid for its operations.

Table 5.23 - Sensitivity analysis of the performance of the PSA reactors of the FT-fuels plant.

PSA hydrogen recovery	**PSA electricity consumption (kW/kg)**	**Synthetized product (ton/year)**			**Electricity produced / Island total electricity produced**	**Electricity consumed / Island total electricity produced**	**FPC (€/kg)**	**Energy efficiency (%)**	**Exergy efficiency (%)**
		Gasoline	**Diesel**	**Kerosene**					
First scenario									
70%	0.31	3,318	4,185	135.30	16%	-	4.79	45	34
	0.62				11%	-	4.91	44	
	0.93				6%	-	5.03	43	
95%	0.31	4,231	5,243		6%	-	4.05	42	42
	0.62				-	1%	4.17	40	
	0.93				-	4%	4.29	39	
Second scenario									
70%	0.31	3,318	4,185	4,292	4%	-	3.31	45	35
	0.62				-	0%	3.39	44	
	0.93				-	3%	3.48	43	
95%	0.31	4,231	5,243	5,378	-	4%	2.80	48	44
	0.62				-	7%	2.89	47	
	0.93				-	10%	2.98	45	

Nevertheless, for all the evaluated cases of the biorefinery for FT-fuels synthesis, the resultant production costs are all still higher than the fuels market prices, making it economically unviable.

5.6. Discussion

Three different plants are assessed using Aspen Plus: hydrogen, methanol and FT-fuels synthesis plants. The results show that hydrogen plant can be economically viable, being its associated production costs (4.36 €/kg) lower than its projected market price for 2025 (7.28 to 9.10 €/kg). The possible utilization of hydrogen as transportation fuel would cover 16% of the currently travelled distance by light-duty vehicles in Azores and, consequently, would reduce the pollutant emissions on the islands from road vehicles. The hydrogen fuel economy is also expected to be more favourable than the actual gasoline one, being the cost per travelled distance 53% of the current one for gasoline. This plant presents the highest energy efficiency (59%), although the lowest exergy efficiency (14%) of the three modelled plants. For the exergy efficiency, this fact is sustained by the limited production capacity of hydrogen when compared to the other plants' yield capacities (methanol, diesel, gasoline and kerosene). In regard to the energy analysis, besides the synthetized hydrogen high energy content, the surplus production of power in the plant also contributes for such numbers. However, this product still finds no relevant market demand in Azores, so its application is projected for a future scenario where hydrogen takes part in the transportation sector. This biorefinery would also be able to produce surplus renewable power, increasing the renewable energy share in Azores. The estimated produced electricity would match up to 24% of the currently thermal power production in the S. Miguel. It is important to highlight that the yearly produced electricity by the hydrogen plant is assumed to be sold to the grid in its totality, which may not be completely true. Since the analysis carried out in this study is not an hourly analysis, but a yearly analysis, there may be times when the power grid is not able to accept the electricity supplied by the plant. However, since a constant power production is being considered, because the biomass flow rate is constant, the supplied power can cover the base load of S. Miguel. Obviously, if there are times when power cannot be supplied to the grid, the revenues from its sale decrease, increasing the hydrogen production cost.

The production costs of methanol (2.90 €/kg) are about eleven times its market price (0.273 €/kg). Even though methanol finds the most varied span of utilizations, currently there is no market in Azores, being its exportation the most valid option. Nevertheless, the possibility of developing activities to synthetize fuels or other commodity chemicals through methanol could be a good opportunity for Azores, that depends heavily on importations.

In the case of the FT-fuels, although the estimates on the production would cover respectively 6%, 10% and 100% of the diesel, gasoline and kerosene current Azores's demand, the expected production costs are prohibitive for both evaluated scenarios (4.91 €/kg and 3.39 €/kg), comparing to its market prices. The lower pollutant emissions of these fuels in terms of SOx and NOx [12], compared to the conventional ones, besides its utilization without need for the existing infrastructures modifications, are the most important features of these products.

Besides being currently non-viable economically, both the methanol and the FT-fuels plants (in the second scenario) require large power consumptions that would increase the power demand of Azores. This can be accomplished by the utilization of conventional fuels and, in the best case, promote the higher share on the island's renewable energy penetration, taking advantage of the periods of overproduction of electricity that currently is not used.

In regard to the CO_2 emissions of the plants, although the hydrogen synthesis plant produces the most CO_2 among the three, the further utilization of hydrogen as fuel is set to produce only water and heat, contrary to the combustion of the other produced materials (methanol or FT-fuels) that are responsible for the emission of a vast quantity of pollutants, mostly CO_2. This way, although the hydrogen plant is set to emit more CO_2, its product utilization is cleaner.

The sensitivity analysis carried out showed that the implementation of a hydrogen plant would be economically viable even for the most unfavourable of the evaluated scenarios. For this plant, although its implementation would be economically viable in any of the islands, the most favourable scenario would be its implementation in the Pico Island. Apart from the theoretical possibility to replace all the thermal electricity production of the island, also it would be possible to reduce the production costs of the plant. Furthermore, this analysis showed that the methanol and the FT-fuels plants would not be economically viable for any of the evaluated scenarios for the Azores archipelago.

Being technologically feasible, the economy of the plants is the most challenging aspect. In this sense, incentives from the government for the installation of the plants, by terms of subsidies or tax reductions for the biorefinery and its associated activities are measures that would decrease the production costs, and therefore, possibly promote the viability of the plants.

6. Closure

6.1. Conclusions

Azores presents a wide variety of endogenous resources that are currently not exploited. In this sense, this work presents the techno-economic assessment of a biorefinery plant in Azores, taking advantage of available biomass resources, namely *Pittosporum undulatum*, to produce energy and chemicals.

Biorefineries are identified as part of the path for a more sustainable future. Nevertheless, their implementation still faces some challenges, mostly regarding their economic viability. The techno-economic assessment carried out in this study shows that from the three evaluated biorefinery plants (hydrogen, methanol and FT-fuels) for the Azores archipelago, only the hydrogen one would be economically viable since its production costs would be 40 to 60% of the hydrogen market value (7.28 to 9.10 €/kg). Nonetheless, since currently no hydrogen is consumed as transportation fuel in the archipelago, its implementation is aimed for a near future when the energy transition takes place. In this sense, the estimated hydrogen production would allow to replace 16 to 22% of the current distance travelled by the current light-duty vehicle fleet of the archipelago, while the fuel economy would be reduced to 53% (0.053 €/km) of the current one for gasoline (0.10 €/kg). In addition, the implementation of such plant would allow to produce surplus electricity that would potentially cover 10 to 25% of the current S. Miguel electricity production. Although technologically achievable, the production of methanol and FT-fuels in the Azores context would be economically unviable. In the case of the methanol synthesis, besides its prohibitive production costs (eight to twelve times its current market value), no current utilization is known in the region for the product. In regard of the FT-fuels, although their production costs are prohibitive (two to ten times its current market values), there is currently a market for these fuel products in Azores archipelago.

Additionally, the sensitivity analysis carried out regarding the location for the biorefinery in different islands of the archipelago proved that the choice over the Pico Island would be both economically and energetically favourable. In terms of economy, this location would allow to reduce the production costs of the plant while energetically it would be possible to theoretically replace all the thermal electricity currently produced in the island.

The implementation of such biorefinery plant in the archipelago would promote the economic, social and technological development of the region by creating a new set of activities related with the operations of the biorefinery. In addition, this plant would make use of a renewable resource, currently with no commercial use, to produce energy and chemical products which would considerably foster the independency of the archipelago from fossil fuels, but mostly from external sources of fuels and other chemicals.

Nevertheless, the exploitation of resources for the operation of the biorefinery must be carefully assessed so that its sustainable exploitation is not jeopardized. Furthermore, the development of such project would represent a considerable capital investment, which can be challenging for its viability.

6.2. Future work

As complement to this study, future work should be done regarding several important issues, such as:

- Assessment and optimization of the biomass distribution and storage systems in the islands;
- Life-cycle assessment of the biorefinery activities;
- Assessment of the possibility of using different feedstocks, mixed or not (agricultural residues, municipal solid waste, other endogenous species);
- *Pittosporum undulatum* archipelago resources chemical and physical characterization and laboratory-scale testing of its gasification;
- Assessment of the use of *Pittosporum undulatum* for the synthesis of other products through bio or thermochemical routes;
- Assessment of the ammonia synthesis from the produced hydrogen for the Azores market;
- Assessment of biomass pre-treatment techniques that promote higher products yields (torrefaction, steam explosion, etc.);

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A. Annex A.

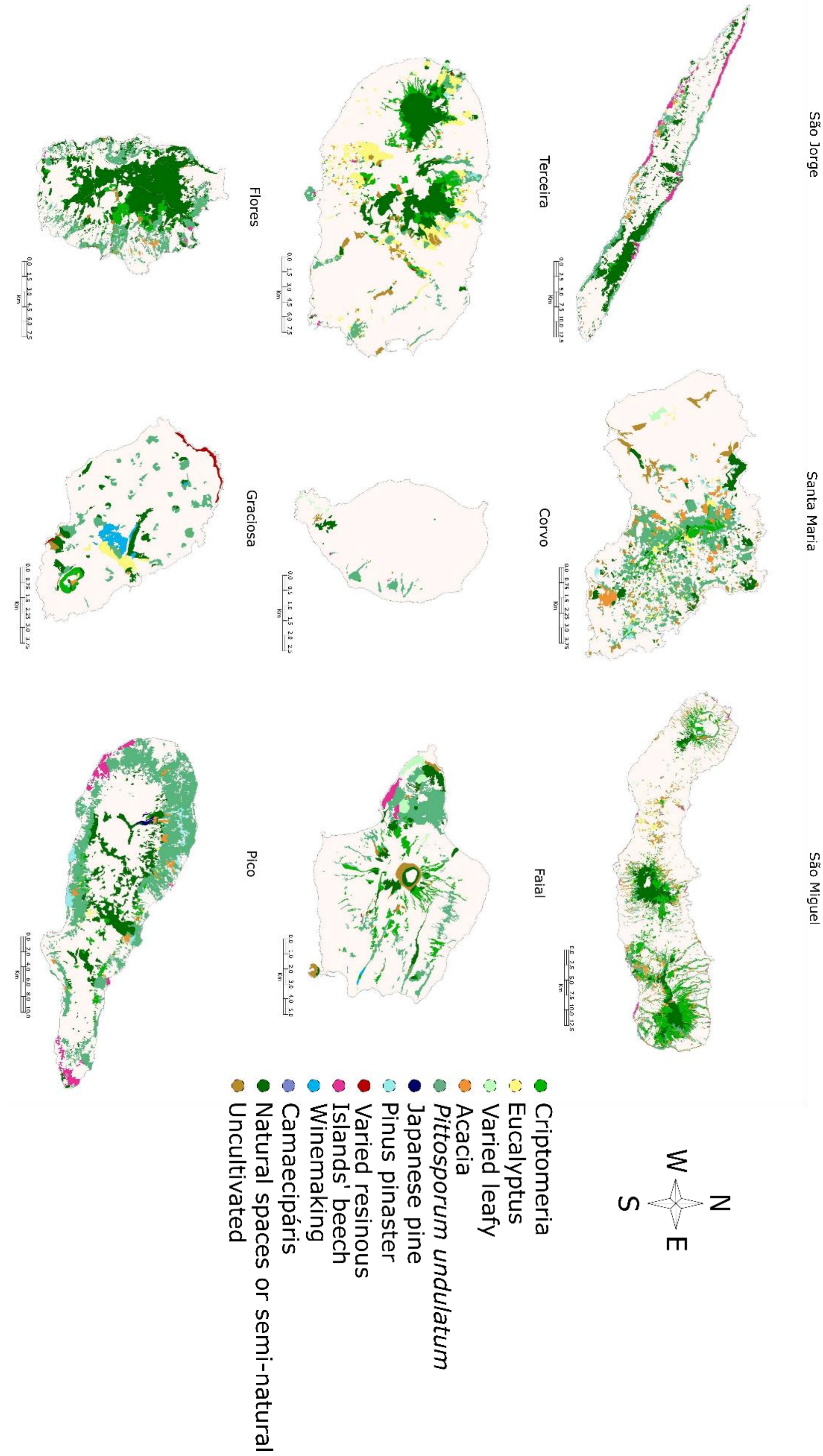


Figure A.1 – Representation of the forest plans of the archipelago, considering the dominant species and the domination of land use, based on [70].

B. Annex B.

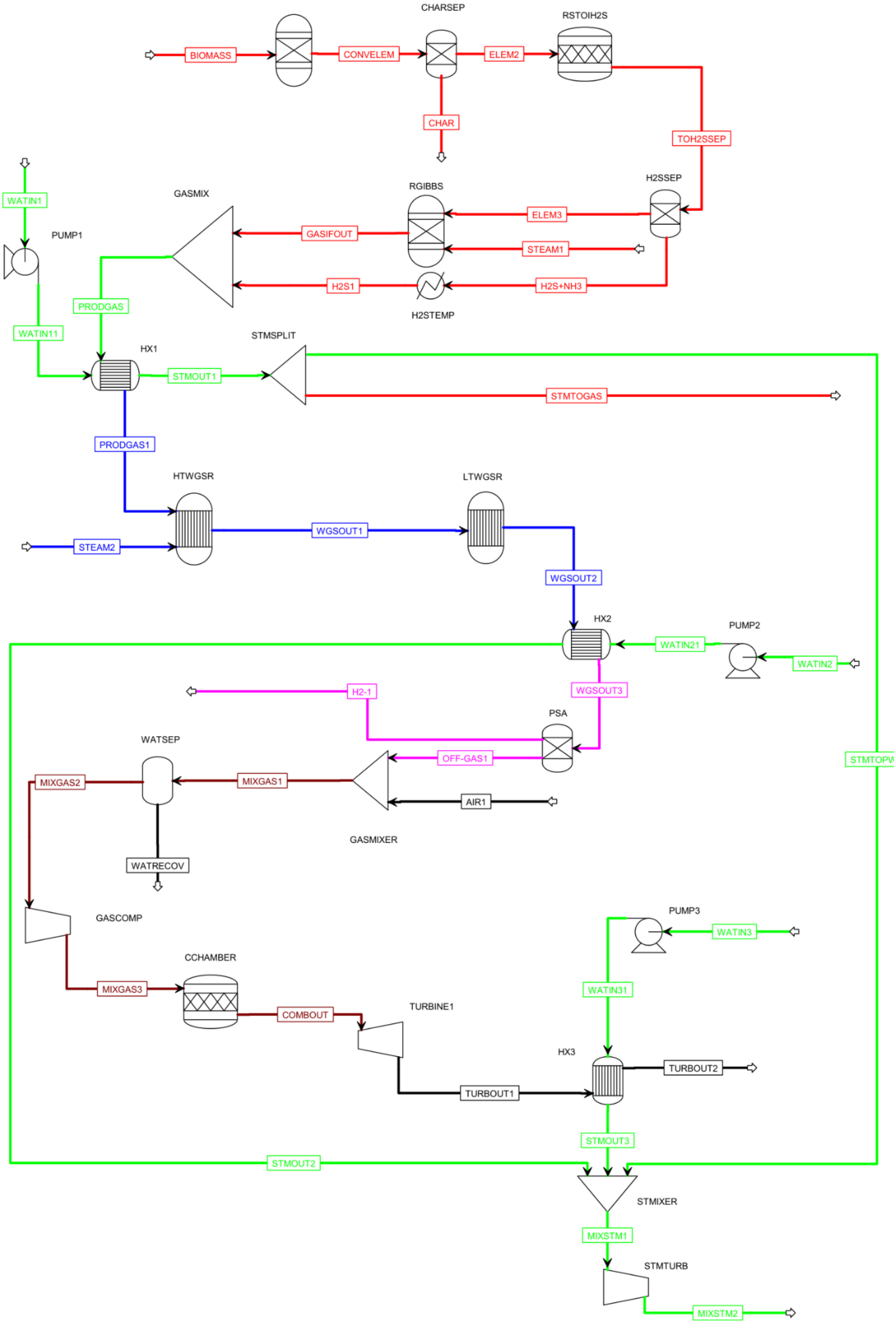


Figure B.1 – Hydrogen synthesis plant flowsheet implemented in Aspen Plus.

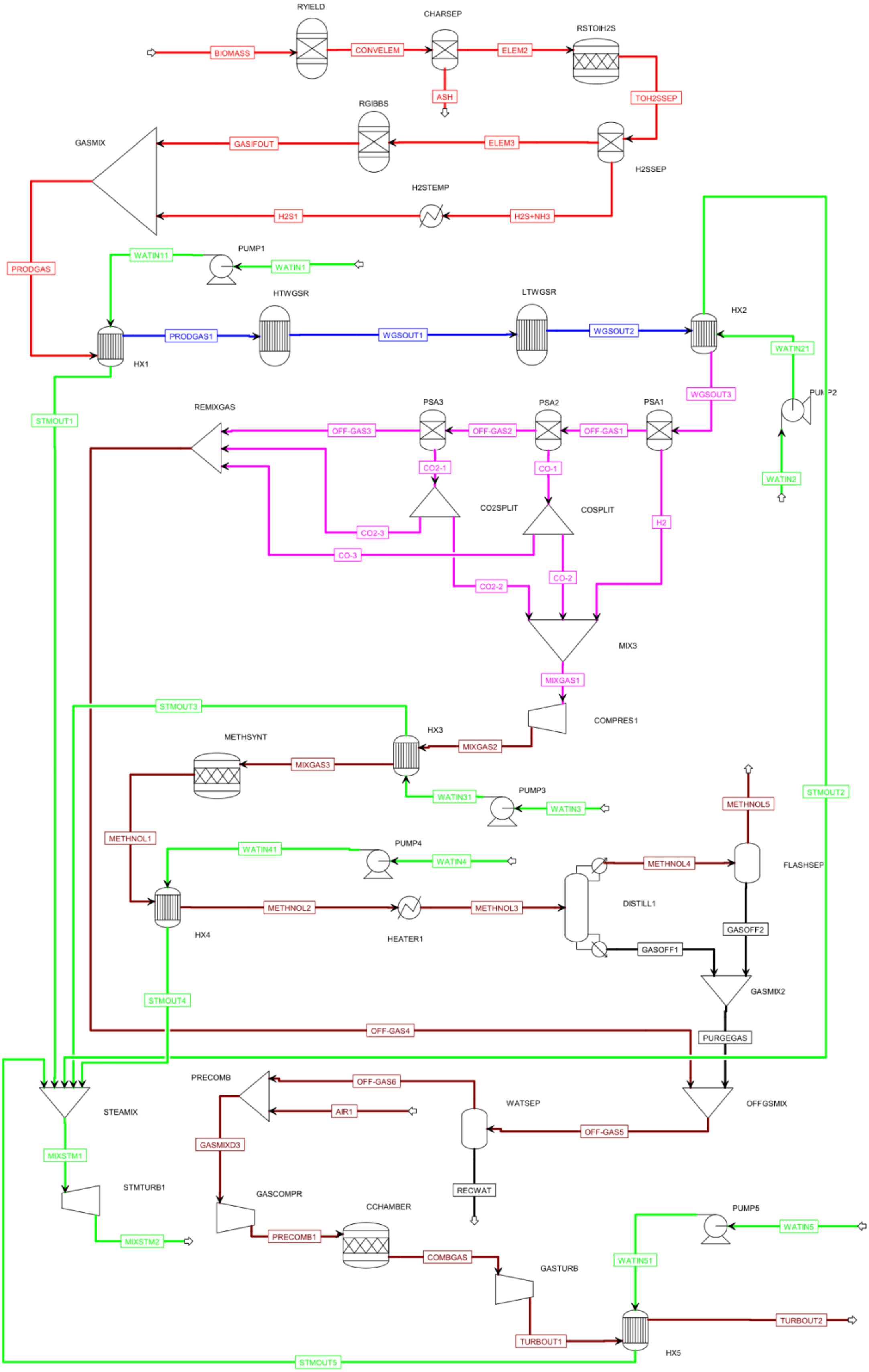


Figure B.2 – Methanol synthesis plant flowsheet implemented in Aspen Plus.

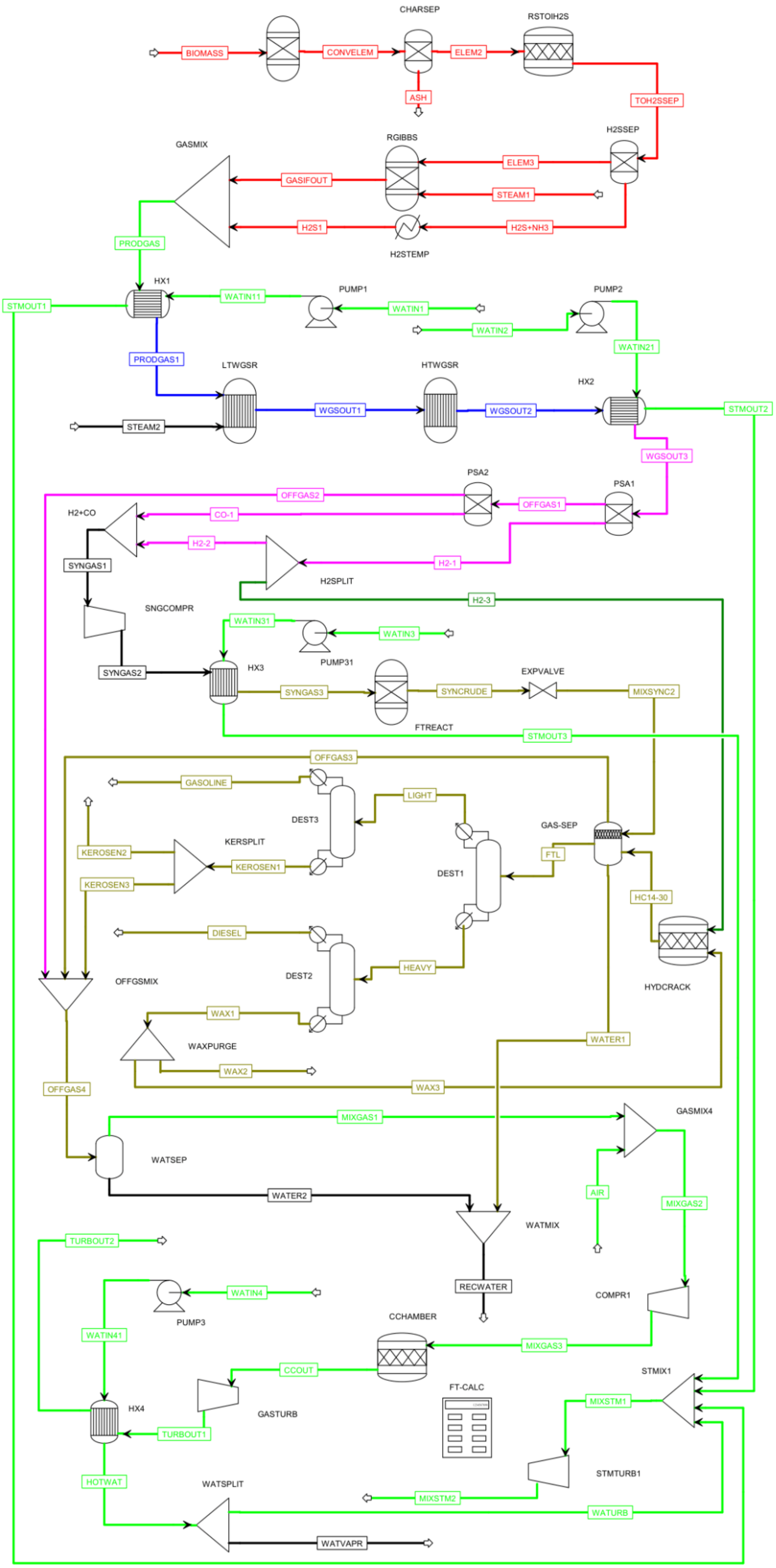


Figure B.3 – FT fuels synthesis plant flowsheet implemented in Aspen Plus (first scenario).

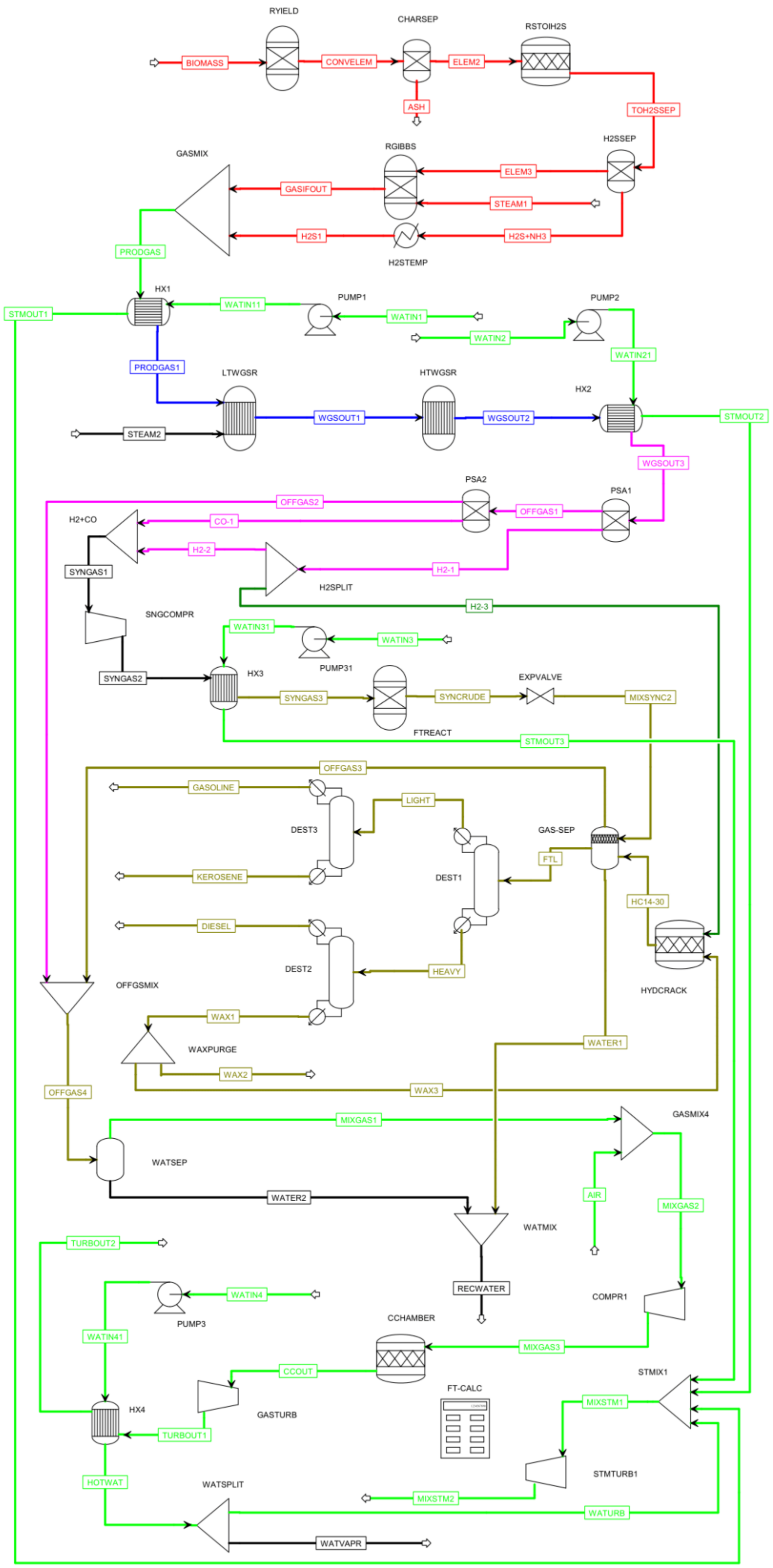
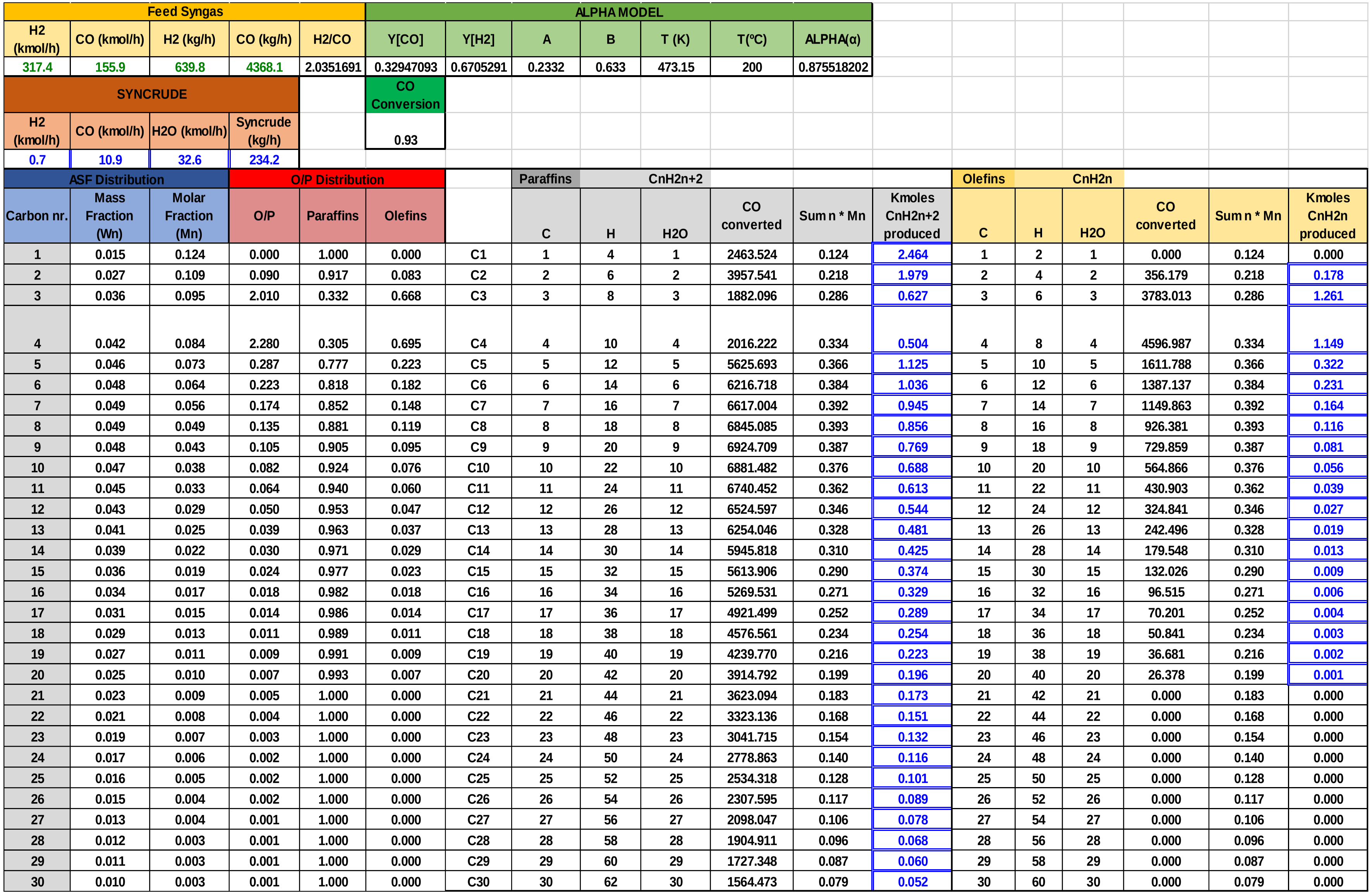


Figure B.4 – FT fuels synthesis plant flowsheet implemented in Aspen Plus (second scenario).



Feed Syngas					ALPHA MODEL						
H2 (kmol/h)	CO (kmol/h)	H2 (kg/h)	CO (kg/h)	H2/CO	Y[CO]	Y[H2]	A	B	T (K)	T(°C)	ALPHA(α)
317.4	155.9	639.8	4368.1	2.0351691	0.32947093	0.6705291	0.2332	0.633	473.15	200	0.875518202

SYNCRUDE					CO Conversion
H2 (kmol/h)	CO (kmol/h)	H2O (kmol/h)	Syncrude (kg/h)		0.93
0.7	10.9	32.6	234.2		

ASF Distribution			O/P Distribution				Paraffins		CnH2n+2				Olefins		CnH2n			
Carbon nr.	Mass Fraction (Wn)	Molar Fraction (Mn)	O/P	Paraffins	Olefins		C	H	H2O	CO converted	Sum n * Mn	Kmoles CnH2n+2 produced	C	H	H2O	CO converted	Sum n * Mn	Kmoles CnH2n produced
1	0.015	0.124	0.000	1.000	0.000	C1	1	4	1	2463.524	0.124	2.464	1	2	1	0.000	0.124	0.000
2	0.027	0.109	0.090	0.917	0.083	C2	2	6	2	3957.541	0.218	1.979	2	4	2	356.179	0.218	0.178
3	0.036	0.095	2.010	0.332	0.668	C3	3	8	3	1882.096	0.286	0.627	3	6	3	3783.013	0.286	1.261
4	0.042	0.084	2.280	0.305	0.695	C4	4	10	4	2016.222	0.334	0.504	4	8	4	4596.987	0.334	1.149
5	0.046	0.073	0.287	0.777	0.223	C5	5	12	5	5625.693	0.366	1.125	5	10	5	1611.788	0.366	0.322
6	0.048	0.064	0.223	0.818	0.182	C6	6	14	6	6216.718	0.384	1.036	6	12	6	1387.137	0.384	0.231
7	0.049	0.056	0.174	0.852	0.148	C7	7	16	7	6617.004	0.392	0.945	7	14	7	1149.863	0.392	0.164
8	0.049	0.049	0.135	0.881	0.119	C8	8	18	8	6845.085	0.393	0.856	8	16	8	926.381	0.393	0.116
9	0.048	0.043	0.105	0.905	0.095	C9	9	20	9	6924.709	0.387	0.769	9	18	9	729.859	0.387	0.081
10	0.047	0.038	0.082	0.924	0.076	C10	10	22	10	6881.482	0.376	0.688	10	20	10	564.866	0.376	0.056
11	0.045	0.033	0.064	0.940	0.060	C11	11	24	11	6740.452	0.362	0.613	11	22	11	430.903	0.362	0.039
12	0.043	0.029	0.050	0.953	0.047	C12	12	26	12	6524.597	0.346	0.544	12	24	12	324.841	0.346	0.027
13	0.041	0.025	0.039	0.963	0.037	C13	13	28	13	6254.046	0.328	0.481	13	26	13	242.496	0.328	0.019
14	0.039	0.022	0.030	0.971	0.029	C14	14	30	14	5945.818	0.310	0.425	14	28	14	179.548	0.310	0.013
15	0.036	0.019	0.024	0.977	0.023	C15	15	32	15	5613.906	0.290	0.374	15	30	15	132.026	0.290	0.009
16	0.034	0.017	0.018	0.982	0.018	C16	16	34	16	5269.531	0.271	0.329	16	32	16	96.515	0.271	0.006
17	0.031	0.015	0.014	0.986	0.014	C17	17	36	17	4921.499	0.252	0.289	17	34	17	70.201	0.252	0.004
18	0.029	0.013	0.011	0.989	0.011	C18	18	38	18	4576.561	0.234	0.254	18	36	18	50.841	0.234	0.003
19	0.027	0.011	0.009	0.991	0.009	C19	19	40	19	4239.770	0.216	0.223	19	38	19	36.681	0.216	0.002
20	0.025	0.010	0.007	0.993	0.007	C20	20	42	20	3914.792	0.199	0.196	20	40	20	26.378	0.199	0.001
21	0.023	0.009	0.005	1.000	0.000	C21	21	44	21	3623.094	0.183	0.173	21	42	21	0.000	0.183	0.000
22	0.021	0.008	0.004	1.000	0.000	C22	22	46	22	3323.136	0.168	0.151	22	44	22	0.000	0.168	0.000
23	0.019	0.007	0.003	1.000	0.000	C23	23	48	23	3041.715	0.154	0.132	23	46	23	0.000	0.154	0.000
24	0.017	0.006	0.002	1.000	0.000	C24	24	50	24	2778.863	0.140	0.116	24	48	24	0.000	0.140	0.000
25	0.016	0.005	0.002	1.000	0.000	C25	25	52	25	2534.318	0.128	0.101	25	50	25	0.000	0.128	0.000
26	0.015	0.004	0.002	1.000	0.000	C26	26	54	26	2307.595	0.117	0.089	26	52	26	0.000	0.117	0.000
27	0.013	0.004	0.001	1.000	0.000	C27	27	56	27	2098.047	0.106	0.078	27	54	27	0.000	0.106	0.000
28	0.012	0.003	0.001	1.000	0.000	C28	28	58	28	1904.911	0.096	0.068	28	56	28	0.000	0.096	0.000
29	0.011	0.003	0.001	1.000	0.000	C29	29	60	29	1727.348	0.087	0.060	29	58	29	0.000	0.087	0.000
30	0.010	0.003	0.001	1.000	0.000	C30	30	62	30	1564.473	0.079	0.052	30	60	30	0.000	0.079	0.000

Figure B.5 – Excel spreadsheet implemented in Aspen Plus for the syncrude stream composition calculation.

Table B.1 - Scales, scale factors, investment costs, installation costs and CEPCI of the different equipment.

Type of process	Equipment	$Scale_{REF}$	f_S	$Cost_{REF}$	f_I	$CEPCI_{REF}$	Source
Equipment used in one or more of the plants analysed	Biomass receiving and unload	198.1 wet ton/h	0.62	3.5 M\$2007	3.63[i]	525.4	[107]
	Biomass storage, preparation and feeding	64.6 wet ton/h	0.77	2.0 M\$1999	3.63[i]	390.6	[108]
	GTI gasifier, gas cooling and gas cleaning including scrubber	483 MW	0.77	208 M\$2007	1	525.4	[108]
	WGS reactor	8819 kmol/h[ii]	0.65	14 M€ 2008	3.63[i]	575.4	[94]
	H_2 PSA	16,616 kmol/h[ii]	0.65	12 M€ 2008	3.63[i]	575.4	[94]
	CO PSA	16,616 kmol/h[ii]	0.65	12 M€ 2008	3.63[i]	575.4	[94]
	CO_2 PSA	16,616 kmol/h[ii]	0.65	12 M€ 2008	3.63[i]	575.4	[94]
	Selexol unit (Acid gas removal)	554 tonCO_2/h	0.7	69 M€ 2008	3.63[i]	575.4	[94]
FT-fuels synthesis	FT synthesis	2420 MW	0.75	246 M\$2011	0.72	585.7	[109]
	Initial fill of FT catalyst	2420 MW	1	7.9 M\$2011	1.86	585.7	[109]
	Syngas compressor	71,360 MW	0.67	13.6 M\$2007	1.86	525.4	[108]
Methanol synthesis	Methanol synthesis	87.5 ton/h[ii]	0.72	3.5 M\$2001	2.1	394.4	[92]
	Syngas compressor	13.2 MW	0.85	12.9 M€2002	1.86	395.6	[83]
	Recycle compressor	13.2 MW	0.85	12.9 M€2002	1.86	395.6	[83]
Power production	Steam turbine	275 MW	0.67	38 M€2008	3.63[i]	575.4	[94]
	Gas turbine	266 MW	0.75	42 M€2008	3.63[i]	575.4	[94]

[i] Lang factor for a solid-fluid processing plant [110].

[ii] Output stream.

C. Annex C.

Table C.1 - Specifications on the individual process units of the simulation for the hydrogen synthesis flowsheet.

EQUIPMENT		CODE	SPECIFICATIONS
Pumps		PUMP1	Outlet pressure: 4 bar; Mass flow rate: 9355 kg/h
		PUMP2	Outlet pressure: 4 bar; Mass flow rate: 4200 kg/h
		PUMP3	Outlet pressure: 4 bar; Mass flow rate: 14400 kg/h
Heat exchangers		HX1	Cold stream outlet temperature: 150ºC
		HX2	Cold stream outlet temperature: 150ºC
		HX3	Cold stream outlet temperature: 150ºC
PSA		PSA	H_2 recovery: 0.7
Flash separator		WATSEP	Outlet temperature: -10ºC; Pressure: 1.01325 bar
Gas turbine	Compressor	GASCOMP	Type: Isentropic; Isentropic Efficiency: 0.85; Mechanical efficiency: 1; Outlet pressure: 10 bar
	Combustion chamber	CCHAMBER	Combustion of all the material that is able to be oxidized; Operating pressure: 10 bar
	Turbine	TURB1	Type: Isentropic; Isentropic Efficiency: 0.85; Mechanical efficiency: 1; Outlet pressure: 1.01325 bar
Steam turbine		STMTURB	Type: Isentropic; Isentropic Efficiency: 0.85; Mechanical efficiency: 1; Outlet pressure: 1.01325 bar

Table C.2 - Specifications on the individual process units of the simulation for the methanol synthesis flowsheet.

EQUIPMENT		CODE	SPECIFICATIONS
Pumps		PUMP1	Outlet pressure: 4 bar; Mass flow rate: 7620 kg/h
		PUMP2	Outlet pressure: 4 bar; Mass flow rate: 3350 kg/h
		PUMP3	Outlet pressure: 4 bar; Mass flow rate: 5000 kg/h
		PUMP4	Outlet pressure: 4 bar; Mass flow rate: 550 kg/h
		PUMP5	Outlet pressure: 4 bar; Mass flow rate: 17500 kg/h
Heat exchangers		HX1	Cold stream outlet temperature: 150ºC
		HX2	Cold stream outlet temperature: 150ºC
		HX3	Cold stream outlet temperature: 150ºC
		HX4	Cold stream outlet temperature: 150ºC
		HX5	Cold stream outlet temperature: 900ºC
PSA		PSA1	H2 recovery: 0.7
		PSA2	CO recovery: 0.98; CH_4 recovery: 0.01; CO_2 recovery: 0.01
		PSA3	CO_2 recovery: 0.9; CH_4 recovery: 0.09; CO recovery: 0.005; H_2 recovery: 0.005
Heater		HEATER1	Outlet temperature: 17ºC; Operating pressure: 1.01325 bar
Compressor		COMPRES1	Type: Isentropic; Isentropic Efficiency: 0.85; Mechanical efficiency: 1; Outlet pressure: 50 bar
Synthesis reactor		METHSYNTH	Operating temperature: 250ºC; Operating pressure: 50 bar
Distillation column		DISTILL1	Total condenser; Operating condenser pressure: 1.3 bar; Operating reboiler pressure: 1.5; Reflux ratio: -1.2Rmin; Methanol recovery (distillate stream): 98%; H_2O recovery (bottom stream): 99.9%
Flash separators		FLASHSEP	Outlet temperature: -50ºC; Pressure: 1.01325 bar
		WATSEP	Outlet temperature: 25ºC; Pressure: 1.01325 bar
Gas turbine	Compressor	GASCOMP	Type: Isentropic; Isentropic Efficiency: 0.85; Mechanical efficiency: 1; Outlet pressure: 10 bar
	Combustion chamber	CCHAMBER	Combustion of all the material that is able to be oxidized; Pressure: 14 atm
	Turbine	TURB1	Type: Isentropic; Isentropic Efficiency: 0.85; Mechanical efficiency: 1; Outlet pressure: 10 bar
Steam turbine		STMTURB1	Type: Isentropic; Isentropic Efficiency: 0.85; Mechanical efficiency: 1; Outlet pressure: 10 bar

Table C.3 - Specifications on the individual process units of the simulation for the FT-fuels synthesis flowsheets-

EQUIPMENT		CODE	SPECIFICATIONS
Pumps		PUMP1	Outlet pressure: 4 bar; Mass flow rate: 9595 kg/h
		PUMP2	Outlet pressure: 4 bar; Mass flow rate: 11000 kg/h
		PUMP3	Outlet pressure: 4 bar; Mass flow rate: 2240 kg/h
		PUMP4	Outlet pressure: 4 bar; Mass flow rate:19300[i] or 13500[ii] kg/h
Heat exchangers		HX1	Cold stream outlet temperature: 150ºC
		HX2	Cold stream outlet temperature: 150ºC
		HX3	Cold stream outlet temperature: 150ºC
		HX4	Cold stream outlet temperature: 150ºC
PSA		PSA1	H_2 recovery: 0.7
		PSA2	CO recovery: 0.98; CH_4 recovery: 0.01; CO_2 recovery: 0.01
Heater		HEATER1	Outlet temperature: 17ºC; Operating pressure: 1.01325 bar
Compressor		SNGCOMPR	Type: Isentropic; Isentropic Efficiency: 0.85; Mechanical efficiency: 1; Outlet pressure: 20 bar
Synthesis reactor		FTREACT	Operating temperature: 200ºC; Operating pressure: 20 bar
Flash separators		GAS-SEP	Outlet temperature: 25ºC; Pressure: 1.5 bar
		WATSEP	Outlet temperature: 20ºC; Pressure: 1.01325 bar
Distillation column		DEST1	Total condenser; Operating condenser pressure: 1.3 bar; Operating reboiler pressure: 1.5; Reflux ratio: -1.2Rmin; C_{13} recovery (distillate stream): 90%; C_{14} recovery (bottom stream): 99%
		DEST2	Total condenser; Operating condenser pressure: 1.3 bar; Operating reboiler pressure: 1.5; Reflux ratio: -1.2Rmin; C_{20} recovery (distillate stream): 90%; C_{21} recovery (bottom stream): 99%
		DEST3	Total condenser; Operating condenser pressure: 1.3 bar; Operating reboiler pressure: 1.5; Reflux ratio: -1.2Rmin; C_9 recovery (distillate stream): 98%; C_{21} recovery (bottom stream): 10%
Hydrotreament reactor		HYDCRACK	Operating temperature: 240ºC; Operating pressure: 35 bar
Expansion valve		EXPVALVE	Outlet pressure: 1.5 bar
Gas turbine	Compressor	GASCOMP	Type: Isentropic; Isentropic Efficiency: 0.85; Mechanical efficiency: 1; Outlet pressure: 10 bar
	Combustion chamber	CCHAMBER	Combustion of all the material that is able to be oxidized; Pressure: 14 atm
	Turbine	TURB1	Type: Isentropic; Isentropic Efficiency: 0.85; Mechanical efficiency: 1; Outlet pressure: 10 bar
Flow spliters		WAXPURGE	Split fraction (purged): 0.05
		KERSPLIT*	Split mass fraction (recovered kerosene): 19.3062 kg/hr
Steam turbine		STMTURB1	Type: Isentropic; Isentropic Efficiency: 0.85; Mechanical efficiency: 1; Outlet pressure: 10 bar

[i] First scenario.

[ii] Second scenario.