POLITECNICO DI TORINO

Corso di Laurea Magistrale in Ingegneria Energetica e Nucleare

Tesi di Laurea Magistrale

Techno-economic analysis of a Fischer-Tropsch fuels and waxes production plant with digestate gasification

Relatore: Lanzini Andrea

Correlatore: Marchese Marco

Candidato: Chesta Simone

A.A. 2019/2020

Index

Legend

AC – Activated carbon
AD – Anaerobic digestion
AGR – Acid gas removal
ASF – Anderson-Schulz-Flory
ASU – Air separation unit
BFB – Bubbling fluidized bed
BOP – Balance of plant
BTX – Biomass to everything
CEPCI – Chemical Engineering Plant Cost Index
CFB – Circulating fluidized bed
CGE – Cold gas efficiency
CHP – Combined heat and power
DFB – Dual fluidized bed
DFBG – Dual fluidized bed gasifier
DMR – Dry methane reforming
DS – Design specification
EF – Entrained flow
ESP – Electrostatic precipitator
FBC – Fluidized bed combustor
FBG – Fluidized bed gasifier
FFB – Fixed fluidized bed
FICFB – Fast internal circulating fluidized bed
FTP – Fischer-Tropsch products
FTS – Fischer-Tropsch synthesis
GT – Gas turbine
GTL – Gas to liquid
HC – Hydrocarbon
HTFT – High temperature Fischer-Tropsch
ICE – Internal combustion engine
IGCC – Internal gasification combined cycle
LCOS – Levelized cost of syncrude
LCOS – Levelized cost of syncrude
LCOW – Levelized cost of waxes
LCOx – Levelized cost of syncrude and/or waxes
LTFT – Low temperature Fischer-Tropsch
MeOH – Methanol
MSW – Municipal solid wastes
Mtoe – Million tons of oil equivalent
NDR – Nominal discount rate
NG – Natural gas
NPC – Net present cost
OFMSW – Organic fraction of municipal solid wastes
ORC – Organic Rankine cycle
PM – Particulate matter
ppb – Parts per billion
ppm – Parts per million
PSA – Pressure swing adsorption
PVSA – Pressure vacuum swing adsorption
PWS – Pressurized water scrubbing
RDR – Real discount rate
RWGS – Reverse water gas shift
SMR – Steam methane reforming
SOEC – Solid oxide electrolyzer cell
TIC – Total investment cost
TOC – Total operative cost
TPEC – Total purchase equipment cost
TR – Total revenue
VS – Venturi scrubber
WGS – Water gas shift
WS – Water scrubber
WTE – Waste to energy

Abstract

A simulation on Aspen Plus for the synthesis of synthetic fuels and waxes is carried out. A 3MW$_{th}$ dual fluidized bed gasifier (DFBG) is employed to produce a syngas and it is fed with digestate or pine wood: the first biomass is the real investigation of the work while the latter is used as a reference. The mass flow of steam used in the gasification process is varied to keep the H_2/CO ratio around 2. The syngas is cleaned removing sulfur compounds, ammonia and chlorine by wet scrubbers, the CO_2 is removed by a pressure swing adsorption (PSA). The Fischer-Tropsch synthesis process (FTS) is simulated adopting the Anderson-Schulz-Flory model (ASF) with a chain-growth probability as a function of the temperature and H_2/CO ratio. The FT products are separated into off-gas and LPG, naphtha, middle distillate and waxes. Three different scenarios are investigated: in two of these, the off-gas and LPG are burnt in a gas turbine (GT) to produce electric energy; in the third, they are recirculated back to the gasifier in order to increase the production. 105-168 kg of syncrude are produced every ton of dry digestate while 144-225 kg using pine wood. The maximum efficiencies found are 54.5% and 51.3% respectively. The minimum levelized cost of syncrude (LCOS) and waxes (LCOW) are 1.71€/kg and 3.38€/kg respectively in case of using digestate and 1.96€/kg and 4.22€/kg using pine wood.

Part I

1. Introduction

Liquid fuels: the humankind development extremely accelerated when they became available. For centuries, the main fuel was the wood: a solid low-energy-density material, also used in buildings and to make several objects and tools. At that time, people did not usually move themselves for long distances. Only a few merchants and officers could travel for hundreds of kilometers on sea by sailboat or on land by horses. Later in time, the coal was discovered: it is still a solid material, but it has a higher density and availability respect to the wood. Industry was born and the rail roads started to connect a growing number of cities. People could travel for thousands of kilometers on mainland if there was the train connection. Also, the sea transports became faster thanks to the Watt engine. However, the real revolution came when the potential of the crude oil was discovered. Individual transports by cars and short time intercontinental travel by plans has transformed the world. Just 120 years ago, to go from a small village in Europe to another one in the United State, a person could spend several weeks. Today, s/he can spend less than half a day. This is possible thanks to the gasoline (or diesel) that powers the cars and thanks to the jet-fuel that powers the plans. Not only the transfers were affected by the oil discovered: plastic, asphalt, waxes, fertilizers, and lubricants are only the most famous crude-derivative products. Without the crude oil, this work probably could not be developed.

Unfortunately, all these comforts and essential products become unsustainable for the environment. The EU has strengthened many strategies to reduce the impact of the humankind development. Here and in other several part of the world, many researches are carried out to try to solve the problem. This work would be a small part of the solution: a way to produce a more sustainable oil, to do not renounce to all the comforts that are available today together with the materials that have become essentials. A possible solution is called syncrude: a synthetic oil produced from a gas. Also, the gas is synthetic and called syngas. The latter is a mixture of hydrogen and carbon monoxide and it can be produced from an electrolyzer cell, from the gasification of coal, biomass, waste and other solid and liquid combustibles or from the reforming of methane or natural gas. If this syngas is produced by a renewable source, such as from a biomass, it can produce a green syncrude.

In literature, many examples can be found treating this topic. Tagomori et al. [1] have analyzed a plant to produce synthetic diesel from a Fischer-Tropsch process using pine and eucalyptus wood residuals in Brazil. They worked on a big-size plant of 750MW$_{th}$ and they found that it is not competitive at all without a strong incentive policy. Another paper on the diesel production from a biomass is the work of Hamelinck et al. [2]: they investigated several variation to the original configuration in order to decrease the final cost of production. In the end, they concluded that the fuel is not competitive with the fossil one with a price 40-50% higher. Hillestad et al. [3] have studied the differences between a conventional biomass to liquid (BTL) plant with respect to a power and biomass to liquid (PBTL) one. They found that the PBTL has a cost of production 30% lower than the conventional BTL, but it still higher than the traditional fuels. Another innovative approach is the one adopted by Im-orb et al. [4]: they investigated a BTL plant with a recirculation of the off-gas that comes out from the fuels formation reactor, to the gasifier in order to increase the production. Neither in this work, the plant is not profitable without incentives. To see the complete list of the works analyzed treating liquid fuels production, see *Table 62* **- Comparison table of the performances of several works**.

The largest part of the works analyzed shows big-sized plants and no profit without incentives. The aim of this study is to investigate the techno-economic feasibility of a small plant exploiting biomass gasification. For *small* it is considered a plant with a thermal power between 1MW$_{th}$ and 10MW$_{th}$. In literature, this kind of plants produce hydrogen as Barisano et al. [5] or power as Chang et al. [6]. Only few example of production of liquid fuels from small plants were found: Kim et al. [7] and Snehesh et al. [8]. This latter is the only work found with a final price comparable with the market value of the fossil fuels and it has a size smaller than $5MW_{th}$.

Small plants are interesting because they are better compatible with the utilization of a biomass. In case of fossil fuels, there are few points where they are extracted and so it is possible to construct plants with large capacities. In case of biomass, the generation is distributed. It is possible to collect big quantities of material, but it requests long transports causing a higher final price and a lower efficiency of the whole life cycle of the fuel produced. From this point of view, small plants seem to be more sustainable.

This work will analyze the gasification of a wasted biomass (the digestate, the exhaust biomass that comes out from a bio-digester for the biogas production) and the utilization of the syngas in a synthesis process to produce a syncrude. This oil will be separated in its four main fractions (LPG, naphtha, middle distillate and waxes) and three of that will be sold. In the study presented, a simulation on Aspen Plus has been carried out in order to get information on the behavior of the plant with different configuration and settings. Two biomasses will be analyzed: a digestate and a pine wood, investigating the differences in terms of efficiency, production and final cost of the products. The size is about $3MW_{th}$ in order to be fed by a biodigester avoiding any transportation. This work wants to be an example of circular economy, using a wasted biomass to produce fuels and waxes.

The present work is organized as follow: in the *Part I*, the theory behind biomass, the way to transform it into energy, the gasification process and the Fischer-Tropsch synthesis process will be explain in detail. The main process to convert biomass into energy will be analyzed with a focus on the gasification, which is one of the core parts of the plant. In addition, the main typology of gasifier will be explained and, in the end, the most appropriate for the purpose will be chosen. In the *Fischer-Tropsch synthesis* chapter, the mechanism that lead to the formation of hydrocarbons will be shown together with the selection of the reactor type and the catalyst.

In the Part II, the plant will be presented together with all the choices and the hypothesis that have been made. In particular, the choice of the biomass is very important for the plant efficiency and economic sustainability. In the *Aspen Plus model*, the four sections of the plant will be presented: the *6.1 Gasifier*, the *6.2 Syngas clean-up and conditioning*, the *6.4 Syncrude production* and the *6.5 Other balance of plant*. In the *6.2 Syngas clean-up and conditioning*, the main methods for the gas cleaning will show. In this way, it will be possible to make the better decision on what equipment is better to employ. In all the chapters, the hypothesis done for the Aspen Plus model will be listed. Furthermore, to find the best efficiency and the lower cost of production, three different configuration will be shown in *Plant layouts*. To conclude this second part, the pinch analysis will be carried out for all the cases. In this way, it will be possible to understand if the plant needs a heat integration and to know the number and the power of the heat exchangers.

In the last part (Part III), the results will be shown: the production and the efficiencies of all the cases will be the first presented, after the mass and energy balance plus the carbon efficiencies will be reported for completeness. A section of comments will be presented in order to explain the results found. Moreover, an economic evaluation will be shown: a brief theory part will be introduced just to better understand the evaluation performed. Then, the result will be presented and commented. Finally, the *Conclusions* will show a comparison with other works and further developments that would be done. On the *Appendix A – Aspen model*, all the details about the model will be displayed.

2. Biomass

Biomass is a plant and animal-originated material suitable for energy use and as a carbon feedstock [9]. Biomass is probably the oldest source of energy after food. Hominids used wood to make light, keep away predators, cook, etc. Earlier, humans understood how to increase energy density of wood making charcoal: in this way it could be possible to reach higher temperature in furnace, useful in metal production. After the "gold age" of wood, coal became the main fuel thanks to the higher availability and wood was relegate to home cooking and heating.

Today wood is still using in domestic application. However other types of biomass such as waste, food residual, industrial bio-waste (e.g. nut shells or grape marc from food processing) have gained relevance in several industrial uses. IEA evaluated that in 2017 10.7% of the global energy demand was satisfied by biofuels and waste (about 1040 Mtoe) [10]. Locally, there are some countries in Europe which have a high penetration of biomass in their energy mix. For instance, Sweden supplies 23% of its energy needs with this source and Finland reaches one fourth [11].

Biomass is an important renewable energy source because it has the advantage of being used on demand, without costly energy storage system (e.g. conversely photovoltaic energy). This is an aspect that is common for all biomass typologies. The most commons are briefly analyzed.

2.1 Types of biomass

2.1.1 Woody biomass

The most common form of biomass is wood. It is used in log, chips, or pellets shape. It is composed of organic matter as cellulose, lignite and hemicellulose and a small part of inorganic matter (ash). The organic matter is the main component of wood fiber and it is basically made of carbon, hydrogen and oxygen with low amount of nitrogen, sulfur and chlorine. Its energy density is lower compared to a fossil liquid fuel as diesel and its lower heating value (LHV) is strongly dependent from its moisture content. It has some historical affinity with coal and there are several examples of uses of wood together with coal. Furthermore, thanks to torrefaction process (a thermal treatment to obtain a high-level drying of a biomass), its energy density increases and it can be powdered easily.

Wood can be extracted from forests or from dedicated plantations. Poplar and willow are two example of trees in these plantations: on flat lands it is simple to irrigate and fertilize the soil and the plants can be cut down every 20-25 years [11]. On the other hand, European forests cover about 182 million of hectares, so the 43% of the total Europe surface [12]. Conversely to the rest of the world, the European soil surface covered by trees, is growing and, between 1990 and 2010, the expansion was been of 11 million of hectares [12]. Finally, the 42% of the total amount of wood produced in Europe is for energy purpose and its contribute to European renewable energy sources (RES) for about a half [12].

2.1.1.1 Forest residuals

The main interesting part of a tree is the trunk: it can be cut in smaller parts and sold to small consumers for their house uses, or to medium and big companies that transform it into timber, wood objects, etc. The small branches are not very interesting for these purposes, but they can be for energy uses. On the other hand, the main disadvantage is the small density due to high volume, which means high transport cost per unit of energy. However, an advantage is that this is a side source and it can be improved without further forest depletion.

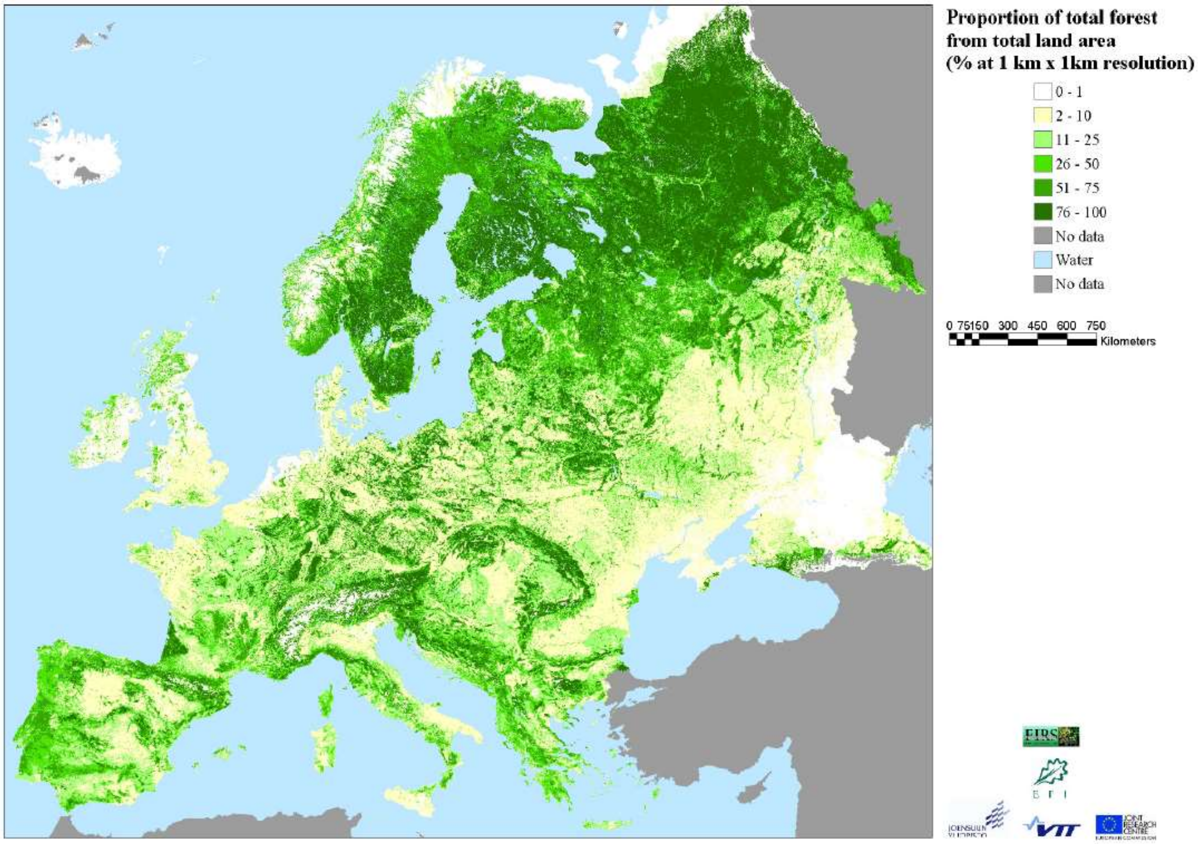

FIGURE 1 - FOREST DISTRIBUTION IN EUROPE [13]

2.1.2 Herbaceous biomass

Differently to woody biomass, herbaceous one has a different composition and often a higher ash content. Some examples of this type of biomass are switchgrass, Miscanthus, sugar cane and they are cultivated. The main advantage is the possibility to have the source near the process plant, so avoid long transportation, and to have a fully production after a sort time. They do not require many years to grow as trees, many of them need just flew months. However, the main disadvantage is the amount of fertile soil taken from food production, together with the environmental damage due to intensive agriculture. Sure enough, the large use of fertilizers and pesticides can lead to soil depletion and water eutrophication.

The main example of crops is definitely the corn (*Zea mays*), which is widely used as food/animal feed or for energy purposes. In 2014, more than one billion tons of corn and over 3 million tons of maize-oil were produced globally [14]. It is possible to produce bio-oil and/or ethanol from it. Furthermore, not only corn is used for that purpose, also wheat, rice, potato, sugar beet, sugar cane, etc. are used. For instance, in Brazil, alcohol is produced from sugar cane to power cars as gasoline substitute. In 2015 the total production of ethanol in the world was almost 100 million cubic meters, United States produce about 60% of that volume and USA plus Brazil have the 85% of the global production [15].

2.1.2.1 Agriculture residuals

As forests, fields produce wastes. All the cereals, as corn, wheat, rice, produce large amount of straw. This material has a considerable amount of energy and it can be used in biodigesters, combustors or gasifiers. Moreover, residuals have no impact on the soil exploitation. However, agriculture wastes have a seasonality and they have to be stored to get a constant supply during the whole year. This storage requests huge volume due to the really low density of the material.

2.1.3 Wastes

There are other biomasses that are neither woody nor herbaceous as organic wastes, animal manure and sewage sludge. These are generally low-grade biomass and the general way to extract their energy is fed a biodigester, a gasifier, or an incinerator. The main advantage of these biomass is the low cost (they are wastes) and it is a great example of circular economy producing energy from wastes. On the other hand, they are difficult to handle due to their high-moisture and high-ash content together with high amount of sulfur, nitrogen and chlorine.

2.1.4 Summary

TABLE 1 - BIOMASS SUMMARY TABLE

Biomass	Pro	Cons
Woody biomass (wood)	✓ Relatively high LHV ✓ Easy to handle	✗ Limited resource
Woody biomass (forestry residuals)	✓ No further deforestation	✗ Low energy density
Herbaceous biomass (crops)	✓ Fast growing	✗ Soil depletion ✗ Food competition
Herbaceous biomass (agriculture residuals)	✓ No further soil utilization	✗ Seasonality ✗ Low energy density
Wastes*	✓ Waste appreciation ✓ Reduce waste environmental impact	✗ Low energy density ✗ High ash content ✗ High moisture content ✗ High S, N, Cl content

* Organic wastes, animal manure and sewage sludge.

2.2 From biomass to energy

Wood is usually used in its solid form as it is, or transformed into smaller shapes, undergoing combustion processed or other thermochemical conversion. On the contrary, the other types of biomasses are preferably converted from their solid form to gas and liquid compounds, though bio-chemical or thermo-chemical processes. Bio-chemical conversion exploits biological processes to obtain such products. For instance, manure is transformed into biogas and sugar cane into ethanol. Thermo-chemical process, such as gasification, pyrolysis and combustion, uses high temperature processes to crack and convert biomass into secondary products.

2.2.1 Fermentation

The fermentation is a metabolic process to obtain energy from organic matter (especially hydrocarbons) in absence of oxygen though the action of enzymes. There are several types of fermentation (lactic acid, butanediol, butyrate, etc.), but the alcoholic one is probably the most used to produce energy.

The complete reaction converts glucose molecules into ethanol, it is the same process to make wine or beer. In these case grape and barley or wheat are used, for the energy production are used low-cost biomass such as sugar cane or corn. Finally, bioethanol is obtained though a distillation process to eliminate water and improve the quality. The solid residual can be used in other processes or as fertilizer.

2.2.2 Biodiesel production

It is a process to convert vegetable oil (from corn, sunflower, soybean, canola, etc.) into a fuel quite similar to the diesel from crude oil. In particular, the process converts fat molecules into long-chain fatty acid esters, thanks to the intervention of methanol (MeOH) or ethanol as solvents. The resulting fuel is used in regular diesel engine without any difference for the user. Lastly, an advantage is the possibility to use exhausted cooking oil that it is recycled from restaurants and domestic kitchen.

2.2.3 Anaerobic digestion

AD is a process where bacteria are employed to degrade a biomass (such as wastes, manure, crops, etc.) in absence of oxygen. These microorganisms break carbohydrates, proteins and fats with water forming monomers (hydrolysis process). Monomers are converted in alcohols and acids in a prime step and further in acetic acid in a second one. Finally, acetic acid is converted into methane and carbon dioxide, which form the so-called biogas. Although, the process has not a complete utilization of the resources: the digestate (so-called the material exiting from the digester) still has an energy content.

2.2.4 Pyrolysis

Pyrolysis is a thermochemical degradation in absence of oxygen, to convert a biomass into a synthetic gas (syngas) made of hydrogen, carbon mono- and dioxide and vapors of aromatic hydrocarbons. Cooling down the syngas, a fraction condenses and it is called pyrolysis oil. This oil is suitable for heat, power generation and as a transportation fuel. The rest of the gas can be burnt as well, used for hydrogen production or in chemical synthesis. It is possible to use woody or herbaceous biomass but also wastes and manure. Lastly, the solid remaining has an high amount of fixed carbon and it is called char (or bio-char) [16].

2.2.5 Gasification

The gasification process is a method to produce gaseous fuel (syngas) from a liquid or solid biomass. It produces a negligible amount of vapor respect to pyrolysis. Char are not produced and a fully-conversion is usually achievable. A furthered treatise of the gasification will be done in the next chapter.

2.2.6 Summary

TABLE 2 - BIOMASS TO ENERGY CONVERSION METHODS

Method	Pro	Cons
Fermentation	✓ Direct liquid fuel production	✗ It uses crops ✗ Production of a restricted number of fuels ✗ Partial conversion of the resources
Biodiesel	✓ Possibility to use exhaust vegetable oil ✓ Direct liquid fuel production	✗ It requests vegetable oil ✗ Other chemicals are needed to complete the synthesis ✗ Production of a restricted number of fuels
AD	✓ Low-cost fuel ✓ It works with wastes	✗ Partial conversion of the resources
Pyrolysis	✓ Fuel flexibility ✓ Direct liquid fuel production	✗ Partial conversion of the resources ✗ Necessity to syngas conversion
Gasification	✓ Fuel flexibility ✓ Fully-conversion of the fuel	✗ Necessity to syngas conversion

3. Gasification

3.1 Introduction

Gasification is defined as the conversion of any carbonaceous feedstock into a gaseous product with a useful chemical heating value [17]. In other words, it is a thermal treatment to transform a solid (or liquid) biomass with a complex chemical structure (e.g. lignocellulose) into a simple gas mixture (mainly composed of H_2, CO, CO_2 and CH_4). Gasification is primarily used with coal due to the low cost and large availability or with petroleum coke. Another common fuel employed for this scope is wood, but also general biomass from agriculture, municipal solid wastes (MSW) or organic fraction (OFMSW) can be used.

First examples of gasifier were commercialized in 1812 and about 70 years later there was the first combination between a gasifier and an internal combustion engine [18]. During 1930s in Italy, Mussolini declared that the Nation would be independent from all points of view and the import of raw materials and goods from abroad were no longer permitted. But without foreign oil, transport industry risked to collapse and other solution had to be found. The only abundant and economic fuel in Italy was wood (gas fields just started to be discovered). An idea was to put a small gasifier, fed by charcoal or directly by wood, in the back of cars, buses, etc. to produce a combustible gas to power the engine [19].

FIGURE 2 - FIAT 1500 POWERED BY A SMALL GASIFIER (1935) [20]

During the last years, many projects were developed. In Figure 3 **- Growth in total gasification power** it is shown the evolution in thermal power of the produced syngas. An important increment appears during oil-crises of 1979, when oil price encourages companies to find other energy sources. In recent years, gasification growth becomes very important. Although it could be associated to the green-transition and renewable sources such as biomass, its growth is mainly due to China industrial development and coal gasification, as shown in Figure 4 **- Gasification capacity by country** and Figure 5 **- Gasification capacity by source**.

Biomass and waste gasification plants have a negligible installed power compared to coal ones. The first ones are usually used to produce chemicals (such as ammonia) or liquid fuels (methanol, ethanol, syncrude, etc.), and there is a large number of planned plants able to produce gas (synthetic natural gas, hydrogen). Finally, gasifiers for power production only are a minority [21].

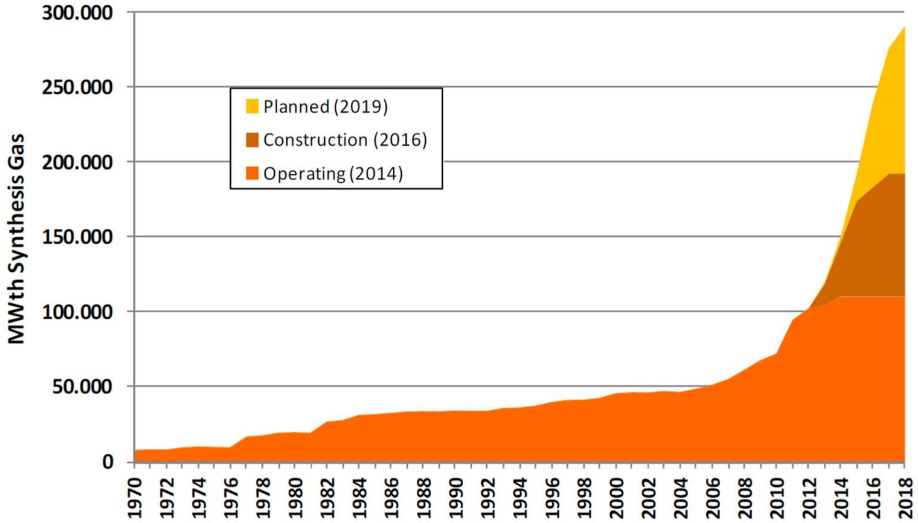

FIGURE 3 - GROWTH IN TOTAL GASIFICATION POWER [21]

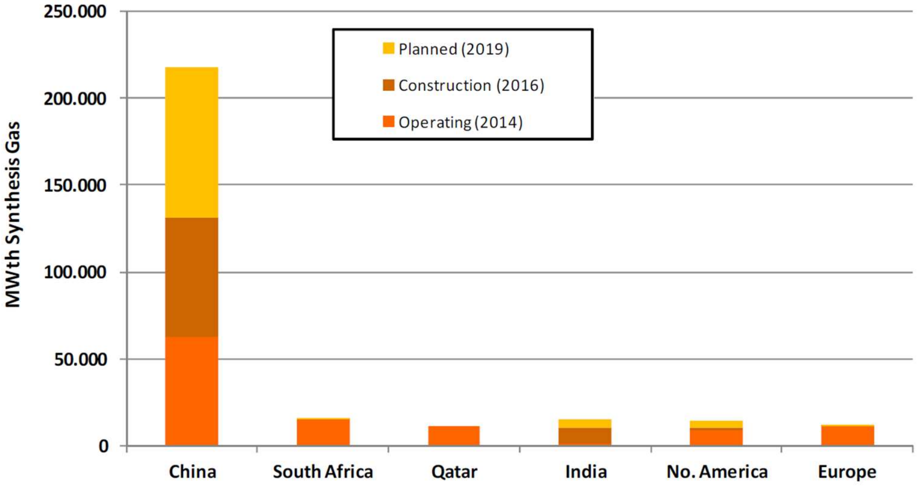

FIGURE 4 - GASIFICATION CAPACITY BY COUNTRY [21]

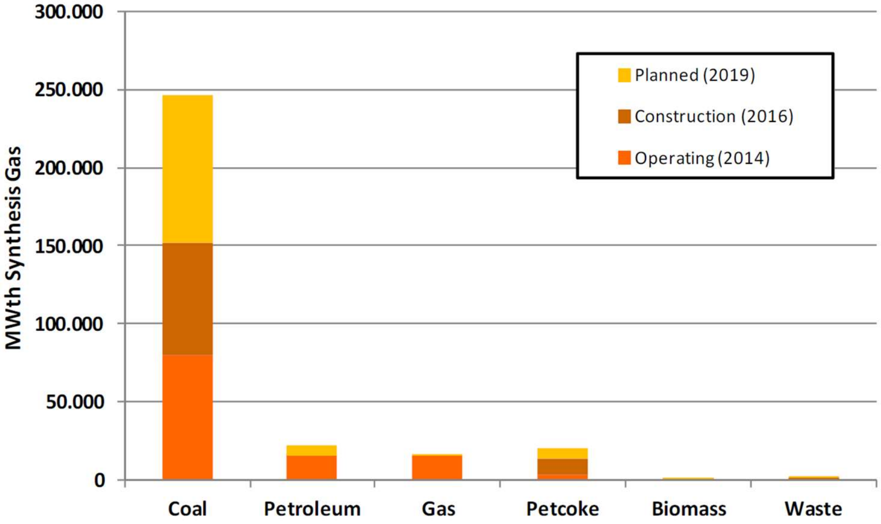

FIGURE 5 - GASIFICATION CAPACITY BY SOURCE [21]

3.2 Principles

The gasification process consists in the conversion of carbonaceous material into gas though high temperature processes with no combustion. The conversion takes place thanks to a gasifying agent such as oxygen or team carrier. It could be pure oxygen or air, but also steam and carbon dioxide or a combination of them. Considering the firsts two, oxygen reacts with molecules of lignocellulose cracking them into light products: this is call partial oxidation and the process is exothermic, so the reaction can be self-sustainable; but it produces a considerable amount of CO_2 and H_2O. Otherwise, by using steam or CO_2, the reaction is endothermic and heat has to be provided from the outside. The latter solution is the most used, since the product syngas has a higher heating value respect to the first case based on oxygen. Moreover, the use of steam is the most relevant in hydrogen production because the molecule of water can react with carbon-rich structure of biomass: oxygen goes from water to a carbon atom forming H_2 and carbon monoxide. This process is similar to coal gasification, the main difference is the lower reactivity of the biomass.

Gasification can be divided in 4 main steps:

1. **Drying**: all biomass types contain water inside. For example, that digestate leaving the digester of manure or food waste has an humidity higher than 60% [22]. This has a huge impact on the performance and the efficiency of a gasifier [23]. When biomass is inserted in the reactor, it undergoes to a fast drying due to the high operating temperature, though an endothermic process. To increase the efficiency of this part, it is possible to apply a pre-treatment of the feedstock called torrefaction. The solid is heated up to a couple of hundreds of Celsius degree for about 30 minutes [24], water evaporates but also a part of useful molecules start to pyrolyzing. Even though this process solution increases the heating value of biomass and changes the reactivity of char [24], it is energetically and economically cost intensive.
2. **Pyrolysis**: it is a thermal degradation of the organic matter. It occurs at temperature higher than 200°C in absence of oxygen [25]. Long-chain molecules are cracked into short ones as gases and hydrocarbon vapors. There are different types of pyrolysis: based on the variation of the biomass resident time in the reactor, the start-up ramping temperature and the possible condensation of a part of bio-oil (a mixture of hydrocarbons and aromatic compound similar to diesel [16]). At the end of the pyrolysis, remaining solid mass is called char.
3. **Oxidation**: oxygen reacts with long-chain molecules cracking them, though a partial oxidation reaction. It can occur also with water or carbon dioxide which bring oxygen to the reaction. This part is generally exothermic and the mass solid remaining is called char (or bio-char from biomass to distinguish it from coal or petroleum char).
4. **Char gasification**: it is usually done with steam or CO_2, but also with oxygen or air. The main reaction here is carbon reacts with the oxygen carriers, following the reactions (1), (6) and (11) [26].
   At the end of the process it is possible to find some unreacted char and ash. Chars are generally interpreted simply as 100% carbon [23], [26]–[30], indeed other authors consider they as a mixture of carbon, hydrogen and oxygen [31].

TABLE 3 – GASIFICATION REACTIONS [32]

Number	Reaction	Energy	Name
(1)	$C + \frac{1}{2}O_2 \rightarrow CO$	-111 kJ/mol	Carbon partial oxidation
(2)	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	-283 kJ/mol	Carbon monoxide oxidation
(3)	$C + O_2 \rightarrow CO_2$	-394 kJ/mol	Carbon oxidation
(4)	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	-242 kJ/mol	Hydrogen oxidation
(5)	$C_nH_m + \frac{n}{2}O_2 \rightarrow nCO + \frac{m}{2}H_2$	Exothermic	C_nH_m partial oxidation

(6)	$C + H_2O \leftrightarrow CO + H_2$	+131 kJ/mol	Water-gas reaction
(7)	$CO + H_2O \leftrightarrow CO_2 + H_2$	-41 kJ/mol	Water-gas shift reaction
(8)	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	+206 kJ/mol	Steam methane reforming
(9)	$C_nH_m + nH_2O \leftrightarrow nCO + \left(n + \frac{m}{2}\right)H_2$	Endothermic	Steam reforming
(10)	$C + 2H_2 \leftrightarrow CH_4$	-75 kJ/mol	Hydrogasification
(11)	$C + CO_2 \leftrightarrow 2CO$	+172 kJ/mol	Boudouard reaction
(12)	$C_nH_m + nCO_2 \leftrightarrow 2nCO + \frac{m}{2}H_2$	Endothermic	Dry reforming

3.2.1 Gasification agents

The choice of a gas (or a mixture) for the gasification process play a key role, because from this it depends the composition of the outlet syngas. As anticipated, the main gases used are:

- **Air**. It is the cheapest, it has not cost of operation (or negligible), the cost of investment is low and it does not require an energy-intensive process to be heated up. The main disadvantage is the syngas dilution: air is made just for one fifth of oxygen, the other part is nitrogen and other inert gas, which has to be heated and transport during the process without any add of energy value. It is also possible to use enriched air (consisted of air with a higher oxygen yield): this solution is more expensive but provides a syngas with higher heating value [2], [33].
- **Oxygen**. It is expensive because it requires an air separation unit (ASU). On the other hand, it increases capital and operating cost and decreases efficiency because of its energy demand. Additionally, it avoids nitrogen dilution, that could reduce cost and volume of gas conditioning. Lastly, oxygen is corrosive when it has a high temperature. So, to avoid the problem, it is normally handled with steam or CO_2 in order to decrease its partial pressure.
- **Steam**. Water molecules react with carbon, oxygen is exchanged forming hydrogen and carbon monoxide. This reaction is endothermic, so it is not possible to carry on a gasifier fed only with steam without any external (or internal) source of heat. There are examples of gasification with air and steam together [22]. When a reactor is fed with steam it produces a syngas with higher LHV with respect to oxygen or air and higher fraction of H_2 [34]. High partial pressure of steam in syngas enhances the reverse water gas shift reaction, which occur at high temperature, reducing CO_2 yield and increasing CO one [35]. Also methane yield is reduced by the presence of water which supports steam methane reforming [27]. The main defect of water is the high energy demand to produce steam: the global efficiency of plant can be affected by this.
- **Carbon dioxide**. This is a method to consume CO_2 producing a useful product. This gas can react with carbon in Boudouard reaction and form two molecules of carbon monoxide. As the steam case, also here the reactions are endothermic. The produced syngas has low H_2 yield and high CO and CO_2 yield [27]. It is used as gas to dilute oxygen due to his lower energy consumption with respect to steam to be heated up and it is possible to be recycled from downstream product upgrades [36].

Table 4 - Gasification agents summary table

Gas	Pro	Cons
Air	✓ Low cost ✓ Low energy intensity ✓ Autothermal reactions	✗ Syngas nitrogen dilution
Oxygen	✓ No syngas dilution	✗ Expansive

	✓ Autothermal reactions	✗ ASU required ✗ Corrosive
Steam	✓ High H_2 yield in syngas ✓ High LHV of syngas ✓ Low methane yield	✗ Energy intensive
CO_2	✓ CO_2 re-utilization ✓ Low energy intensity	✗ Low H_2 yield in syngas

3.3 Types of gasifiers

During history, many gasifier typologies have been developed. Gasifiers can be divided into three main categories: fixed or moving bed, fluidized bed, or entrained flow (so bed-free) reactors. In general, fixed-bed downdraft (flow from top to bottom) gasifiers are used in small application, fluidized and fixed-bed updraft (flow from bottom to top) for medium ones and entrained flow for very large plants.

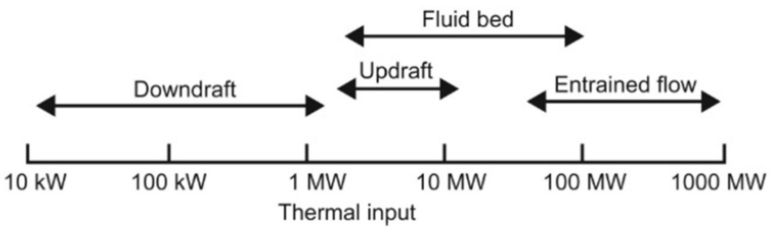

FIGURE 6 - RANGE OF APPLICABILITY FOR BIOMASS GASIFIER TYPES [37]

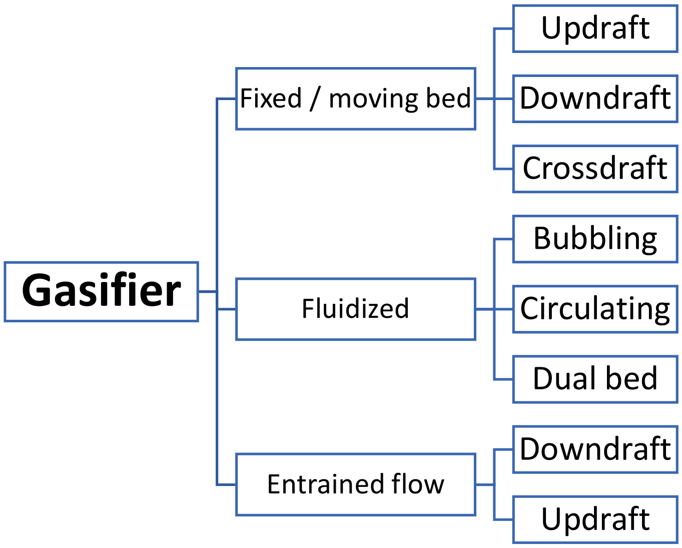

FIGURE 7 - GASIFICATION TECHNOLOGY

3.3.1 Fixed and moving bed

This type of gasifiers has a bottom which is solid. It is a grate where biomass is supported. The gasification agent can be injected from the top or the bottom of the reactor depending on downdraft or updraft configuration. They are inexpensive and of simple construction, so perfect for small size application.

Generally they work with temperature about 1000°C or less [37]. The partial load are usually well-tolerated up to 20% of the design power [38].

The updraft type has high tolerability for ash and moisture of biomass, high efficiency and production of high LHV. Air is fed from bottom (counter current respect to biomass) and exits from the top at relatively low temperature. Biomass feeding system is not very simple due to the fact that the solid enters near hot flammable gas. Finally, the produced syngas is generally used directly in a burner due to the high amount of tars [37] [39].

In downdraft gasifiers, the fuel is injected from the top, air (or oxygen) is fed together with biomass and/or in oxidation zone, gas flow downward so it passed through high temperature zone which cracks tars and make it one of the cleanest gasifier. The reactor is usually kept in slight low pressure. It has the advantage of easy gas and solid feed, but the high operating temperature could melt the ash. The syngas exits from the bottom at high temperature and it could be used to recover heat. It has a fast start-up compared to the updraft configuration [37] [39].

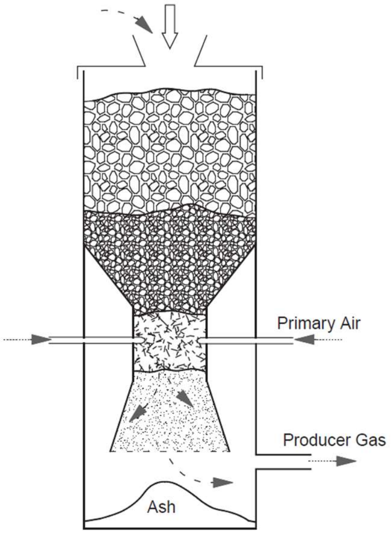

FIGURE 8 – DOWNDRAFT GASIFIER [39]

3.3.2 Entrained flow

Entrained flow (EF) gasifiers had been developed for coal gasification. They work only with powdered fuel, so pulverized coal and torrefied biomass can be used. This type of gasifiers works with high temperature, usually higher than ash melting point (higher than 1250°C), so the latter have to be maintained liquid and be discharged from the bottom. Such high temperatures lead to complete tars conversion and almost total carbon conversion [17], [40]. They work with steam/water and oxygen, which requires an air separation unit. Given their high affinity with coal, this technology has been thoroughly studied and developed, reaching high capacities and low specific costs. On the other hand, EF gasifiers are relegated to large plants. They are normally used in IGCC (internal gasification combined cycle) plants because they work under pressure (20-80 bar) and this allows reducing their sizes with respect to the same-power other gasifier typologies providing the same power. Even though, working with high pressure brings some counterpressure issue on the solid feeder. A solution is to mix powered coal with water forming a slurry, this could be handled as a liquid. A pump brings the slurry to the right pressure and it is injected in the gasifier. Although, this solution requires a huge amount of energy due to the fact that the water is liquid and it has to be vaporized. The plant overall efficiency is affected by this [17], [40].

Finally, there are two main types of EF gasifiers: top-fed or side-fed. Depending on where the fuel is injected from, the syngas exits from the bottom or the top of the reactor, respectively [17], [40].

3.3.3 Fluidized bed

Fluidized bed gasifiers (FBG) have a uniform temperature distribution. They use an inert solid (e.g. silica sand) or a catalytic solid (e.g. olivine, dolomite) with the fuel and gas. The gasification agent is injected from the bottom area through perforated plates, while the fuel can be introduced from either the side or top areas of the reactor. It is important that the hot gas does not flow back through the biomass loader, so a purge gas (generally N_2 or CO_2) is used to maintain a counterpressure. The syngas usually exits from the top and all the solid matter (ash, unreacted char and sand) exits from the side or from the bottom depending on gasifier type.

Thanks to the efficient heat flux exchange between the solid and the fuel, the operating temperature of this gasifier is lower than the one of the moving bed or the entrained flow gasifiers (800-900°C). Moreover, the tars production takes place in between the updraft and the downdraft gasifier section and has a strong dependence from bed composition [41]. If the residence time is short, the production of tars increases together with light hydrocarbon and condensable compounds. Furthermore, a cyclone is employed to divide the solid from the gas material. This component has to be maintained at high temperature to prevent from tars condensation on walls [37], [39]. Finally, partial loads are achievable up to 50% of the nominal power and working in overload is tolerated up to 120% [38].

FBGs have a high fuel flexibility, they can use coal or biomass of every kind, dried or with a high moisture content. Fuel can have a high or low heating value and ash content does not affect functionality: biomass chips are generally used, but there are example using MSW or manure [see Table 5 **– Some examples of FB gasifier, just one example per fuel type.** for references]. Also the grading is not a limitation and it is possible to introduce in the gasifier pieces with different size and form [32].

The main issue of this type of gasifiers is the difficulty to match heat required to keep temperature constant and the production of gas. In addition, the velocity of the gas inside the reactor is crucial: if it goes below a certain threshold, the bed become fixed and some hotspot can appear increasing the risk of ash melting and agglomeration with the sand. To solve this problem, it is possible to reduce the cross section of the gasifier, so gas velocity is increased and in the extreme case bubbling fluidized bed (BFB) becomes circulated fluidized bed (CFB). In this case all solid goes out and it is re-injected from bottom together with gasification agent and fuel [37], [39].

TABLE 5 – SOME EXAMPLES OF FB GASIFIER, JUST ONE EXAMPLE PER FUEL TYPE.

Plant name	Country	Gasifier type	Fuel	References
Güssing	Austria	FICFB	Biomass chips	[18]
Milena	Nederland	DFB	Wood pellet	[18]
The JOULE–MFCF	Italy	DFB	Almond shell	[18]
Blue tower	Germany	DFB	Waste	[18]
?/Clausthal Institute of Environmental Technology	Germany	CFB	Straw	[7]

?/ThermoChem Recovery International	USA	BFB	Black liquor	[7]
?	Spain	FCB	Forestry, olive and grape pruning, grape marc and sawdust	[42]

An investigation on a 100kWth fluidized bed gasifier fed with several types of fuels is reported by Pfeifer et al. [43]: they used wood chips, wood pellets, bark, straw, sewage sludge, lignite, coal and mixture of some fuels.

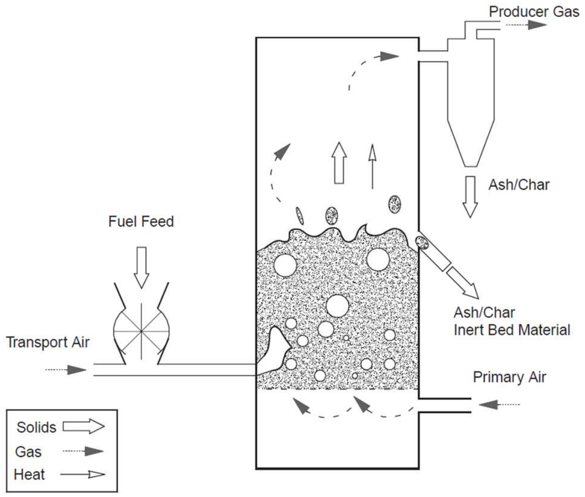

Figure 9 – BFB gasifier [39]

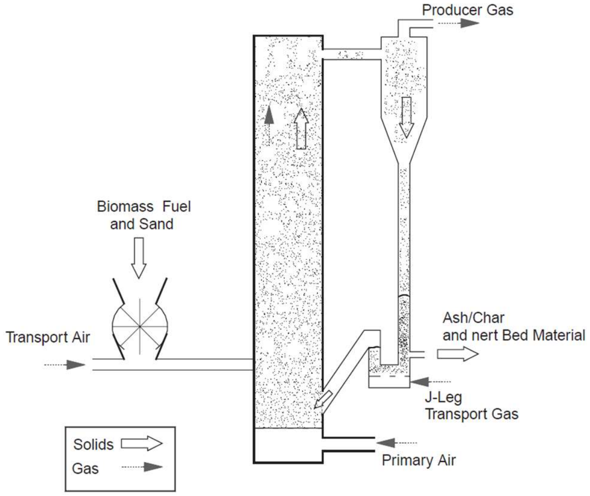

Figure 10 - CFB gasifier [39]

3.3.3.1 Dual fluidized bed

A hybrid configuration of gasifiers between BFB and CFB ones is the dual fluidized bed gasifier (DFB or DFBG): it is composed of two reactors that could be both BFB, both CFB or one and one. In the first reactor (the gasifier) the biomass is gasified with steam or carbon dioxide (or a mixture of both) while a fraction of the produced char is circulated to the second reactor (the combustor). In this second reactor, char is thus combusted and the generated heat is transferred to the gasifier through the circulating material. DFBs are interesting because they can work as gasifiers but also as pyrolizer thanks to their capacity to supply the heat necessary to sustain the pyrolysis.

In the combustor, air is injected to the bottom and char are burnt increasing sand temperature. At the top, the sand is separated from the gas and further recirculated back into the first reactor. The exhaust gas exits separately from syngas, so it is possible to use air to generate heat that the gasifier needs without syngas nitrogen dilution. Moreover, the flue gas can also be also recirculated back to the combustor when low power is requested, in order to maintain the volume flow constant and guarantee sand circulation. During partial load working, low amount of air is used to burn the char. The flow could not be enough to sustain the accurately circulation of the sand and the gasifier could be damaged (for instance due to hot spot creation). Using an excess of air can be a solution, however it has to be heated up losing energy. Instead, using exhaust gas which is at high temperature, it is possible to recirculate back a fraction of this gas, keeping the right flow inside the combustor and using only strictly necessary air to complete the combustion [31].

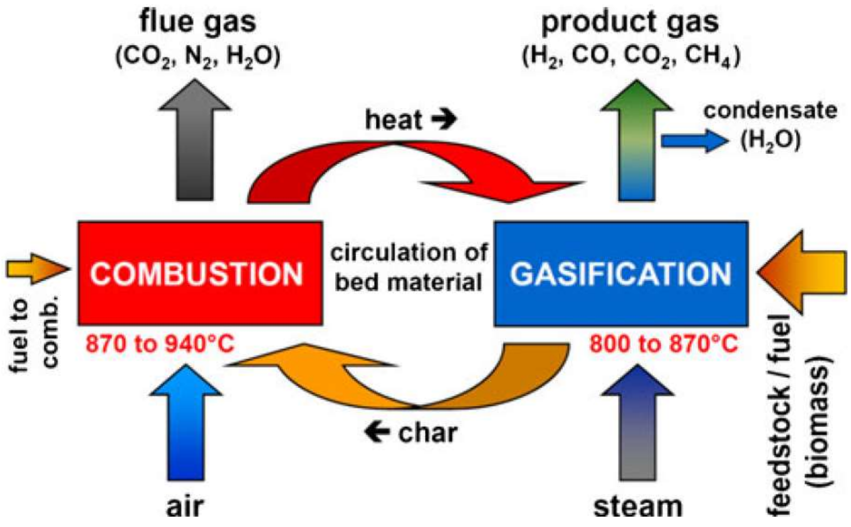

FIGURE 11 - BASIC PRINCIPLE OF DFB PROCESS [44]

In fluidized bed combustors (FBC), in general, and thus in the char-combustor part of the DFBG, the hottest component of the whole gasifier, cannot reach high temperature due to ash-melting and sintering problems. If temperature reaches a certain value, the ash particles that enter in contact with each other withstand a sintering process and a clump is formed. FBs do not tolerate conglomerate formation and this process has to be avoided. Additionally, ash melting is not tolerated due to the impossibility to maintain the ash liquid until the discharge.

Lastly, there are several example of DFB plants, three of these are in Austria (Güssing 8MWth, Oberwart 8.5MWth and Villach 15MWth[44]) but there are other example of smaller size (e.g. 100kWth at Vienna University [43]). This shows that dual fluidized bed gasifier can be used for a wide range of sizes. This is an advantage, given the avoidance of moving biomass through long distances due to his low energy density.

Thus, both small and large biomass producers can benefit from this gasifier (e.g., local biomass producers or wastewater treatment plants and paper mills that produce syngas to generate electric energy needed to reach their self-sufficiency).

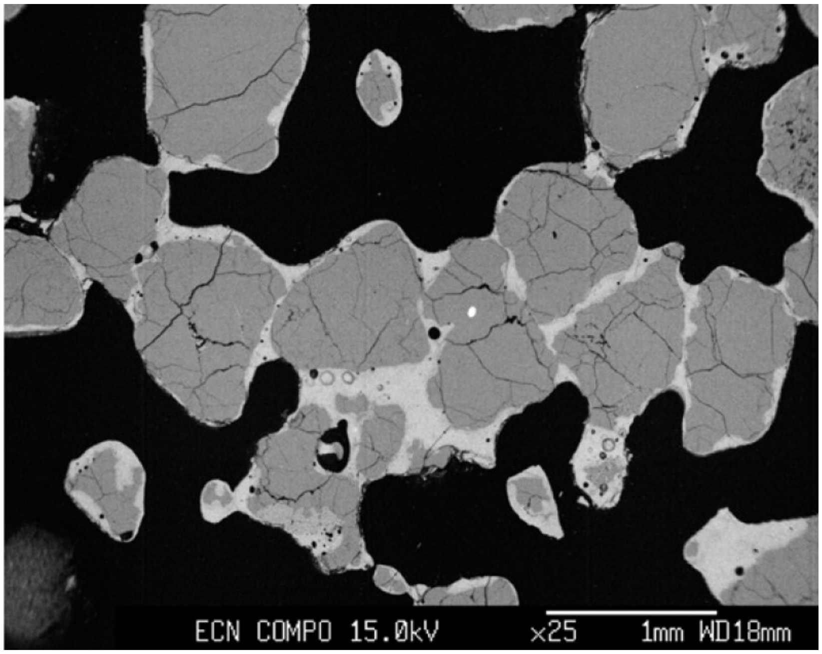

FIGURE 12 - AGGLOMERATE FORMATION-BINDING MATERIAL RICH IN POTASSIUM [45]

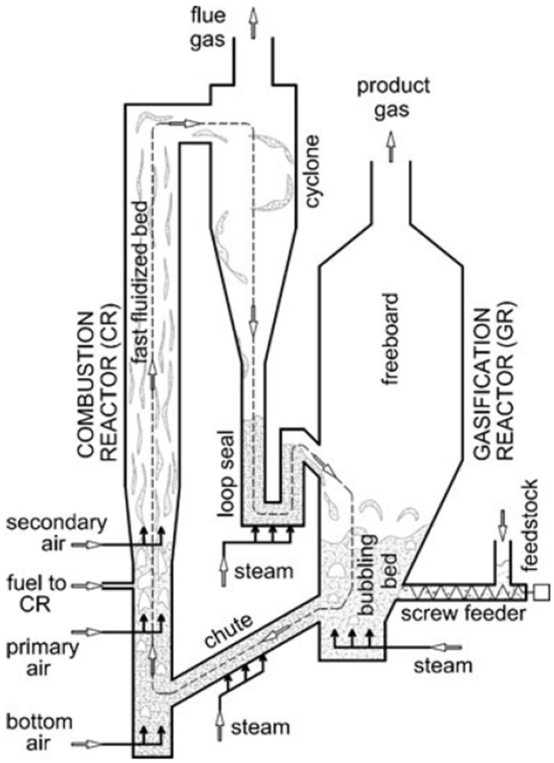

FIGURE 13 – SCHEME OF A DFB GASIFIER [44]

3.4 Summary

Table 6 - Gasifiers summary table

Gasifier	Pro	Cons
Fixed bed	✓ Suitable for small applications ✓ Construction simplicity ✓ Low cost	✗ Necessity to use oxygen if syngas nitrogen dilution has to be avoided
Entrained flow	✓ Working in pressure (avoid syngas compressor) ✓ No tars production	✗ Suitable only for large application ✗ Necessity to use oxygen ✗ Biomass pre-treatment required ✗ Complex feeder for solid fuel
Fluidized bed	✓ Suitable for small-medium application ✓ Possibility to add catalysts ✓ High fuel flexibility ✓ Possibility to use air even though syngas nitrogen dilution has to be avoided	✗ High start-up time ✗ Fluidized condition has to be maintained ✗ No tolerability to ash melting/agglomeration

4. Fischer-Tropsch synthesis

4.1 Introduction

Franz Fischer and Hans Tropsch had been working at the Kaiser Wilhelm Society (Weimar Republic) when, in 1930, the US patent office published a patent [46]. The two men explained their discovered in the paper: a method to produce methane starting from carbon oxide was already known, however nobody had already found a way to produce heavier hydrocarbon. They found a way to increase the chain-carbon number of hydrocarbons produced: in this way it was possible to produce liquid fuel and waxes starting from a syngas (made of H_2 and CO). This process took their names: Fischer-Tropsch synthesis (FTS). The very revolution that this discovered brought in the world, was the possibility to produce liquid fuels (for trucks, cars, planes, ships, etc.) starting from a gas, which could be made by partially burning coal (gasification process), wood, natural gas, etc. So, a nation with low or no availability of oil but with large reservoir of coal (e.g. Germany or South Africa) could produce fuels.

During 1930s, a 1000-tons-per-year plant was built in Germany. In the '40s three plants appeared in Japan with a capacity of 110 thousand tons per year. During WWII also the United State started to construct their plants. After the war, South Africa got some difficulties to import oil, but thanks to its large reservoir of coal, the Sasol company started to synthetize Fischer-Tropsch products (FTP) [47].

Starting from the '90s, some gas to liquid (GTL) plants appeared in Qatar, Malaysia, South Africa, etc. They used natural gas (NG) to produce the syngas required for the FT synthesis (by steam or dry reforming). The use of NG has many advantage respect to coal, primarily due to the absence of dust, low amount of sulfur and other impurities. Today, it becomes fashionable once again due to global warming and targets to reduce greenhouse gases emission: it is possible to use wood or a general biomass as well, to produce the syngas needed to FTS as explained in the chapter before, or use a biogas in substitution of the NG.

4.2 Reactions

The FTS is a catalyzed hydrogenation-alike reaction of carbon monoxide and it produces alkanes, alkenes and oxygenated compound (e.g. alcohols) depending on the catalyst type and reaction condition. The global formation reaction formulae are reported below:

Alkanes
$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \qquad \textbf{(13)}$$

Alkenes
$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \qquad \textbf{(14)}$$

Alcohols
$$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O \qquad \textbf{(15)}$$

These reactions occur in presence of a catalyst which could be cobalt, ruthenium, iron, nickel, or a mixture of them. To better understand the mechanism of catalysis, see the section 4.5 Catalysts.

The FTS is influenced by the temperature and the partial pressure of the reactants, not only from the kinetics point of view (the higher is the temperature, the higher is the probability that molecules can interact with each other), but it also considering the molecular distribution of the products. FTS can produce a wide spectrum of hydrocarbons, from methane to heavy waxes passing through gasoline, kerosene and diesel. If the FT reactor works at high temperature (300-350°C), the products will contain a high yield of light fraction as NG or liquified petroleum gas (LPG), while working at low temperature (200-250°C) it is possible to get a high fraction of diesel and waxes. Moreover, high pressure has the effect of increasing high-molecular-weight compounds yield. Another important aspect that working parameters such as pressure and temperature can influence, is the branched molecules formation: avoiding these products is important to get a high quality diesel and kerosene (with high cetane number which led to shorter ignition time). So, low temperature and high pressure are employed. On the other hand, high-quality gasoline has to have a high-octane number and so riches in aromatics and branched molecules. It is not possible to use FT gasoline such that, it requires an upgrade process.

In general, the aim is to produce long-chain molecules because in most of the cases, the interest is to produce fuels for engine (mainly diesel and kerosene) and/or lubricant and waxes. Light fractions, such as LPG, are cheaper that the others and if the aim is to produce a gas (e.g. synthetic NG or SNG), FTS is not the most suitable choice (methane synthesis from syngas is feasible and preferable). Liquid fuels are usually considered C_{5+}, with a boiling temperatures higher than the environment one.

4.3 Mechanism

Fischer-Tropsch kinetics is intricate due to the several compounds involved and the complexity of CO catalyst chemistry. In the next section, a briefly explanation of the synthesis mechanisms is reported.

4.3.1 Methylene polymerization

Main FTS products are linear hydrocarbons (HC), so the treatise will focus on the formation of these ones. Fischer and Tropsch proposed that the synthesis is a polymerization of methylene groups. CO is absorbed from the catalyst and it is dissociated on the surface forming carbide and oxides. Also hydrogen undergoes the same process forming hydride (see Figure 14 **- Chain-growth mechanism [48]**) [48]. Carbon and hydrogen react with each other and form a methyne group (CH), further upgraded into a methylene (CH_2) and so on. When a methyl compound (CH_3) is formed, hydrocarbon starts to grow, reacting with others methylene groups. The higher is the number of contacts which occurs between these functional groups and the hydrocarbon molecule, the longer is the chain formed, determining higher formation of heavy hydrocarbons. The process ends in two ways:

- β-hydride elimination: a hydrogen atom of the molecule is exchanged between a carbon of the HC molecule and the metal catalyst, which is bounded with a carbon of the HC molecule. Finally, the metal is bound with a hydrogen and the molecule is free. When this occurs, an α-olefin is formed (carbon double bond between the lasts two carbon atoms).
- Reduction by surface hydride gives a paraffin (only single bonds through carbon atoms).

The parameter α (called chain-growth probability) measures the probability that these two processes do not occur, so molecule can continue to growth up. The oxygen atoms react mainly with hydrogen forming water.

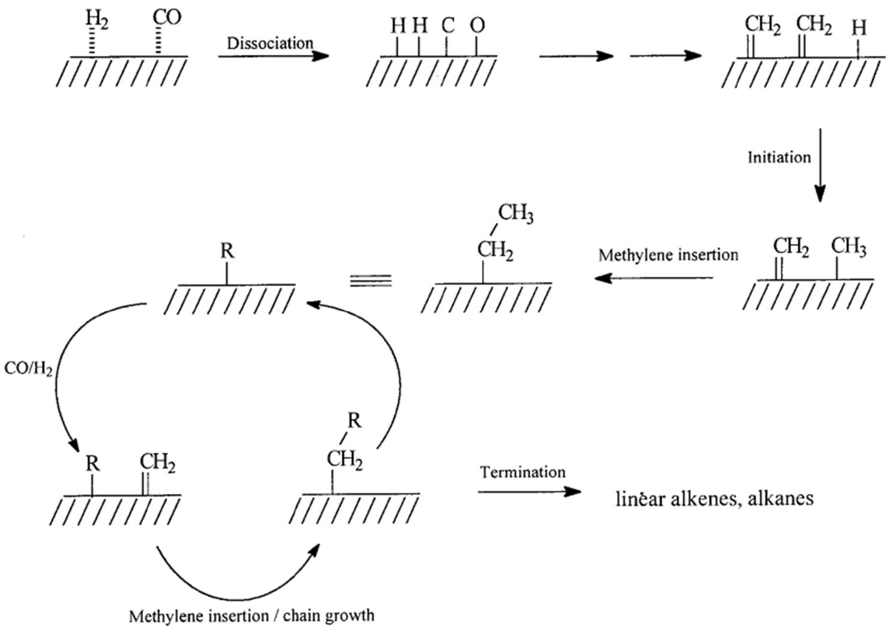

FIGURE 14 - CHAIN-GROWTH MECHANISM [48]

4.3.2 FT products characterization

It is important to understand the composition of the syncrude. A mathematic description of the hydrocarbons spectrum is provided by the Anderson-Schulz-Flory model (ASF):

$$x_n = (1-\alpha)\cdot\alpha^{n-1} \quad \textbf{(16)}$$

$$w_n = n\cdot(1-\alpha)^2\cdot\alpha^{n-1} \quad \textbf{(17)}$$

Where x_n is the molar yield of the hydrocarbon with carbon chain number equal to *n*, w_n is the mass fraction and α is the chain-growth probability. Methane yield is not well represented from this distribution [49].

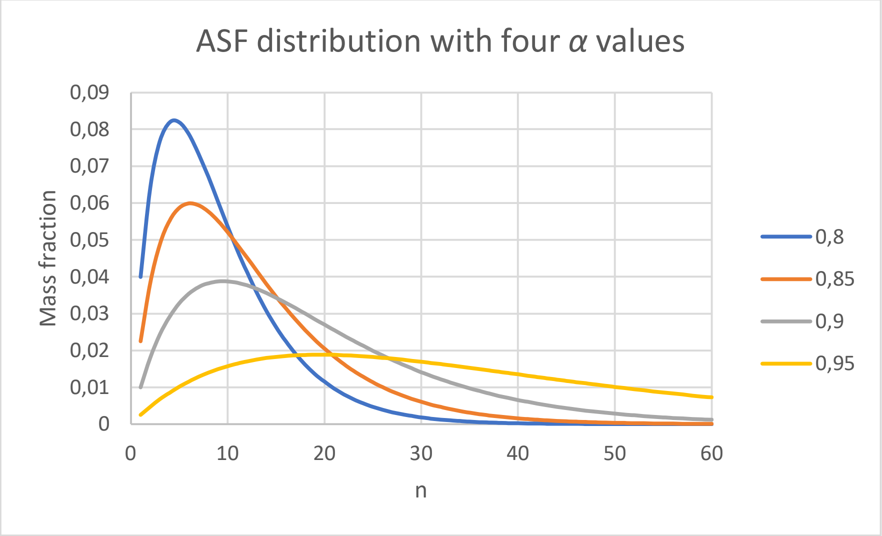

FIGURE 15 – ASF DISTRIBUTION FOR DIFFERENT ALPHA VALUES

The graph shows how α is important in syncrude composition.

The parameter α depends from many kinetics factors, although a linear approximation, keeping into account only temperature and syngas composition, is reported from Panahi et al. [50] for cobalt catalyst.

$$\alpha = \left(0.2332\,\frac{y_{CO}}{y_{H2} + y_{CO}} + 0.663\right) \cdot \left(1 - 0.0039\,(T - 533)\right) \tag{18}$$

Where y_{CO} is the carbon monoxide yield, y_{H2} is the hydrogen one and T is the reactor temperature.

If iron or cobalt are employed for FTS, alcohols formation is negligible but not the alkenes one. A relation between alkenes and alkanes (also call olefins and paraffins respectively) is provide by Cinti et al. [51]:

$$\left(\frac{O}{P}\right)_n = e^{-kn} \tag{19}$$

Where O is the olefins yield, P the paraffines one and k a constant parameter with value of 0.3 in this case (Co catalyst). In the graph is shown the fraction of alkenes with respect to the total production (α = 0.9).

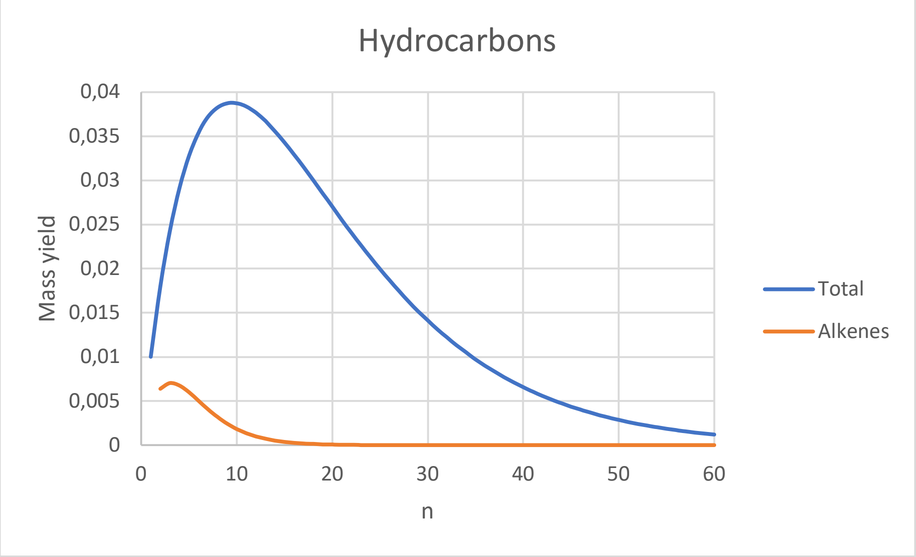

FIGURE 16 – TOTAL HC VS. OLEFINS

After n = 15/20, the amount of alkenes is almost zero and negligible.

In order to produce high molecular weight molecules, low temperature and low H_2/CO ratio is preferable. Despite this, it is not possible to go under a certain temperature, due to the slowing down of the kinetic, and under a certain hydrogen-to-carbon monoxide ratio, due to carbon deposition which can be formed on catalyst. This is a big issue because it can deactivate the catalyst and the whole reactor can be compromised. Generally, a ratio about 2 is employed, but there are some investigation of ratio near 1 [49], [52].

High pressure is employed to increase chain-growth probability and to increase the CO consuming ratio [53].

4.4 Reactors

The choice of a FT reactor is important because it has two main function: firstly it supports the catalyst; secondly, it removes the heat produced in the reaction. Several types have been developed and they can be divided in 3 categories: fixed, fluidized and slurry bed reactors.

4.4.1 Fixed bed reactor

The fixed bed reactor is made of tubes to make easier the cool-down process: syngas passes through the tubes within the catalyst and coolant flows on shell side. This configuration is used for small application, but size can be improved adding more tubes. It is scalable and the most used also thanks to its simple design [47], [54]. Off-gas and HC flow downstream, exiting from the bottom and the liquid phase formed trickles down and it is simply separated. On the other hand, fixed bed required catalyst particle size of about 1mm, which is huge for this synthesis, and the surface activity is not so high respect to the other reactor types. Finally, pressure drops are substantial [54].

A successfully HTFT reactor of this type is the Sasol Advance Synthol reactor used for more than 30 years. The reasons of its success are several among which low catalyst consumption, low maintenance and simplicity to design and construct [54].

The catalyst has to be supported in fixed bed reactors and the role of this is very important. It has the main scope to transfer heat from the surface of the catalyst to the external coolant fluid. There is the necessity to avoid hot spot points, where the temperature rises and selectivity is moved towards light products. In the worst case, the catalyst can be damaged. For example, zeolite supported catalyst decrease CH_4 production and increase C_{5+} selectivity. Metal oxides and non-metal oxides are usually used, like alumina- or silica-based, and they can increase the catalyst stability. For instance, silicon carbide is more effective than alumina-based support thanks to its very high thermal conductivity [47].

4.4.2 Fluidized bed reactor

It can operate at higher pressure and temperature with respect to fixed bed and it can have a better efficiency. Fluidized bed reactor has a higher heat transfer, making it easier to reach isothermal condition just as the temperature control. Additionally, the catalyst handling is easier [47]: metal particles are smaller than in fixed bed and this increases the activity. These reactors are usually bubbling column (BFB) or fixed (FFB) for LTFT (three-phases reactor) and circulating fluidized bed (CFB) for HTFT due to the presence of only two phases (gas and solid) [54]. Despite the higher complexity, it costs less than a fixed bed of the same size [55].

4.4.3 Slurry bed reactor

This typology was developed to avoid the criticalities of fixed bed reactors. In particular, it is easier to design and also much cheaper to construct. Thanks to the slurry (catalyst plus liquid products), the temperature control is higher and hot spot are eliminated, so average higher temperature could be achievable. The activity is high due to the large catalytic area and pressure drops are low. Nevertheless, the separation of the catalyst from waxes is difficult. Finally, the poisoning risk is higher: whole the catalyst is exposed fairly to sulfur or other contaminants while in fixed bed reactors, the first part acts as guard bed and prevent the complete deactivation of the catalyst [56].

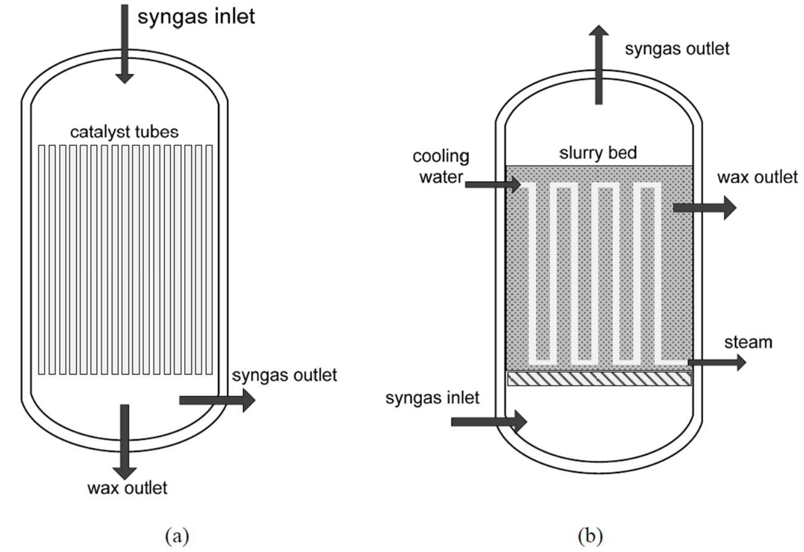

FIGURE 17 - (A) FIXED BED REACTOR, (B) SLURRY BED REACTOR [55]

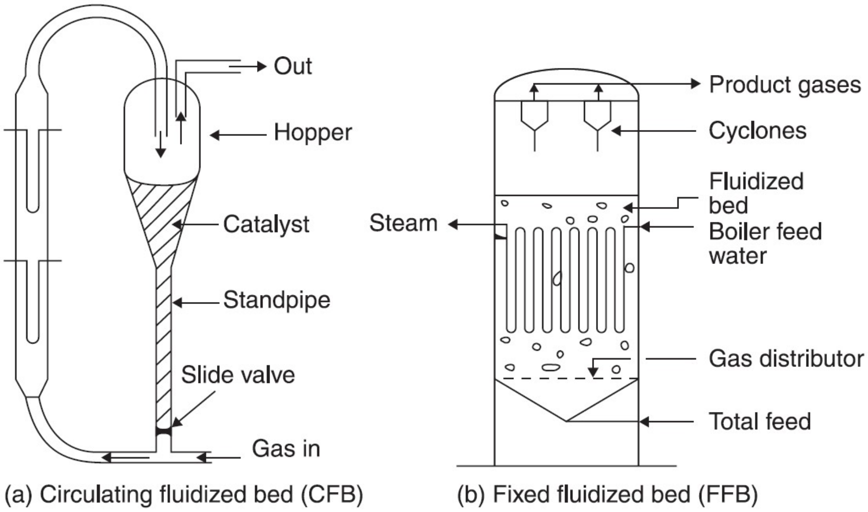

FIGURE 18 - FLUIDIZED BED REACTORS [57]

4.4.4 Summary

TABLE 7 - FTS REACTORS SUMMARY TABLE

Reactor	Pro	Cons
Fixed bed	✓ Suitable for small applications ✓ Scalable ✓ Simple design	× Low surface activity × Possible hot-spot formation × High pressure drops
Fluidized bed	✓ Low probability of hot-spot formation ✓ Easy thermal control ✓ High catalyst activity	× Complex design × Catalyst poison risk
Slurry bed	✓ No hot spot formation	× Catalyst poison risk

	✓ High catalyst activity	✗ Difficulty to divide catalyst from waxes

4.5 Catalysts

A good catalyst material for FTS has to satisfy some main characteristics:

- High resistance to water
- High selectivity to desired products
- Resistance at temperature employed in FTS

There are several materials that could be used in the FTS. Following, the most famous are described.

4.5.1 Nickel

Nickel is a metal, it is not expensive and it is a quite common material. Nickel has been used in methanation process before Fischer and Tropsch discovered the long-chain hydrocarbon synthesis, as it could be seen in the 1930 patent [46]. Unfortunately, this metal is not very used in FTS due to its large production of methane and its selectivity for light hydrocarbons.

4.5.2 Ruthenium

Ruthenium has a very high cost and its use is more limited than nickel. It is an excellent material for FTS thanks to its selectivity to heavy products. Despite its high cost, it is used together with other materials such as cobalt to increase the performance of the reaction.

4.5.3 Cobalt

Cobalt is become popular mainly due to lithium batteries. There are many types of Li-based batteries, some of these require cobalt in the cathode fabrication. The fast-growing market of this type of energy storage creates a huge hunger of cobalt and this conditions its price: it is grown of about 3 times since 2008 [58].

Co as catalyst for FTS was used as one of the firsts materials for this scope. Today there are many documents which investigate its catalyst potential and several plants had employed Co [47]. For instance, it is usually employed in LTFT thanks to its high surface activity and high selectivity for heavy products. FTS with cobalt catalyst produces high fraction of waxes and diesel, although it has the disadvantage to produce a large part of methane. Another problem is the difficulty to regenerate the catalyst once that it is deactivated, so it has to be substituted. However, the high cost makes this effect even worst [47].

Finally, cobalt has a higher tolerability to water and an investigation shows that it could have a positive effect on its selectivity to liquids (C_{5+} selectivity). Moreover, the WGS reaction does not occur and so carbon monoxide is not converted into carbon dioxide loosing carbon molecules useful for the reaction [47].

4.5.4 Iron

Iron was the first material employed for FTS [46]. Iron is a good material thanks to its low cost and good tolerability to high temperature. It has a high flexibility to the syngas composition: it tolerates a H_2/CO ratio as low as 1. This is possible thanks to the high WGS reaction, that occurs and reduce the amount of useful CO. Conversely to cobalt, Fe has a low methane production, but FTS with Fe catalyst produces a non-negligible amount of olefins and oxygenated compounds [47]. However, it has also a low chain-growth probability and a FTS with Fe-catalyst produces a high amount of light hydrocarbons. Furthermore, it has a higher thermal resistance compared to cobalt and this could bring some issues in reactor cooling, increasing temperature and selectivity for C1-C4 hydrocarbons. Finally, another problem is the tendency of iron to react with water, making preferable to work with low amount of steam.

To conclude, iron tolerability to poisons is low and sulfur is not tolerated [47], [52].

4.5.5 Summary

TABLE 8 - CATALYSTS COMPARISON [47], [54]

Material	Pro	Cons
Nickel	✓ High surface reactivity	✗ Small chain-growth probability ✗ High CH_4 production
Ruthenium	✓ High C_{5+} selectivity	✗ Very high cost
Cobalt	✓ Good activity ✓ Good C_{5+} selectivity ✓ High corrosion resistance ✓ High chain-growth probability ✓ Low olefin production ✓ Steam has a positive effect on C_{5+} selectivity ✓ No effect of water on CO conversion	✗ High cost ✗ High CH_4 production ✗ Difficulty to regenerate the deactivated catalyst
Iron	✓ Low cost ✓ Good in high temperature application ✓ Low CH_4 production ✓ High tolerance to low H_2/CO	✗ Moderate thermal resistance ✗ High sulfur sensibility ✗ Limited life ✗ High sensibility to water ✗ WGS reaction occurring ✗ Low selectivity for heavy products ✗ Production of oxygenated compounds

Some metals can be used together: e.g. ruthenium is used as promoter in Co catalyst. In particular, it increases selectivity for high molecular weight hydrocarbons. Potassium is used in iron catalyst as well as manganese. Moreover, K improves carbon chemisorption on catalyst and reduce hydrogen one. Finally, copper can be used with Co despite the global activity reduction, but platinum can be a substitute [54].

4.5.6 Deactivation

Syngas used to feed the FTS can transport some impurities which can damage the catalyst. This risk is high especially when the syngas is produced from gasification of solids as coal, biomass or MSW. The catalyst is made of metals which have a high tendency to react with acids forming salts (e.g. $CoCl_2$ and FeS). Furthermore, dust or vapors can bring alkali metals and when they are deposited on the surface, catalyst is deactivated.

TABLE 9 - GENERAL FTS POISONS TOLERANCE [7], [18]

Substances	Limits
S (H_2S, COS, etc.)	<1ppm
NH_3	<1ppm
Halogens	<10ppb
Alkaline metals	<10ppb
Organic compounds (tars)	Below drew point

However, using perfectly cleaned syngas cannot preserve completely the catalyst: carbon deposits can be formed when syngas has ratio of C/H and C/O too high. The first parameter to control is the H_2/CO ratio which should not go below a certain threshold depending on the material used and the operative conditions.

Part II

5. Choice of the biomass

5.1 Biomass

Biomass is the fuel and the raw material for the plant. It has a crucial role in the synthesis and the economic sustainability depends on it. A diverse selection of the biomass for the FTS can be made. The most popular choice for is wood, thanks to the simplicity to handle it and the low level of pollutants. Other possibilities comprise wood or agricultural residues or even wastes. Furthermore, there are some applications that investigate the use of digestate, sewage sludge or MSW. In the *Table 10* - **BTX plants**, several plants are reported: it is specified the type of feedstock biomass, the type of gasifier, the size and the final aim. The biomass does not influence the aim of the plant, conversely of the size. Generally, for small-sized plant, the production of power is more interesting, while big-sized plants consider the synthetic fuels production. However, there are some exceptions such as the 200kW$_{th}$ of Kim et al. [7] and the 1MW$_{th}$ of Barisano et al. [5] that produce FT diesel and hydrogen respectively.

TABLE 10 - BTX PLANTS

Authors	Feedstock biomass	Gasifier	Size	Final aim	Ref.
Barisano et al.	Refuse derived fuel	DFB	1MW$_{th}$	H_2	[5]
Chang et al.	Rice straw	BFB	4MW$_{th}$[2]	Power	[6]
Dietrich et al.	Generic biomass	EF	400MW$_{th}$	FT fuels	[59]
Dussan et al.	Digestate of sewage sludge	DFB	3-6MW$_{el}$[1]	Power	[60]
Dutta et al.	Generic biomass	DFB	350MW$_{th}$[2]	EtOH	[61]
Elsner et al.	Wood pellets and sewage sludge	Downdraft	360kW$_{el}$[1]	Power	[62]
Francois et al.	Wood chips	DFB	10MW$_{el}$[1]	Power	[63]
Hamelinck et al.	Generic biomass	CFB	400MW$_{th}$	FT diesel	[2]
Henao et al.	Sawdust	DFB	200kW$_{th}$	Power	[64]
Hillestad et al.	Wood chips	EF	435MW$_{th}$	FT fuels	[3]
Im-orb et al	Rice straw	Downdraft	393MW$_{th}$	FT fuels	[4]
Kim et al.	Pine pellets	DFB	200kW$_{th}$	FT diesel	[7]
Martín et al.	Switchgrass	n.a.	150MW$_{th}$[1]	EtOH	[65]
Menin et al.	Wood chips	DFB	13MW$_{th}$	SNG	[66]
Prins et al.	Sawdust	n.a.	210MW$_{th}$	FT fuels and power	[67]
Rafati et al.	Woody biomass	BFB	400MW$_{th}$	FT fuels	[68]
Salkuyeh et al.	Canadian pine	FB/EF	630MW$_{th}$[2]	H_2 and power	[69]
Snehesh et al.	Casuarina wood chips	Downdraft	4.9MW$_{th}$	FT fuels and power	[8]
Spyrakis et al.	Woody biomass	n.a.	4.8MW$_{th}$[2]	FT fuels	[70]
Swanson et al.	Corn stover	BFB/EF	350MW$_{th}$[2]	FT fuels	[55]
Tagomori et al.	Pine/ Eucalyptus	EF	750MW$_{th}$	FT diesel	[1]
Thunman et al.	Woody biomass	DFB	20MW$_{th}$	SNG	[71]
Tijmensen et al.	Wood	CFB	100MW$_{th}$	FT fuels and power	[72]
Trippe et al.	Wood residues/straw	EF	1GW$_{th}$	FT gasoline	[73]
Tuomi et al.	Biomass residues	DFB	100MW$_{th}$	FT fuels	[74]

[1] The power is referred on the output fuel/power produced.

[2] Estimated on the input biomass mass flow rate.

As reported, the biomass typology does not affect the plant purpose. A short review on the pros and cons of the most common of biomasses is reported in *Table 11* - **Biomasses pro and cons review**.

Table 11 - Biomasses pro and cons review

Biomass	Pros	Cons	References
Wood chips/pellets	✓ Easy to handle ✓ High LHV ✓ High availability	× Cost × Not always sustainable [75] × Overexploited [76]	[1], [3], [7], [23], [24], [30], [36], [43], [62], [63], [68], [70]–[73], [77], [78]
Crops	✓ High availability ✓ Production on demand (annually)	× Food competition × Anaerobic digestion (AD) competition	[65], [79]
Forest residues (including sawdust)	✓ Low cost ✓ Low environmental impact	× Difficulty to transport for long distances × Low energy density	[42], [64], [67], [67], [79]
Agricultural residues[1]	✓ Low cost ✓ Low environmental impact	× Difficulty to transport for long distances × Limited availability × Low energy density	[4], [6], [24], [30], [33], [34], [42], [55], [59], [80], [81]
MSW	✓ Low cost ✓ Circular economy ✓ High availability ✓ Reducing use of landfills	× High ash contents × Difficult to handle × High moisture contents × Varying composition × Low LHV × Possible presence of heavy metals	[16], [32]
OFMSW/food waste	✓ Low cost ✓ Circular economy ✓ High availability	× High ash contents × AD competition × Difficult to handle × High moisture contents × Varying composition × Low LHV	[30]
Sewage sludge	✓ Low cost ✓ Circular economy ✓ High availability ✓ Reducing use of landfills	× High ash contents × AD competition × Difficult to handle × High moisture contents × Low LHV	[43], [62], [77], [82]
Manure	✓ Low cost ✓ High availability ✓ Reducing eutrophication	× High ash contents × AD competition × Difficult to handle × High moisture contents × Low LHV	[27], [30], [83]
Digestate	✓ Low cost ✓ Circular economy ✓ High availability ✓ Reducing eutrophication	× High ash contents × Difficult to handle × High moisture contents × Low LHV	[22], [25], [60], [84]–[87]

[1] including nut or almond shells, grape marcs, stover, etc.

The references indicate the papers using a certain type of biomass feedstock in a gasifier for different purpose. In the presented study, two different type of biomasses are selected. The first one corresponds to wood as many other works. For second type, different biomasses could be used as feedstock to produce liquid fuels. Agricultural and forest residues are also explored in many works and they seem to be a promising source of energy. However, in this paper, the digestate is preferred due to the absence of concurrency with other technology (e.g. biodigester) and the necessity of long transport. There are many papers that investigate the digestate gasification (see [60], [83]–[87]). Finally, a pine woody biomass is considered as reference.

5.2 Digestate

The digestate is the solid residue of the anaerobic digestion. A large part of biodigesters works with animal manure and crops or agricultural residues. This kind of plants take usually place in a farm, so the digestate produced can be use as fertilizer by the same farm. Even though, there are several digesters working with sewage sludge or OFMSW that are collected by a firm. In this case, the company has probably no way to use the biomass and it has to found a method to dispose (or to sell) the matter.

5.2.1 Landfill

As anticipated, the digestate is a residue, so it can be considered as a waste and landfilled. Generally, this material has a high moisture content and, in many cases, it is liquid with a solid yield less than 15% [88]. For this reason, it is not possible to landfill it without a drying process, which has a cost in economic and energy terms. In addition, the disposal is not free, so another cost has to be taken into account.

5.2.2 Incineration

Since the digestate has a non-negligible LHV, it can be burnt together with MSW in incinerators. Similar to the disposal, it has to be dried even at higher level with respect the landfilling, since the LHV strictly depends by the moisture content.

5.2.3 Fertilizer

This biomass contains many minerals and organic matter which can contribute to enrich the soil [89]. However, it can contain several pollutants as heavy metals, organic compounds, improper material (such as glass or plastic) and general substances or organisms dangerous for the humans or for the environment.

5.2.4 Costs

The cost of the digestate is variable. The disposal makes a negative value of the digestate and so it becomes a cost, also the incineration can be similar to the landfill. On the other hand, the use as fertilizer can have a positive price because it can substitute the use of a standard one.

A study shows that the cost depends mainly from the moisture content and from the form (randomly or pellets): it goes from 0€/ton to 150€/ton, with the average price of a dried mass of 5-30€/ton. For this study, the value of 30€/ton is considered [89].

5.2.5 Analysis

A review of the works already done on the possibility to gasify the digestate is performed and summarized in the table below.

TABLE 12 - DIGESTATE GASIFICATION PAPERS REVIEW

Authors	Gasifier	Size	Aim	Reference
Antoniou et al.	Downdraft	40.5 kW_{el}	Power	[86]
Chen et al.	Downdraft	-	Lab.	[87]
Dussan et al.	DFB	12 MW_{th}	Power	[60]
Freda et al.	Rotary kiln	70.6 kW_{th}	Pilot	[22]
Lacroix et al.	-	168 kW_{th}	Pilot	[85]
Opatokun et al.[1]	Fixed bed	-	Lab.	[25]
Wisniewski et al.	Bach reactor	-	Lab.	[84]

[1] pyrolysis.

In order to gain information on the biomass feeding rate to the gasifier reactor, two methods could be applied: taking the reference from existing digesters or evaluating the biomass flow rate knowing the CO_2 (or the CH_4) flow rate content in biogas after the digester process. In this study, a typical biogas upgrading unit is considered: the gas is produced using OFMSW and sewage sludge together in a biodigester. To evaluate the size of the gasifier needed for the complete disposal of the biomass, the work of Marchese et al. [90] is considered, where a flow rate of CO_2 from biogas was identified as 1 ton/h. The data for the biodigester mass balance are not provided in the paper above-mentioned. Hence, the methodology proposed by Blank et al. [91] is used to size the correct amount of digestate, knowing the carbon dioxide flow rate. The reasons behind our sizing choice can be identified as the need to fully consume the digestate material leaving the digester, maximizing the production of FT material otherwise obtained only from the CO_2 stream above-mentioned. This solution allows for direct use of digestate from already existing plants. Results of the sizing are found in Table 13 **- Variables and parameters for the digestate mass flow calculation**.

$$\dot{V}_{bio} = \frac{\dot{m}_{CO_2}}{\rho_{biogas}} = \frac{\dot{m}_{CO_2}}{\rho_{CO_2} \big/ (1 - x_{CH_4})} \tag{20}$$

$$\dot{m}_{conv} = \frac{\dot{V}_{bio}}{x_{bio}} \tag{21}$$

$$\dot{m}_{in,d} = \frac{\dot{m}_{conv}}{x_{mass}} \tag{22}$$

$$\dot{m}_{out,d} = \dot{m}_{in,d} - \dot{m}_{conv} \tag{23}$$

TABLE 13 - VARIABLES AND PARAMETERS FOR THE DIGESTATE MASS FLOW CALCULATION

Name	Symbol	Value	Unit
CO_2 mass flow rate	$\dot{m}_{CO_2}$	1000	kg/h
CH_4 yield[2]	x_{CH_4}	60.00	%
Biogas flow rate	$\dot{V}_{bio}$	1384	m^3/h
Specific biogas production	x_{bio}	0.8461	m^3/kg_{dry}
Mass flow converted in the digester (dry)	$\dot{m}_{conv}$	1636	kg/h
Digester mass conversion (dry)	x_{mass}	65.00	%
Digester inlet biomass (dry)	$\dot{m}_{in,d}$	2517	kg/h
Digester outlet biomass (dry)	$\dot{m}_{out,d}$	881.0	kg/h
Thermal power of the digestate[2]	$P_{th,dig}$	3.108	MW_{th}

[1] supposed.

[2] LHV from Freda et al. [22].

Finally, the proximate and ultimate analysis of the digestate, together with the LHV, are provided by Freda et al. [22] and they are reported in the tables below. The paper analyzes a digestate deriving from a similar initial mixture with respect to the one supposed before.

TABLE 14 - ULTIMATE ANALYSIS OF THE DIGESTATE

Ultimate analysis	Value	
C	35.0	wt% dry basis
H	4.00	wt% dry basis
N	3.07	wt% dry basis
O	24.6	wt% dry basis
S	0.87	wt% dry basis
Cl	0.1	wt% dry basis
LHV	12.7	MJ/kg

TABLE 15 - PROXIMATE ANALYSIS OF THE DIGESTATE

Proximate analysis	Value	
Ash	32	wt% dry basis
Volatile matter	55	wt% dry basis
Fixed carbon	13	wt% dry basis
Moisture	9.9	wt% wet basis

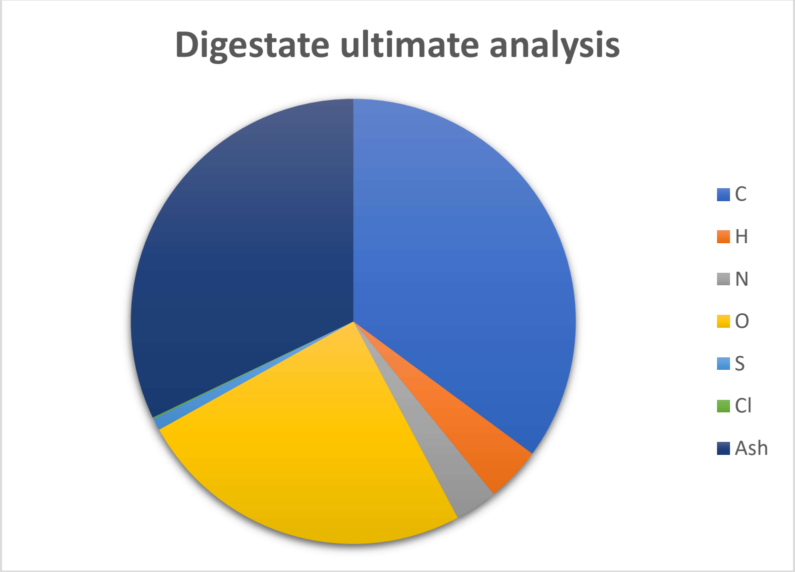

FIGURE 19 – PIE GRAPH OF THE DIGESTATE ULTIMATE ANALYSIS

5.3 Pine wood biomass

Wood is taken as reference feedstock biomass. So, the data provide by Doherty et al. [23] about the wood chips are taken into account.

TABLE 16 - ULTIMATE ANALYSIS OF THE PINE WOOD

Ultimate analysis	Value	
C	51.19	wt% dry basis
H	6.08	wt% dry basis
N	0.2	wt% dry basis
O	41.3	wt% dry basis

S	0.02	wt% dry basis
Cl	0.05	wt% dry basis
LHV	19.09	MJ/kg

TABLE 17 - PROXIMATE ANALYSIS OF THE PINE WOOD

Proximate analysis	Value	
Ash	1.16	wt% dry basis
Volatile matter	80	wt% dry basis
Fixed carbon	18.84	wt% dry basis
Moisture	20	wt% wet basis

FIGURE 20 - GRAPH OF THE PINE WOOD ULTIMATE ANALYSIS

The ultimate analysis of the digestate and wood are very different especially for the amount of ash. In addition, the nitrogen and sulfur yields are higher in the digestate and this will lead to a high level of pollutants in the syngas produced.

Lastly, the mass flow of woody biomass is taken to produce the same thermal power input, so 733.1 kg/h of as-biomass.

6. Aspen Plus model

The gasifier, the cleaning and conditioning system, and the FT reactor, together with the main components of the balance of plant (BOP), have been modeled on Aspen Plus. In the following pages, an accurate description of all the components is reported.

For the description of the blocks, the design specifications and the calculators used in the Aspen Plus program, see the *Appendix A* – Aspen model.

6.1 Gasifier

6.1.1 Choice of the gasifier

A medium-small gasifier (~3MWth as calculated before) is needed for the scope of gasifying the biomass, so the entrained flow technology has to be excluded because there is no example of this type of gasifier working with so small power. The choice is between fluidized bed and fixed bed reactors. In addition, the syngas has to be nitrogen-free in order to a proper working of the FTS reactor. So, the latter type is rejected due to the oxygen required to operate, while a fluidized bed (DFBG type) seems to be the best choice.

The main motivations which have led to this choice are summarized below:

- High LHV of the syngas.
- No nitrogen dilution due to air use.
- Low tars production.
- Fuel flexibility over the biomass type.
- Temperature self-stabilizing.
- Possibility to use simple air (no oxygen enrichment required).
- Possibility to use a catalytic bed to improve the syngas quality.
- Low initial cost [18].
- Possibility to use catalytic candle filter inside the reactor to reduce tars production and methane yield [92]–[94].

The main cons of the DFBG are:

- Long start-up time.
- No ash melting/sintering tolerability, thus requires good ash management.

A good review about DFBG is reported by Göransson et al. [18] and many examples of working plants and theoretical papers are shown in the *Table 10* **- BTX plants**.

Finally, steam is selected as gasification agent. The use of CO_2 was also investigated, however it generally brings to lower H_2/CO ratio with respect to steam [27] and this can cause some problems to the FTS reactor.

6.1.2 Model

The DFBG is modeled after Doherty et al. [23] research work.

6.1.2.1 Hypothesis

The hypothesis of the model are the followings:

1. Isothermal and steady state gasifier conditions.
2. Heat losses of the gasifier are neglected (adiabatic conditions).
3. Gasifier works at atmospheric pressure (1 bar).

4. Pressure drops are considered only for inlet air and steam according to Kraft et al. [95] (from Güssing plant).
5. Negligible pressure drops in heat exchangers or other components.
6. S, Cl and N present in biomass are fully converted into H_2S, HCl and NH_3.
7. Whole sulfur is converted in H_2S, the amounts of COS and CS_2 are considered negligible.
8. No production of SO_x and NO_x neither in the gasifier nor in the combustor.
9. Char are made only of carbon and ash.
10. Char are completely burnt in burner, no carbon residual in flue gas.
11. No tars production.
12. Only production of methane is considered, no other hydrocarbons are produced.
13. No interaction between minerals in ash and other substances.
14. Whole ash is removed from flue gas.
15. No formation of CO in the combustor.

The scheme of the Aspen Plus model is reported in the *Appendix A* – Aspen model.

6.1.3 Validation

To validate the model, the paper of Doherty et al. [23] is taken into account. Using the same boundary conditions (temperatures, biomass composition and steam to biomass ratio), the syngas compositions are compared below.

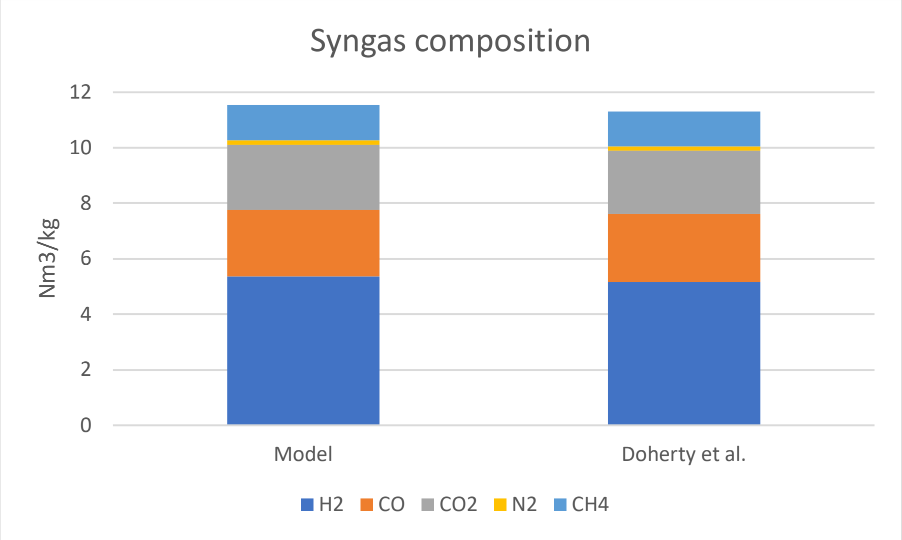

FIGURE 21 - SYNGAS COMPOSITION COMPARISON

From the *Figure 21* **- Syngas composition comparison** it is possible to see that the differences between the two compositions are negligible. Considering the mean squared error done on the major components shown (H_2, CO, CO_2 and CH_4), it is 2.16%.

TABLE 18 - SYNGAS COMPARISON

Component	Model	Doherty et al.	MSE	Güssing plant
H_2	46.4%	45.8%	1.3%	45.8%
CO	20.7%	21.6%	4.1%	21.6%
CO_2	20.2%	20.2%	0.0%	21.2%
CH_4	11.0%	11.0%	0.1%[1]	10.0%

H_2S	70ppm	66ppm	6.0%	21.5-170ppm
NH_3	1600ppm	1510ppm	5.7%	1100-1700ppm
HCl	158ppm	150ppm	5.4%	100ppm

[1] Approximation hides an error.

Nitrogen is not reported in the table because its yield was specified with a design specification and so it is correct by definition.

The LHV of the syngas is calculated as Fernandez-Lopez et al. [27] in their work:

$$LHV\ \left[{}^{MJ}/_{m^3}\right] = 10.8 \cdot y_{H_2} + 12.6 \cdot y_{CO} + 35.8 \cdot y_{CH_4} \qquad \textbf{(24)}$$

Where y_{H_2}, y_{CO} and y_{CH_4} are the gas yield of hydrogen, carbon monoxide and methane respectively. The model presented shows a LHV of 11.6 MJ/m^3 and Doherty et al. [23] of 11.3 MJ/m^3 so an error of 2.4%.

6.1.3.1 Sensitivities

A sensitivity analysis on the syngas composition with respect to the gasification temperature (T_G) variation was conducted. Increasing the temperature, methane is cracked and its yield goes sharply to zero. Similar result comes up for the carbon dioxide. Although, standard temperatures of operation are between 700°C and 900°C [23], higher and lower temperature are reported only to show the behavior of the model. In real applications, a T_G higher than 900°C is not achievable in a fluidized bed gasifier. In following graphs, all the yields are on dry basis except for the steam one.

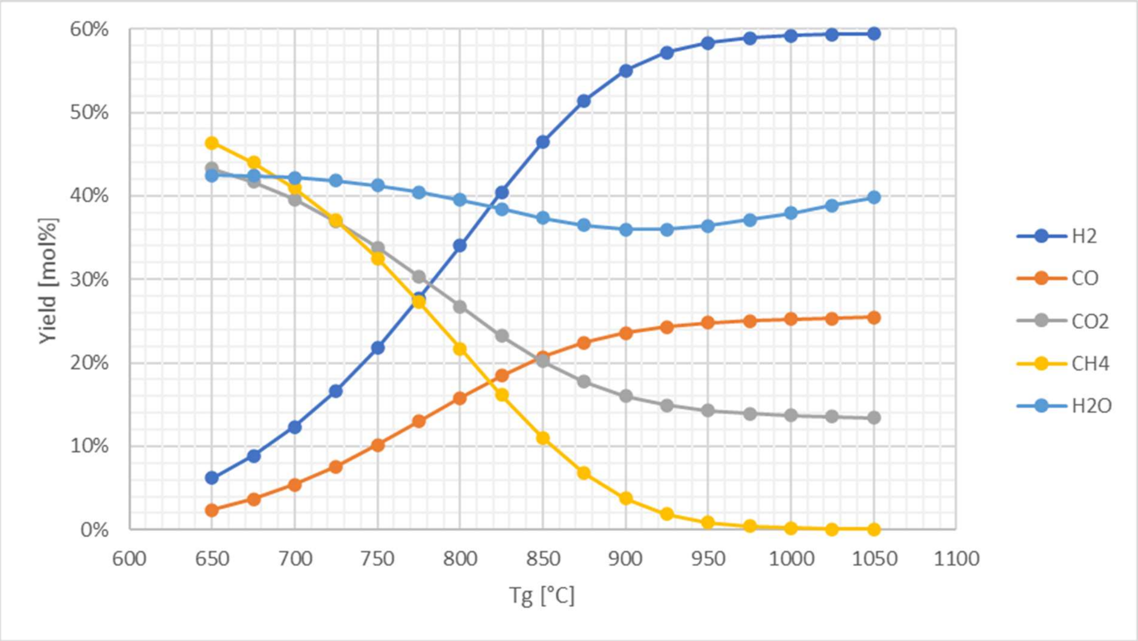

FIGURE 22 - GASIFICATION TEMPERATURE SENSITIVITY

Between 900 and 950°C these is the maximum production of useful syngas (without CO_2). It is important to get the higher mass flow from the gasifier because the final syncrude production depends on it. Higher temperatures support endothermic reactions, so the conversion of H_2O and CO_2 in H_2 and CO is enhanced, but the amount of char combusted to maintain the thermal balance increased too. So, at a certain point, the biggest fraction of solid sent to the combustor reduces the amount of char gasified and the mass flow is reduced.

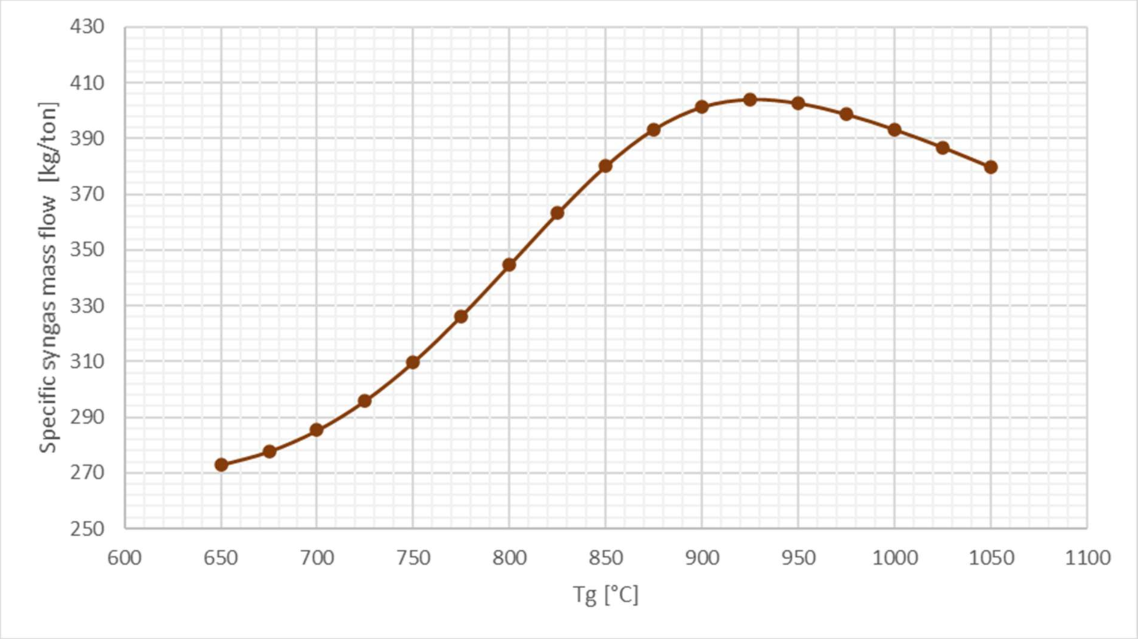

FIGURE 23 – SPECIFIC MASS FLOW OF USEFUL SYNGAS

It seems convenient to show the fraction of char split together with the LHV of the syngas: it is almost constant varying T_G, so the heating value does not depend on the temperature. It must be said that it is not possible to multiply the mass flow in the Figure 23 **– Specific mass flow of useful syngas** with the LHV in the Figure 24 **- Char and LHV sensitivities**, because the latter is calculated on the dry syngas mass, while the mass flow represent only the syngas without the inert (CO_2, N_2, etc.). To conclude, both LHV and char fraction behaviors are comparable to Doherty et al. [23].

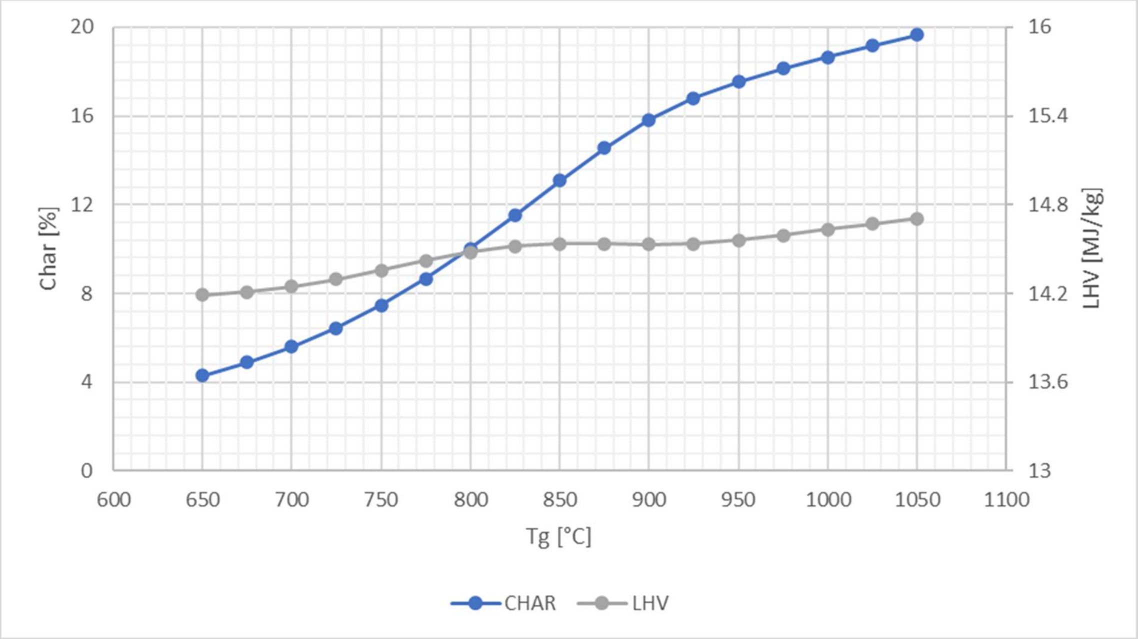

FIGURE 24 - CHAR AND LHV SENSITIVITIES

Additionally, a sensitivity analysis on steam to biomass ratio is performed. It starts from 0.25, this is the value where steam mass flow is zero because the humidity in biomass is enough to satisfy the water requirement.

Methane yield decreases when more steam is injected in the gasifier, this was predictable due to the moving of equilibrium point of the SMR reaction towards H_2 and CO.

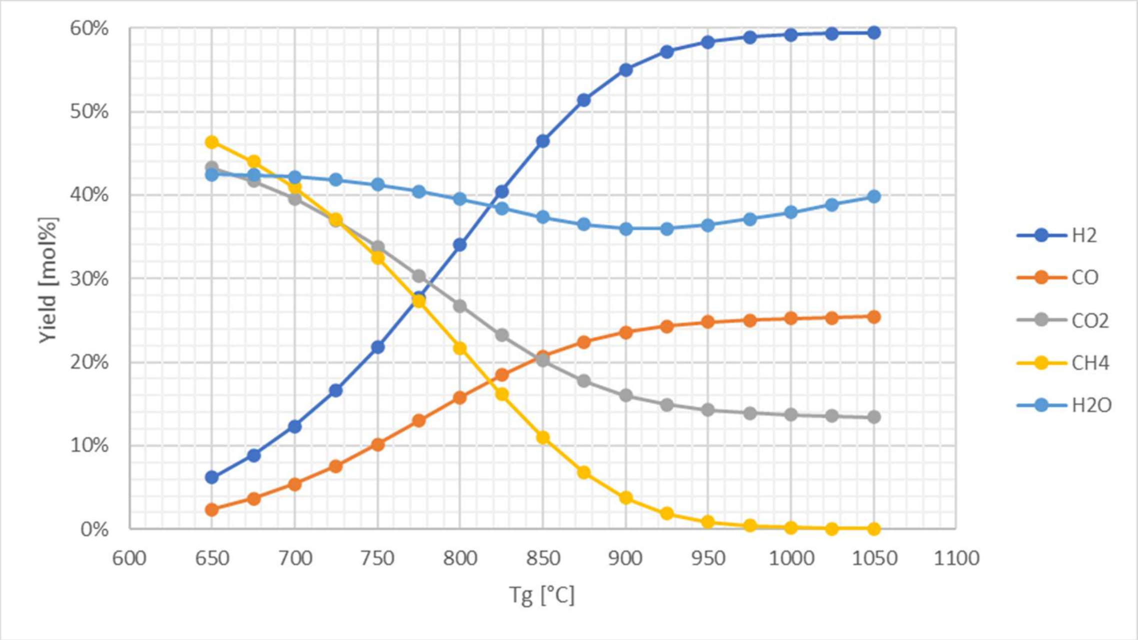

FIGURE 25 - STEAM TO BIOMASS RATIO SENSITIVITY

The H_2/CO ratio is very sensible to the steam to biomass ratio. This leads to use the steam mass flow to get the desired H_2/CO value.

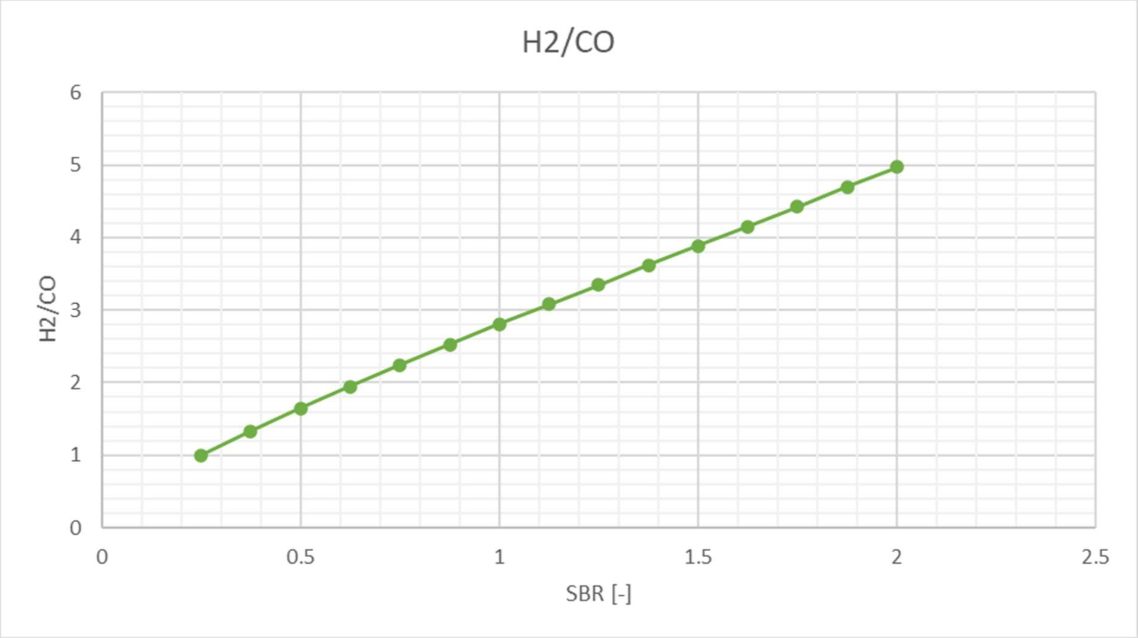

FIGURE 26 - H_2/CO VARIATION RESPECT TO THE S/B

Considering the small quadratic error respect to the Doherty et al. [23] and the sensitivity behaviors similar to the proposed work, the model is considered validated. For further information, see Doherty et al. [23] and Appendix B – Gasifier validation.

6.2 Syngas clean-up and conditioning: technologies overview

Gas condition section is important because the catalyst inside the FT reactor is extremely sensible and it might be deactivated by some impurities. In particular ammonia, halogen acids and sulfur are poisoning compounds for the precious metal catalysts. In addition, solid carbon deposition as dust or solidification of vapors on the catalyst surface, have to be avoided. The FT reactions require a pressure higher than the atmospheric one (>20bar), so a syngas compression section is requested. Finally, a low partial pressure of CO_2 in the syngas is advised in order to get a better working of the downstream components [2], [4], [54], [96], [97]. A review of the main pollutants and their removal methods is reported below.

6.2.1 Dust removal

When a solid (or a liquid) is gasified (or combusted), it generates dust particles with a diameter ranging from a value lower than 1µm to about 100µm. The particulate matter (PM) can be divided in two categories:

- **Primary particulate**. It is formed in the gasifier and it is further divided in two types:
    - Ash. PM produced by the elutriation of the inert matter, these are called *fly-ash* to distinguish them from *bottom-ash*, so the ash remaining in the gasifier/combustor. The proportion between them is variable.
    - Soot. A small fraction of the solid does not react and the smaller part can enter in the gas stream.
- **Secondary particulate**. It is formed after the gasification chamber where the syngas contaminants can react with each other and form solid particle (e.g. $HCl_{(g)} + NH_{3(g)} \rightarrow NH_4Cl_{(s)}$ under 300°C).

Dust has to be removed almost completely from the syngas when it is used in downstream application differently from the combustion in a furnace. Internal combustion engines (ICE) or gas turbines (GT) request low level of dust, while all the applications involving catalysts (as FTS, methanol production, etc.) require an amount even lower. Otherwise, it causes fouling, corrosion and erosion problems in heat exchangers, pipes and in all the other components, especially where the gas has a high velocity (e.g. turbine blades) [98]. The systems for the dust-removal are several:

- **Bag filter**. When the gas has a temperature lower than 150-200°C, it is possible to use bag filters in order to remove all the kinds of dust particles (from the biggest to the smallest). It is a mature technology and it is possible to find bag filters in both small and huge plants. Nevertheless, it requires wash-cycles (with air) to remove the PM collected and a periodical substitution. Finally, the materials are cotton or polypropylene for low temperature applications or fiber glass or Teflon for high ones.
- **Cyclone**. It consists of a vertical cylinder and it works with the gravity. The dirty gas in injected from a nozzle in the wall to create a vortex inside the cylinder. The big particles cannot follow the gas during the narrow curve and they hit the wall loosing kinetic energy. The gravity attracts them, and without the support of the inertia, they drop down and are collected. The disadvantages of this system are the need of big particles and it can provide high pressure drops. On the other hand, it can work continuously without any wash-cycles or short-term substitutions, and with high temperature gas.
- **Electrostatic precipitator (ESP)**. When particles enter the system, they are loaded with an electrostatic charge. The ESP system generates an electric field and the particles are attracted from several plates arranged on the gas path. When they enter in contact with the wall, they lose the charge but also their kinetic energy. So, they drop down and can be collected. The ESP system requires electric energy to work and some wash-cycles. However, it has a high removal efficiency also with small particles and it can work with medium temperature (300-400°C).
- **Water scrubber (WS)**. There are many types of WSs:

    - Wash tower. The gas enters from the bottom of the tower while water is nebulized from the top in countercurrent mode. The water droplets have a certain probability to enter in contact with the particulates, absorbing them and drop down in a tank.
    - Venturi scrubber. It is similar to a wash tower, but water is nebulized in co-current. After, the gas passes through a Venturi channel (a channel with a narrowing) improving the velocity. In this way, the water droplets become smaller and the interaction with the tiny dust particles is improved. Finally, water droplets with dust are removed by gravity or cyclones. The absorption power increase respect to the wash tower, but pressure drops are higher.
- **Ceramic filters**. Ceramic filters are similar to a bag filter, but they are made of ceramic material in order to tolerate high temperature. It is not a common solution, but it is very promising due to the possibility to insert a catalyst for the tars cracking or the methane reforming. Lastly, there are some examples of treatise of this technology [41], [93], [94].

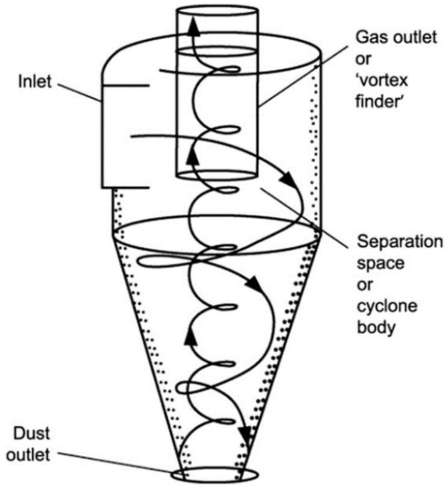

FIGURE 27 - CYCLONE [98]

6.2.2 Tars removal

Tars are aromatic compounds that are generated by coal or biomass thermal decomposition (both during pyrolysis and gasification). The amount of tars in a syngas depends on the residence time and the temperature of the reactor. There are four types of tar:

1. **Primary tars**. They derive from cellulose decomposition. They are formed especially at low temperature (below 600-700°C). E.g. furfurans.
2. **Secondary tars**. They derive from lignite decomposition. The temperature of formation is higher than primary (between 600 and 900°C). E.g. phenols, light olefins.
3. **Tertiary tars**. They are produced from further reaction inside the gasifier/pyrolizer at temperature between 800 and 1000°C. E.g. toluene.
4. **Polynuclear aromatic hydrocarbon**. They are very difficult to decompound also at high temperature (>1000°C). An example of these compounds is the naphthalene. Studies on their decomposition are available in literature: under certain conditions, increasing the gasification temperature (from 750 to 840°C) in a fluidized bed gasifier, the total amount of tar decrease, but the naphthalene yield in the syngas increases [99], [100].

Tars are tolerated in applications where the syngas is directly burnt in a furnace without a cooling process. However, if the aim is to power an ICE or a process working with a catalyst, they are a sensible problem. If they are present in the syngas, they can also condensate on heat exchanger forming fouling.

A first way to reduce the tar is to properly set the gasification conditions. Using high temperature, high steam to biomass ratio and a proper bed material (for FBGs), the tar yield can be reduced [41], [99]. Although, this is not enough, so other methods have to be employed.

- **Tars cracker**. Catalyst for the tar cracker are made of a nickel or dolomite bed. The syngas flows inside and, thanks to the large surface together with a high catalytic power, the tars are decomposed. It has the main advantage of using low-cost material. However, the presence of dust and sulfur can reduce its efficiency. Another typology is the thermal cracker which brings the syngas up to 1100-1300°C to decompose tars [98]. It requires energy and it can reduce the LHV of the gas (given the injection of oxygen to increase the temperature).
- **Wet scrubber**. When water is injected in hot syngas, the latter is cooled down and tars condense on water droplets. Not all the tars are soluble in water and this leads to a low efficiency. However, it is possible to remove tars and dust together. The direct water-quench is used to avoid the presence of a heat exchanger. On the other hand, it produces wastewater with hydrocarbons contamination.
- **Venturi scrubber** (VS). It is the same technology explained in *6.2.1 Dust* removal. The tars removal efficiency can reach 90% [101].
- **Bio-oil scrubber**. It is a scrubber feed with an oil, since the organic vapors are soluble in organic liquids, tars are absorbed. The tars removal is almost compete and their drew point can reach values quite lower that 25°C. The most famous is the OLGA system. Olga is a Dutch acronym for oil-based gas washer [101].

More than 98% of lignocellulose-derived tars are soluble in organic solvent as methanol [102]. There are applications that use MeOH in scrubbers for carbon dioxide absorption and, if the syngas still contains some tars, they can be washed out from the syngas [102].

6.2.3 Ammonia removal

Nitrogen is present in biomass in a fraction different for each type (e.g. wood, OFMSW, etc.) and, during the gasification process, it can form ammonia. It has to be removed from the syngas because it is corrosive and it can reacts with metal catalysts. The simplest way to remove it, is to wash the gas with water in a wash tower (ammonia is highly soluble in water) or with an acid solution in a Venturi scrubber [103]. In the first case, water has to be regenerate to avoid the ammonia saturation. In the second case, sulfuric acid (H_2SO_4) can be used in a water solution: ammonia reacts with the acid forming a salt.

6.2.4 Halogen acids removal

The most common halogen present in biomass is chlorine. It forms hydrochloric acid which is very corrosive also in low concentration [98]. Additionally, chlorine can react with other syngas pollutants forming solid salt and creating secondary dust. It is possible to remove HCl together with ammonia in a wash tower, or with other acids (like sulfur-based ones) with sodium hydroxide (NaOH) in a Venturi scrubber. In any case, a guard bed made of high-reactive metals is advised to further reduction to ppb order of magnitude.

6.2.5 Sulfur removal

The sulfur content in a syngas is manly in form of sulfuric acid (H_2S) with lower content of sulfur oxides (i.e., SO_2 and SO_3). It can cause corrosion problems and it is a poison for catalyst materials. To remove it, several ways are possible:

- **Ammonia scrubber**. A scrubber with a solution of aqueous ammonia is used to wash the syngas. Sulfuric acid reacts forming ammonium sulfide $(NH_4)_2S$.
- **Sodium hydroxide scrubber**. Similar to the previous system, the syngas is washed with an aqueous solution of NaOH, the salt produced is sodium sulfide (Na_2S).
- **Organic solvent scrubber**. There are several processes involving organic solvents such as methanol, glycol etc. Examples of commercial names are Selexol, Rectisol and Purisol. These systems can also

remove carbon dioxide together with sulfur. For a further explanation, see *6.2.7.1 Absorption* processes.
- **Guard bed**. The syngas passes through a bed of metal oxide (such as zinc- or copper-oxide) and the sulfuric acid reacts with that forming a solid salt. At the exit, the syngas has a very low content of sulfur. This method is generally used downstream together with one of the others.

There are conflicting opinions on water scrubber to remove H_2S. Many studies consider that it is not absorbed by the WS, others adopt just one WS to remove ammonia, hydrochloric and sulfuric acid [1], [63], [66], [104]. In this work, the worst case is considered, so water scrubber does not absorb sulfuric acid.

6.2.6 Alkali and alkaline earth removal

Biomass, especially herbaceous one, contains alkali and alkaline-earth materials such as potassium and sodium. The biggest part remines in the gasifier in form of ash, but some elements with a low melting point, can evaporate and leave the reactor together with the syngas. They are generally hydroxide or bonded with chlorine or sulfur, however, they can produce corrosion problem, condense in heat exchanger causing fouling problems and deactivate the catalysts [105]. The main methods to remove these substances are:

- **Solid sorbets bed**. A bed of material where vapors can nucleate and condense. It is used in hot gas cleaning.
- **Water scrubber**. A direct water quench of the syngas leads to the condensation of the vapors on the water droplets.

6.2.7 CO_2 removal

Carbon dioxide capture systems are interesting for many applications such as improving natural gas or coal syngas quality. Also, for hydrogen production from methane reforming or coal gasification, there is the need to remove CO_2. Another more recently application is the carbon capture from flue gas to decarbonize the energy and non-energy sectors (e.g. steel or concrete production). In syngas cleaning and conditioning after gasification, its removal can increase the efficiency of downstream components where CO_2 would otherwise be an inert compound.

There are several systems to remove carbon dioxide from a gas stream. All the systems can be divided in two categories:

- **Absorption**. In absorption process, molecules are trapped by volume of a solid or, more frequently, a liquid. It is possible to further divide in physical and chemical absorption.
  - Example: gas washing separation. Gases have a certain solubility in liquids depending on the temperature, the gas partial pressure and the nature of both. It is called “Henry’s law”. The syngas enters in a scrubber, a low-CO_2-dissolved liquid (lean solvent) is injected in counter current with respect to the syngas and CO_2 is absorbed. The liquid is collected and it enters in another reactor (called “stripper”) where the CO_2 is removed from the liquid and it is regenerated. The processes can be divided in physical absorption, working with high-CO_2-affinity liquids (e.g. methanol, glycol, ethers, etc.), and chemical absorption, working with liquids which molecules are able to form chemical bond with CO_2 (e.g. amines) [104], [106]–[108].
- **Adsorption**. In adsorption process, molecules are attracted by surface of a solid or a liquid and they remain there (they do not enter inside volume).
  - Example: mechanical separation. Gases have not only a solubility in liquids, but they can be also adsorbed by solid. Strength of Wan-der-Waals forces, which make gas molecules attach at a solid surface, depend on the solid and gas nature. Some gases have weak attraction forces and others have strong ones. When the gas flows out, first the weak-forces gases are

released, after the stronger one. In this category can also enter the microfiltration by membrane or nano-filter [109], [110].

6.2.7.1 Absorption processes

General characteristic for a chemical-physical sorbent are:

- Low toxicity
- Low cost
- Low vapor pressure
- Low corrosivity
- High thermal and chemical stability

Below, a review of the most used and famous technology for carbon capture are reported.

6.2.7.1.1 Selexol

It is a process involving dimethyl ether of polyethylene glycol. It works with high pressure and low temperature (20-50°C). The process is not energy intensive, especially from thermal energy point of view. The power consumption is moderate high thanks to the high viscosity of the fluid, especially if the syngas contain a high amount of water [1], [111]. This process reduces the carbon dioxide partial pressure (about 90-95% of reduction [1], [112]) and can remove also hydrogen sulfide. The solvent has a low toxicity, low vapor pressure and a low corrosivity. Moreover, it dries almost completely the gas due to the high affinity with water, and it is able to remove also hydrocarbons [113]. It is usually adopted when the gas to clean up has a high partial pressure of CO_2 and for large plants. It is easy to find plants using Selexol process of hundreds of MW, no example has been found for medium and small size.

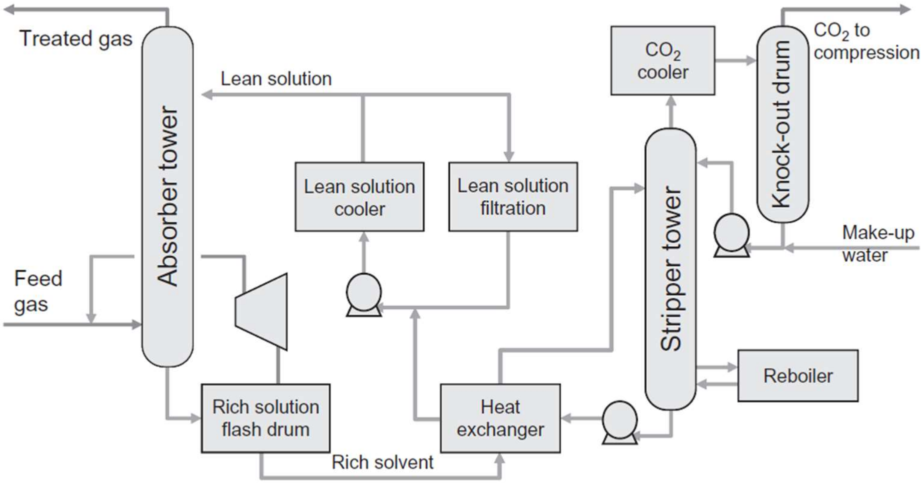

FIGURE 28 - SELEXOL PROCESS SCHEME [113]

6.2.7.1.2 Rectisol

This process uses methanol as solvent. The working principle is similar to the Selexol, with the main different to use refrigerated liquid at about -30°C [7] and so it requests a chiller. The affinity with the Selexol process are several, as the high working pressure and the sulfur removal power, but it can reduce more than Selexol the CO_2 partial pressure [68], [106]. Rectisol is widely used [113] and there are many examples of applications in large plants. However, a lab-scale methanol scrubber for acid gas removal is reported by Seo et al. (2014) [102] and Kim et al. (2016) [7] successfully using that system in the syngas cleaning unit for small-sized BTL plants (1bbd-size plant).

6.2.7.1.3 Amine-based

Amine-based processes have a plant structure similar to Selexol and Rectisol (based on scrubbing-stripping of a liquid). They are a chemical-physical process since amine can form bond with CO_2. There are several types of amines that it is possible to use: amines are organic compound based on ammonia, used in water solution. The simplest type is the methylamine (CH_3NH_2), instead the most used that is the ethanolamine, also called MEA ($2R\text{-}NH_2$).

$$2RNH_2 + CO_2 \leftrightarrow {RNH_3}^+ + RNHCOO^- + heat \qquad \textbf{(25)}$$

The energy released is 2.0 MJ/kg-CO_2 and it occurs already at ambient pressure. To reverse the process is sufficient to increase the temperature at about 100-150°C [55], [114] and CO_2 is released. The disadvantage is the high amount of energy request for the regeneration: the consumption is about 2.2-3.5 MJ/kg-CO_2 [107], [115]. On the other hand, it is possible to reach a high CO_2-removal efficiency. H_2S is also removed thanks to the high solubility of that compound in organic solvents (such as amines). This technology is suitable for medium-size plant [115]. Lastly, the other two negative bullets are the necessity of water/solvent integration and the corrosive and volatile issues of some types of amines (such as MEA) [90], [114].

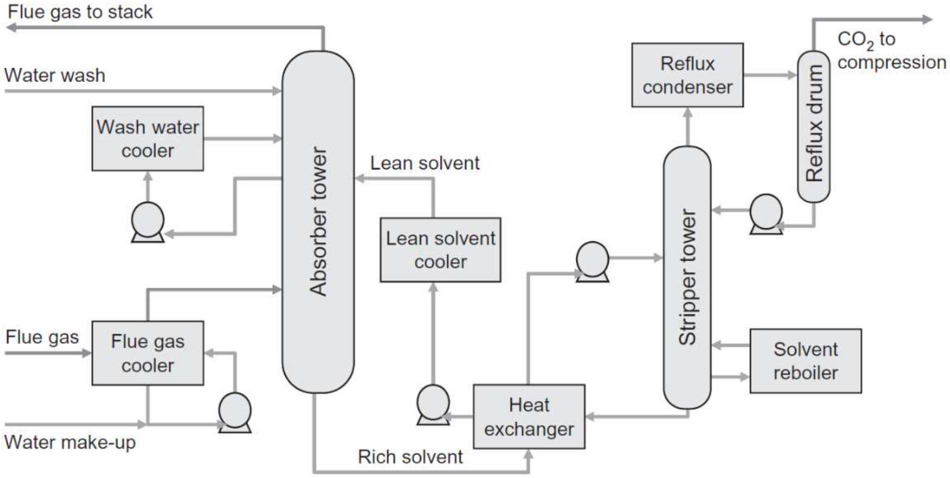

FIGURE 29 - AMINE-BASED CO_2 ABSORPTION PLANT SCHEME [113]

6.2.7.1.4 Pressurized water scrubbing (PWS)

Carbon dioxide is slightly soluble in water, but increasing the pressure, the solubility increases. Nock et al. [104] investigated this system in biogas upgrading. It does not request any dangerous substances, only simple water. However, a problem is the fact that the H_2S absorbed from the liquid, when it is regenerated with air, forms sulfuric acid that is corrosive. Another negative aspect is the low selectivity of the water toward syngas elements and it risks of absorbing also other components like hydrogen or methane. The efficiency in the reduction of the acid gas is not high as the previous cases investigated. Moreover, the gas exits saturated in water.

6.2.7.2 Adsorption processes

6.2.7.2.1 Pressure swing adsorption (PSA)

A gas mixture that enters in contact with a material shows different tendency to remain attached to the surface. It depends on the typology of both solid material and gas. The PSA system compresses a gas mixture in a tank containing activated carbon, silica gel, zeolite, or others. After it is released and the molecules with weak affinity with the solid exit before the others. So, choosing the right material, it is possible to separate a certain gas from a mixture. It is widely used for oxygen and nitrogen separation from air, to isolate hydrogen from a syngas or to remove hydrocarbons vapors from a gas [65].

It is not a continuous process; it is made of four basic phases:

- **Feed**: gas enters from the bottom of a tank (already pressurized) and a certain type of molecules are adsorbed on the solid surface.
- **Blowdown**: gas is released from the top; some molecules have higher reluctance to leave the solid surface (desorption) and they spend more time to exit. So, the first gas released is made by molecules with low affinity with the solid.
- **Purge**: the remaining gas is pushed back (exiting from the bottom) using the low-affinity gas to wash the tank in low pressure.
- **Pressurization**: the original pressure is restored with low-affinity gas and the cycle restarts.

There are other phases added for improve recovery and purity of both gas streams. For example in *Figure 30* **- PSA with five stages working at 30bar [116]** there is another phase called “rinse”. This is useful to remove the syngas in the tank using carbon dioxide. It reduces the syngas dispersion in the CO_2 stream, increasing the purity of the latter. In the figure, each tank represents one stage. Using one tank per phase, it is possible to have a continuous production.

This process does not require big thermal load as amine scrubbing, it consumes only electrical power to drive compressors and requires a small cooling. It consumes less energy than Rectisol process and it is suitable for CO_2 removing from syngas [116] also in medium-size plants. The removing efficiencies can reach values up to 95% [115].

A variation of that system is the pressure-vacuum swing adsorption (PVSA) where the purge phase is carried out under vacuum [115], [116].

There are examples of the zeolites and activated carbon (ACs) used in PSA process (see *Table 22* **- Some examples of PSA application**). Zeolites have a higher adsorption power respect to ACs for low CO_2 partial pressure. If it is higher than 1.7 bar, the situation becomes the opposite and ACs have better performance [110]. ACs can easily release CO_2 at low pressure, contrary to zeolites which require pressure also lower than atmospheric to work properly, so are preferable in PVSA.

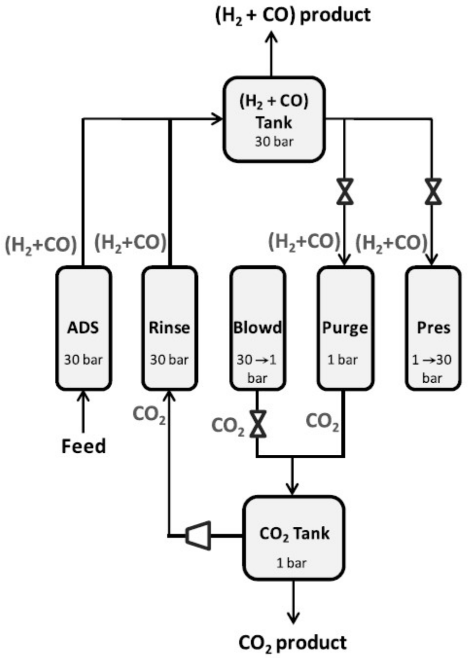

FIGURE 30 - PSA WITH FIVE STAGES WORKING AT 30BAR [116]

6.2.7.3 Miscellaneous

6.2.7.3.1 Membrane

Membranes for gas separation act as a filter: some molecules can pass though, others cannot. This technology involved organic (or inorganic) membrane permeable at a certain type of gas. It is a simple system with high reliability, low capital and operational cost and low energy consumption [117]. There are many examples of application in CO_2 removal from natural gas in large plants [117]. The lifetime is very short and it is possible to have a annually substitution [96]. Another problem is the selectivity: membranes have a low selectivity and if that is improved, the permeability is generally decreased [108]. Membranes usually work with low temperature (ambient conditions), but the ceramic (inorganic) membranes are able to work at about 350°C [108].

6.2.7.3.2 Cryogenic distillation

The principle is simple and quite similar to what is done to remove water from a gas. In cryogenic distillation process, the gas is pressurized and cooled down up to the point where carbon dioxide becomes liquid. After it is separated easily from the rest of the gas. Unfortunately, other component can also condense or solidify making some problem on heat exchanger. For example, water solidify below 0°C, so the gas has to be completely dried before the cryogenic process. It requests also very low temperature, so the energy consumption is very high. To avoid extremely low temperature, pressure has to be important to increase the condense temperature, but also this process requests a lot of energy [108].

6.2.7.4 Summary

TABLE 19 - CO_2 CAPTURE PROCESSES SUMMARY

CO_2 capture process	Pros	Cons
Selexol	✓ Low energy consumption ✓ High CO_2 capture	× Only for large plants*

	✓ H_2S capture	
Rectisol	✓ High CO_2 capture ✓ H_2S capture	✗ Low temperature cooling
Amine-based	✓ High CO_2 capture ✓ H_2S capture	✗ High energy consumption ✗ Corrosive issues
PWS	✓ Low-cost solvent	✗ Low selectivity ✗ Low CO_2 capture
PSA	✓ Suitable for small application ✓ No thermal consumption	✗ No H_2S capture power ✗ High CO_2 initial concentration requested
Membrane	✓ Very simple	✗ Short lifetime ✗ Low selectivity
Cryogenic distillation	✓ No solvents required	✗ Low temperature cooling

* No data for small plants was found.

There are several other methods for CO_2 removal, here only the major and the most interesting for this work was reported.

6.2.8 Summary

TABLE 20 - GAS CLEAN-UP SYSTEMS SUMMARY TABLE

Pollutant	Problems	Removal methods
Dust	Fouling, corrosion, erosion	Filter (bar or ceramic), cyclone, ESP, WS
Tars	Fouling, corrosion	Cracker, WS, VS, oil scrubber
Ammonia	Corrosion	WS, VS (H2SO4)
Halogens	Corrosion	WS, VS (NaOH), guard bed
Sulfur	Corrosion	VS (NaOH), guard bed
Alkali/alk. earth	Fouling, corrosion	WS, sorbent bed
CO_2	Syngas dilution	Scrubber, PWS, PSA, membrane, cryogenic distillation

6.2.9 Choice of the system

In this section, an analysis on what had been done in other works is carried out. The purpose is to have an idea of what the most common systems of gas cleaning are. It is avoided to report plants using EF gasifier for the reason that the production of tars is negligible. However, both fluidized and fixed bed are taken into account due to the similar amount of pollutants generated.

- **Francois et al. (2013)** [63] provides a model of a wood gasifier (DFB) to power a combined heat and power (CHP) system with a $10MW_{el}$ ICE-generator. The syngas cleaning system involves:
    - Cyclones
    - Catalytic tar cracker (olivine based)
    - Bag filter (for dust and condensate tars both)
    - Water scrubber (NH_3, HCl and tars removal)

  Sulfur is not removed from the syngas. The authors do not mention the reason why they do not remove it.
- **Kim et al. (2016)** [7] provides an experimental treatise of a FT-diesel-production laboratory-scale plant. A $200kW_{th}$ DFBG is employed. The syngas cleaning system involves:
    - Cyclone
    - Gravitational dust collector
    - Wet scrubber

  - Bag filter
  - MeOH scrubber to remove acids gas as CO_2, H_2S and COS

  The methanol scrubber required a chiller to bring the solvent temperature up to -30°C. The scrubber works at 60 bar, the compressor stages are between the filter and the scrubber.
- **Hamelinck et al. (2004)** [2] describes a huge gasification plant. A CFB gasifier of about $400MW_{th}$ is employed and it investigates the FTS production. It is a theoretical analysis and the authors evaluate the difference through several configuration as three gasifier pressure, the use of air or oxygen and different syngas cleaning and conditioning pathway. Furthermore, they find that the carbon dioxide capture from the syngas improve the efficiency but not the final cost of production. The better performance and the lower cost of production are achievable when pressurized gasifier is used (at 25 bar).

  First way (tar cracker + wet):
  - Tar cracker
  - Cyclones
  - Bag filter
  - Water scrubber (NH_3 and HCl removal)
  - Guard bed (ZnO)

  Second way (tar scrubber + wet):
  - Cyclones
  - Oil scrubber
  - Water scrubber (NH_3 and HCl removal)
  - Guard bed (ZnO)

  Third way (tar cracker + dry):
  - Tar cracker
  - Cyclones
  - Candle filters
  - Dry absorption (NH_3 removal)
  - Dry absorption (HCl removal)
  - Dry absorption (H_2S removal)
  - Guard bed (ZnO)

  In case of excess of carbon dioxide, they use a Selexol system to decrease its yield. The work shows that the investment cost for wet cleaning is lower, but the overall cost of production is almost the same for both dry and wet cleaning.
- **Tijmensen et al. (2002)** [72] considers a CFB gasifier with $100MW_{th}$ of input biomass in a FTS plant. The cleaning system involves:
  - Tar cracker
  - Cyclones
  - Bag filter
  - COS hydrolyzation
  - Water + NaOH scrubber (HCl and H_2S removal)
  - H_2SO_4 scrubber (NH_3 removal)
  - Guard bed (ZnO)

  They consider the tar cracker with a very high efficiency and the small amount of tar that still in the syngas, condense on the heat exchanger. They specify that it could be a problem.
- **Martín et al. (2011)** [65] provides a mathematical model of a switchgrass gasification for bioethanol production. The size is about $150MW_{th}$ of ethanol produced. The syngas cleaning involves:
  - Cyclones
  - Steam reforming (for tars and NH_3 removal)

    - Wet scrubber
    - PSA (HC and NH_3 removal)
    - Amine scrubbing (H_2S removal)
    - PSA/membranes (CO_2 removal)
- **Im-orb et al. (2016)** [4] describes a downdraft gasifier (about 400MW$_{th}$) fed with rice straw in a FTS plant. The syngas cleaning system involves:
    - Sand bed filter (dust removal)
    - Steam reformer (nickel catalyst, for tar removal)

  The work does not consider sulfur in biomass and ammonia production.
- **Dussan et al. (2018)** [60] considers a gasification (DFB or FICFB, deduced from a scheme) of a sewage sludge and its digestate (through AD) and use it to power a 6MW$_{el}$ ICE. The syngas cleaning presented is not complete, but it involves:
    - Amine scrubber
- **Swanson et al. (2010)** [55] describes a BFB gasifier feed with corn stover (2000ton/day, it means about 300-400MW$_{th}$). The produced syngas is used in a FTS plant. The authors investigate the difference between an entrained flow gasifier and a circulating fluidized bed. The syngas cleaning system involves:
    - Cyclones
    - Water scrubber (direct water quench)
    - Amine scrubber (CO_2 and H_2S removal)
    - Guard bed
    - SMR reactor
    - WGS reactor

  There is also a PSA to separate a fraction of hydrogen needed for the products upgrades.
- **Spyrakis et al. (2004)** [70] considers a 1ton/h biomass gasifier (4.8MW$_{th}$) that produces a syngas to feed a FTS. The syngas cleaning system involves:
    - Tar cracker
    - Ceramic filter
    - Hydrolysis
    - Dry absorption (HCl and H_2S removal)
    - Dry absorption (NH_3 removal)
    - Guard bed (ZnO)

  There is no further information on what the dry sorbents are.
- **Dutta et al. (2011)** [61] describes a DFBG working with biomass (2000ton/day, it means about 300-400MW$_{th}$) for alcohols production. The syngas cleaning system involves:
    - Cyclones
    - Tar cracker
    - Venturi scrubber with water
- **Menin et al. (2020)** [66] considers a gasifier (13MW$_{th}$) for SNG production. The syngas cleaning system involves:
    - Cyclones
    - Methyl ester tar scrubber
    - Bag filter
    - Water scrubber (HCl, NH_3 and H_2S removal)
    - PWS (partial CO_2 removal)

TABLE 21 - SYNGAS CLEANING METHODS SUMMARY TABLE

Paper	Purpose	Dust	Tars	NH_3	HCl	H_2S	CO_2	Ref.
Francois et al.	ICE	Cy + BF	CC + WS	CC + WS	WS	-	-	[63]
Kim et al.	FTS	Cy + GDC + BF + WS	WS	WS	WS	MeOH	MeOH	[7]
Hamelinck et al.	FTS	Cy + BF	CC	WS	WS	GB	Selexol	[2]
Tijmensen et al.	FTS	Cy + BF	CC	VS	VS	VS + GB	-	[72]
Martín et al.	EtOH	Cy + WS	SR	SR + WS + PSA	WS	AS	PSA	[65]
Im-orb et al.	FTS	SB	SR	-	-	-	-	[4]
Dussan et al.	ICE	-	-	-	-	AS	-	[60]
Swanson et al.	FTS	Cy + WS	WS	WS	WS	AS + GB	AS	[55]
Spyrakis et al.	FTS	CF	CC	DA	DA	DA + BG	-	[70]
Dutta et al.	EtOH	Cy	CC	VS	VS	-	-	[61]
Menin et al.	SNG	Cy + BF	MES	WS	WS	WS	PWS	[66]
This work	FTS	Cy + WS	CC + WS	WS	WS + VS	VS	PSA	-

Table legend: Cy → cyclone, BF → bag filter, GDC → gravity dust collector, CC → catalytic cracker, GB → guard bed, WS → water scrubber, SR → steam reforming, SB → sand bed, AS → amine scrubber, CF → ceramic filter, DA → dry absorption, MES → methyl ester scrubber

6.2.9.1 Final considerations

To select the proper equipment combination for the syngas cleaning and conditioning, it is useful to start from carbon dioxide removal. There is not a common line: several systems are employed. Many papers describe how the Rectisol process is the most used, but it is difficult to find a small plant that use this system. Regarding Selexol process, the same problem subsists: only big-size plants have been found adopting this technology. Furthermore, amine scrubbing is too energy expensive and PWS has a low selectivity towards CO_2. Finally, PSA is adopted, due to the simplicity of the system and the high removal efficiency. On the other hand, there are some obstacles in the removal of sulfur components together with carbon dioxide, so another component has to take care of that.

For sulfur removal system, the same evaluations already done for CO_2 are still valid. So, MeOH, amine and water scrubbing are not feasible, the dry absorption seems to be a low-maturity technology and it is rejected. In addition, the only use of a guard bed leads to a high consumption of material due to the high presence of sulfur in the syngas. The most promising system is the Venturi scrubber with NaOH combined with a zinc oxide guard bed. The first one removes the major of the H_2S, while the second one guarantees that the level of sulfur is below 1ppm.

Hydrochloric acid can also be removed from the basic Venturi scrubber. However, for ammonia, dust and tar, a standard-water scrubber is employed, so also HCl is absorbed from the water.

Anyway, the tar reduction by the water scrubber is not so high, as reported by Francois et al. [63]. Many papers report a tar conversion system that can be a regular or a steam reforming catalytic tar cracker. In this work, an olivine catalytic cracker is employed without the addition of steam. This is also useful to reduce the amount of ammonia and hydrocarbons [63].

In order to prevent a fast pollution of the tar cracker by fouling, a group of cyclones is adopted to get a first dust removal. The finest PM are supposed to be completely removed by the scrubbers [63].

To conclude, the PSA system is working at 6.7 bar (6.25 bar at the exit of the machine) and it is collocated between the two compressor stages. In this way, the second compressor brings the syngas up to 30 bar and at a temperature of about 210°C, in order to save a heat exchanger before entering the FT reactor.

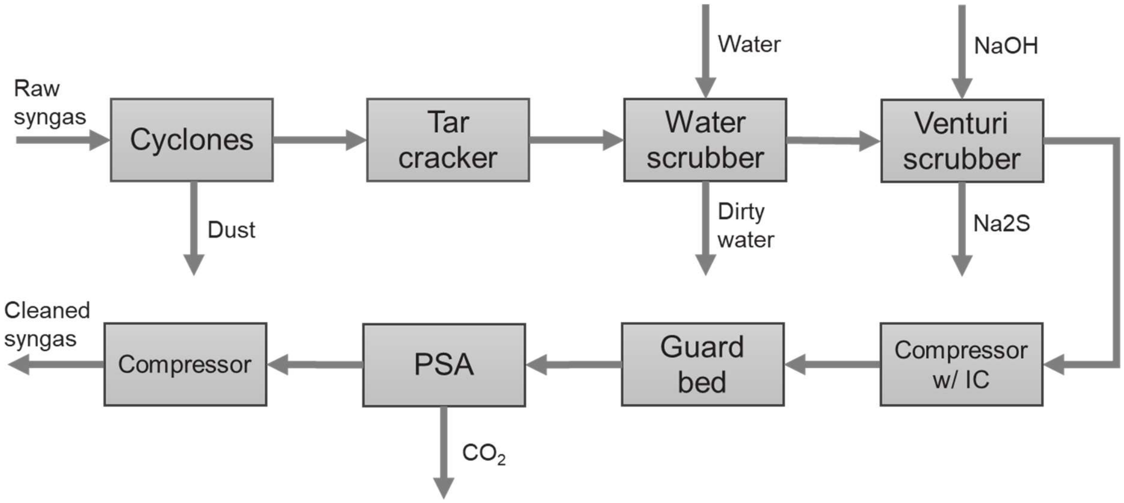

FIGURE 31 - SYNGAS CLEANING AND CONDITIONING SCHEME

6.3 Syngas clean-up and conditioning: technologies selection

6.3.1 Cyclones

In the gasifier model on Aspen Plus, dust does not appear for simplicity. Otherwise, in a real plant it is produced and so it has to be considered in the economic analysis.

6.3.2 Catalytic tar cracker

In the process model, tars are not modelized for simplicity, but in the reality, they are present in the syngas stream. Olivine, that is inside the tar cracker, has the side effect of decomposing ammonia and hydrocarbons. This has to be taken into account. In the Aspen Plus simulation, an stoichiometric adiabatic reactor is used with a pre-defined level of conversion (70%) taken from Francois et al. [63].

6.3.3 Wet scrubber

The kinetic modelling of a water scrubber is complex and out of the aim of this analysis. In this work, a separation block has considered (Sep2 in Aspen Plus), where ammonia and hydrochloric acid are fully removed. After that, a heat exchanger cools down the syngas to 40°C, that is an acceptable temperature for a gas exiting from a wet scrubber. Finally, the syngas exits saturated in moisture, without introducing other water.

6.3.4 Venturi scrubber

Similarly to the previous case, a separator is used to divide sulfuric acid from the syngas stream. Sodium hydroxide is not modelled because it is not strictly useful; however, it will keep into account in the economic balance.

6.3.5 PSA system

There are several examples of PSA systems utilization in CO_2 removal as reported in the table.

TABLE 22 - SOME EXAMPLES OF PSA APPLICATIONS

Authors	Bed material	Pressure	Pressure drop	Removal efficiency	Specific energy	Ref.
Hernandez et al.	Zeolite 5A/13X	5 bar	-	95%	-	[96]
Martín et al.	Zeolite 5A	4.5 bar	0.45 bar	95%	-	[65]
Oreggioni et al.[1]	Zeolite 13X	1.5 bar	-	90%	0.10 kWh/kg$_{CO2}$	[115]
Ribeiro et al.	Activated carbon	30 bar	Negligible[2]	>90%	0.19 kWh/kg$_{CO2}$	[116]

[1] PVSA

[2] Supposed by scheme

For other plants, it is suggested to see the work of Riboldi et al. [110], which reports many examples with different working pressures and adsorbent materials.

In this work, the PSA system in Martín et al. [65] is considered as reference. The PSA unit works with zeolite 5A at 4.5 bar and a 0.45 bar of pressure drop. In the present work, the pressure is increased up to 6.7 bar. This is done in order to simplify the plant and to avoid a heat exchanger at the outlet of the PSA: compressing the syngas from 6.25 bar (PSA discharge pressure) up to 30 bar (FTS reactor working pressure), the compressor increases the syngas temperature from 35°C to 210-215°C. This is the same of the FTS reactor and the syngas can be used directly.

The energy consumption of the PSA system (suppose different with respect to the work lost for the pressure drop) is in the range of 0.1 – 0.2 kWh/kg$_{CO2}$ according to Oreggioni et al. [115]. In this work, an average value of 0.15 kWh/kg$_{CO2}$ is taken into account.

6.3.6 Hypothesis

The hypothesis of the model are the following:

1. 20% of methane and 70% of ammonia are converted in the catalytic tar cracker [63].
2. The catalytic tar cracker is adiabatic.
3. Methane in tar cracker undergoes steam reforming only.
4. No interaction through syngas components (e.g. reaction between ammonia and acids).
5. 100% of removing efficiency of NH_3, HCl in the wet scrubber [63].
6. Syngas exits from the wet scrubbing saturated in water.
7. No sulfur compounds or carbon dioxide is removed by the water scrubber.
8. H_2S is completely removed by the Venturi scrubber.
9. No carbon dioxide is removed by the Venturi scrubber.
10. 100% of Na_2S and unreacted NaOH is recovered and no traces leak in the syngas stream.
11. 95% of CO_2 is removed [65].
12. 0.45bar of pressure drop is considered at the PSA system.
13. No gases different from CO_2 are removed by PSA system [65].
14. All the heat produced or absorbed by ammonia and hydrochloric acid dissolution in water and hydrogen disulfide reaction with sodium hydroxide are neglected.

The scheme of the Aspen Plus model is reported in the *Appendix A* – Aspen model.

6.4 Syncrude production

The aim of the plant is to produce syncrude, so there is the necessity to transform the syngas into synthetic oil though an FTS.

6.4.1 Choice of the system

The different systems for FTS have been analyzed previously. Keeping into account that the plant is small compared to a standard coal or gas to liquid (CTL or GTL) plants, the choice goes towards the simplicity. A fixed-bed multi-tubular reactor is employed as Marchese et al. [90], with an off-gas recirculation to increase the production. The catalyst employed is cobalt, given its higher heavy-hydrocarbon selectivity and the low olefins and oxygenated compound production.

6.4.2 Model

A Fischer-Tropsch synthesis process is complex to model and it is generally required a kinetic modeling [118]. A low-computational-time-consuming way to get a result is to use the Anderson–Schulz–Flory distribution as anticipated in the introduction about FTS (see *4.3 Mechanism*).

The reactor for the hydrocarbons formation is a yield reactor working with an Excel datasheet. The ASF distribution returns a formation probability for each paraffin molecules (up to infinity). In the reality, it is not possible to handle infinite quantities. Additionally, Aspen Plus has a limited range of paraffins and olefins. So, only flew molecules are taken into account and reported in the *Table 23* **- Summary of the molecules taken into account**.

TABLE 23 - SUMMARY OF THE MOLECULES TAKEN INTO ACCOUNT

Hydrocarbons	Paraffins	Olefins	Molecules considered
C_1 to C_4	Yes	Yes	All the molecules
C_5 to C_{19}	Yes	Yes	Only even
C_{20} to C_{31}	Yes	No	Only even
C_{32} to C_{35}	Yes	No	Only even (C34 does not appear on Aspen Plus library, so it is not modelled)
C_{36+}	Yes	No	Only C36 are representative of all the heavier molecules

It can be possible to keep into account only one molecule to represent a group as done in Cinti et al. [51], but the way presented can be more accurate.

To represent the olefins yield, it is used the formula contained in the paper of Cinti et al. [51] and already presented in the introductive chapter on FTS (see *4.3.2 FT products characterization*).

Regarding the oxygenated compounds, they are neglected.

6.4.2.1 Hypothesis

The hypothesis of the model are the following:

1. ASF distribution for C_{2+}.
2. Methane yield of 20% [90].
3. Olefins distribution according to Cinti et al. [51].
4. Oxygenated compounds are neglected.
5. Reactions occur isothermally.
6. The formula to calculate the chain-growth probability is taken according to [50].
7. The H_2/CO ratio variation inside di reactor is supposed negligible.
8. Recirculation is made with one part of the gas fraction (gas and liquid are separated).
9. Pressure drops are neglected.

10. 60% of per-pass CO consumption.
11. Methane, ethane and ethene are completely removed from the syncrude.
12. The heat produced by the synthesis reaction is calculated as Comidy et al. [119]

The scheme of the Aspen Plus model is reported in the *Appendix A* – Aspen model.

6.4.3 Syncrude products and cuts

The natural oil, as the synthetic one, is made of several fractions. The most important ones are reported below:

- **LPG**: liquified petroleum gases, also called improperly liquid propane gas, is the lightest fraction of the oil and it is formed by $C_3 – C_4$. LPG is a gas at ambient condition of temperature and pressure, but it can be easily liquified increasing the pressure between a couple of bar and 10 bar depending from its composition.
- **Naphtha**: it is a general name to indicate the mix of molecules from C_5 to C_9. It is liquid at ambient pressure and temperature, but it has a high volatility. From naphtha is possible to extract the gasoline, but in FTS syncrude, this cut has a low quality (low octane number) due to the absence of branched and cyclic molecules. To produce a useful fuel to power cars, it has to be upgraded.
- **Middle distillates**: it is a liquid with low volatility. The fractions of the middle distillates go from C_{10} to C_{19} and they form the light oil. From the middle distillates, it is possible to extract diesel and kerosene. These two are very interesting in FTS, because they are sulfur-free and have a high cetane number.
- **Heavy fractions**: they are liquids and/or solids. They are made of heavy oils and waxes with a chain number higher than 20. They can be treated in a cracking process producing diesel or used as lubricant, in pharmaceutical/cosmetical application or many other applications.

These fractions are generally separated with a fractional distillation, so the real fractions are not distinguished by the chain length or the molecular weight but by the boiling temperature.

The yields of these fractions forming the crude oil are different for different oil and this influences its price. The same happen for the synthetic crude. Middle distillates and the heavy fractions are the most expansive [96], for that reason, cobalt has been selected as catalyst, due to its selectivity toward heavy molecules.

6.5 Other balance of plant

There are other components that are not inside the three main parts described before, such as the steam generation, the air blower, etc. These auxiliary systems are briefly described below.

6.5.1 Steam generation

The system is supposed to work with the steam generated in the FTS reactor cooler. The steam is generated at 12bar in order to have a boiling point of about 190°C. This is done because the FTS reactor works at 210°C and a temperature difference between the two sides (hot and cold) of about 20°C is employed. The saturated steam is laminated to bring it at 1.11 bar needed for the gasifier injection [95] and then superheated up to 450°C.

6.5.2 Air blower and conditioning

The combustor needs air to oxidize the char, but the circulated fluidized combustor has a pressure drop of 0.2 bar [95], so air has to be blown. For this purpose, an electric blower is employed. Before entering the combustor, the air is pre-heated up to 450°C to increase the efficiency.

6.5.3 Gas turbine

The off-gas can be burnt in a gas turbine. The size is very small for that kind of machine (hundreds of kilowatt), but it is better than a piston engine because the turbine discharges hot gas, which can be necessary for the thermal balance of the plant. On Aspen Plus, it is modelized with a compressor, a combustor (stoichiometric reactor with fully conversion of the fuel) and a turbine. The pressure ratio of the compressor is 6.7 [120], the maximum temperature in the combustor is 1000°C and all the pressure drops are neglected.

6.5.4 Hypothesis

The hypothesis of the model are the following:

1. The steam is generated at 12bar.
2. The water used is pure and it does not contain any traces of gas dissolved.
3. Efficiency of the GT does not depend on its size.
4. No nitrogen oxides are generated in the GT.
5. Air has no moisture.
6. All the other electric energy utilities are considered negligible

The scheme of the Aspen Plus model is reported in the *Appendix A* – Aspen model.

7. Plant layouts

There are several possibilities of components arrangements in the plant. From the layout, it depends the efficiency, the productivity and the economic balance of the system. In this section, the four most significant layouts are reported and commented.

7.1 Case A

Case A is the basic configuration. It is taken into account to have a reference when another configurations will be investigated. This layout is popular and it has been analyzed by many papers. Just a couple of example are reported as reference: Tagomori et al. [1] and Tijmensen et al. [72].

The biomass (pine wood or digestate) enters the gasifier as it is received, so without any conditioning. The gasifier exchanges char and sand with the combustor. The formed raw syngas passes through the cleaning system, where all the pollutants are removed (*6.2 Syngas clean-up and conditioning*). The cleaned syngas enters the FTS reactor, where syncrude is produced. The recirculation is omitted in the drawing to keep it simple, but it is implied. Finally, the whole off-gas is sent to the power generation group (the gas turbine) to produce electric energy, that is enough to satisfy the plant demand and the remaining part is sold. In addition, also the LPG fraction of the produced syncrude is used for the power generation. It has a lower cost with respect to the liquids and furthermore it has to be recompressed to become a liquid with additional costs.

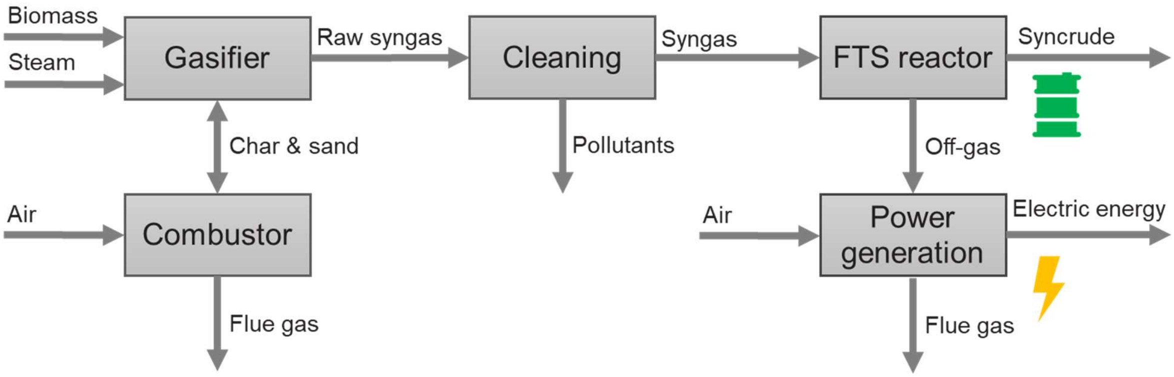

FIGURE 32 - CASE A PLANT LAYOUT

The working temperature of the gasifier is 850°C as in the model of Doherty et al. [23] and the recirculation of the FTS reactor is 80%.

Advantage:

- ✓ Configuration tested in several papers
- ✓ Co-production of fuel and power
- ✓ Possibility to get incentives for the power produced
- ✓ Plant energy self-sufficiency

Disadvantage:

- × Low efficient of the power generation especially for small plant
- × Production of electricity when the price is low

7.2 Case B

This is the same configuration of the case A, but it has undergone an optimization process. Increasing the working temperature, the syngas increases in quantity and in quality as shown in the sensitivity analysis in *6.1.3 Validation*. The gasifier temperature is brought to the maximum possible (900°C) and the recirculation on the FTS is set to 90%, which is considered the highest possible value.

Advantage:

- ✓ Co-production of fuel and power
- ✓ Possibility to get incentives for the power produced
- ✓ Plant energy self-sufficiency

Disadvantage:

- × Low efficient of the power generation especially for small plant
- × Production of electricity when the price is low

7.3 Case C

The last case considers that electric energy is not produced inside the plant. The gas turbine efficiency is low, so it can be more interesting to recirculate the off-gas and LPG stream. Surely, it is not possible to send the whole flow to the gasifier because there is a fraction of inert gases such as nitrogen. This can be collected in the loop and it makes the plant out of work very quickly, so a fraction is sent to the combustor. A side effect is the reduction of the amount of char sent to the combustor that are necessary to maintain the plant thermal balance. Furthermore, a sensitivity analysis is performed with the aim of selecting the right fraction of gas split between the gasifier and the combustor. The choice is 80% to the first and 20% to the latter, according to *Figure 33* **- Sensitivity on the fraction split between the gasifier and the combustor**.

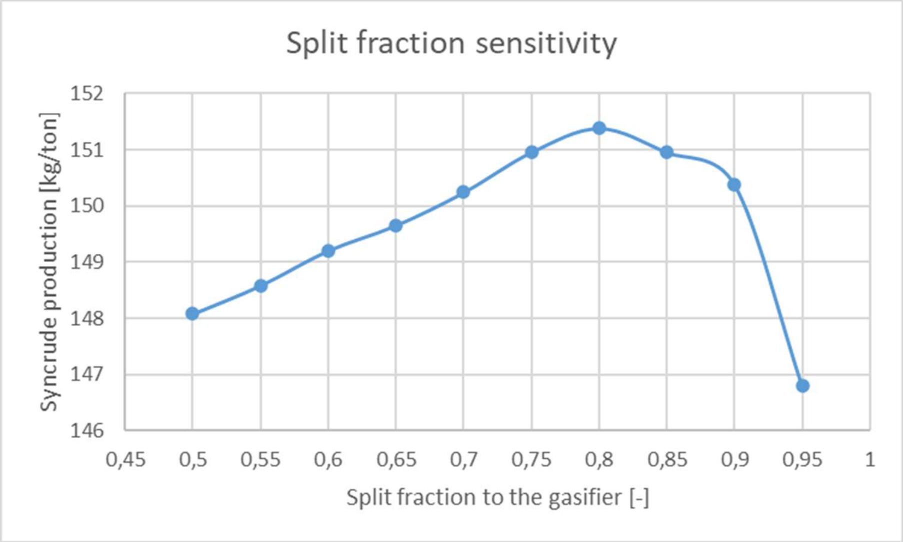

FIGURE 33 - SENSITIVITY ON THE FRACTION SPLIT BETWEEN THE GASIFIER AND THE COMBUSTOR

A similar configuration is reported by Im-Orb et al. [4]. It recirculates back to the gasifier a fraction of off-gas though a turbine to recovery the small amount of energy released when the gas is expanded from the high pressure of the FTS reactor to the low pressure of the gasifier. In the present work, the expander is not used because it increases the initial cost, although it can improve the efficiency.

Advantage:

- ✓ Syncrude producibility improved
- ✓ High energy efficiency
- ✓ Lower capital cost due to the absence of the gas turbine
- ✓ Whole the flue gases are on one stream, it means only one system for the thermal recovery

Disadvantage:

- ✗ Energy dependence from the outside

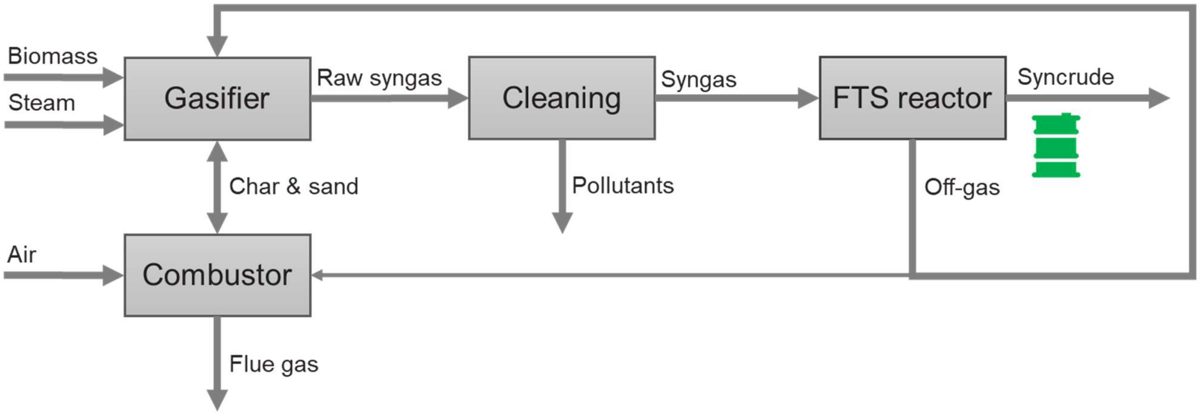

FIGURE 34 - CASE C PLANT LAYOUT

8. Pinch analysis

A pinch analysis for each case is performed to understand if the plant needs a thermal integration and to know the size and the number of the heat exchangers requested. Performing the analysis, the target is to reduce the number of components and avoid any splitting of the streams, which makes complicated the plant.

It is necessary to remember that in the graphs, the hot and cold curves are drown keeping into account the ΔT_{PP}. The red (hot) curve has to be over the blue (cold) one, but if there is an overlapping it is acceptable (it is the pinch point).

Moreover, for the cases C (both digestate and wood), hypothesis of steam production is taken into account in order to increase the thermal recovery. Certainly, the heat cannot be sent for long distance like electric energy. So, the production of steam is depending to the site-proximity demand. If the plant is collocated inside an industrial complex, it is possible to sell the steam. Otherwise, if there is a district heating/cooling grid, it is possible to sell heat at low temperature. Finally, when none of these possibilities is doable, it is possible to feed an organic Rankine cycle (ORC) and produce electric power for the internal consumption and/or to sell to the grid.

Lastly, for all the exchanger, a temperature variation of pinch point of 15°C is assumed.

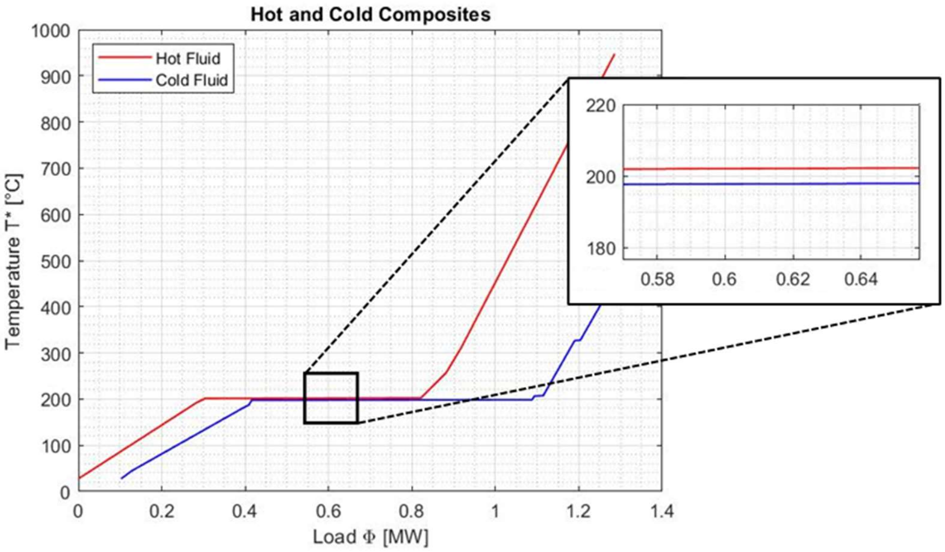

FIGURE 35 - EXAMPLE OF CORRECT GRAPH

8.1 Digestate

8.1.1 Case A

TABLE 24 - STREAMS FOR CASE A WITH DIGESTATE

Component	Stream	Typology	T_{in} [°C]	T_{out} [°C]	Thermal power [kW]	Gc_p [kW/K]
Air pre-heater	1	Cold	37.0	450	127.4	0.3085
Flue gas cooler	2	Hot	905	200	255.2	0.3620
Economizer	3	Cold	20	180	59.93	0.3746
Steam generator	4	Cold	190	191	169.7	169.7
Steam superheater	5	Cold	173	450	45.16	0.1630
Intercooler	6	Hot	253	35	74.75	0.3429
FTS reactor cooler	7	Hot	210	209	324.5	324.5
FTS products cooler	8	Hot	210	35	129.6	0.7406
Flash tank MT	9	Cold	199	200	12.93	12.93
Flash tank HT	10	Cold	319	320	8.383	8.383
Light products cooler	11	Hot	200	35	5.348	0.03241
Middle products cooler	12	Hot	320	35	9.203	0.03229
Heavy products cooler	13	Hot	320	35	6.301	0.02211
TG discharge cooler	14	Hot	611	100	755.6	1.479

Heat required at high temperature: 0 kW

Cool required at low temperature: 1137 kW

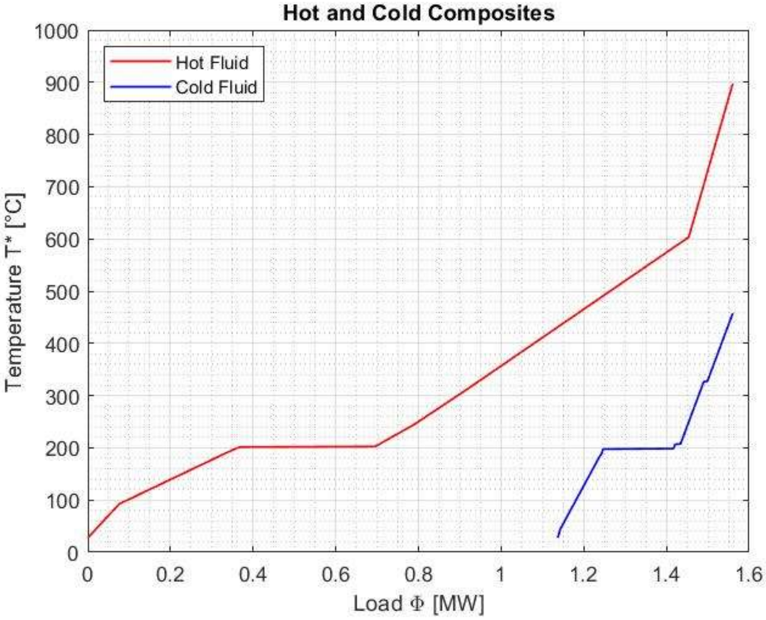

FIGURE 36 - COMPOSITE CURVE FOR CASE A WITH DIGESTATE

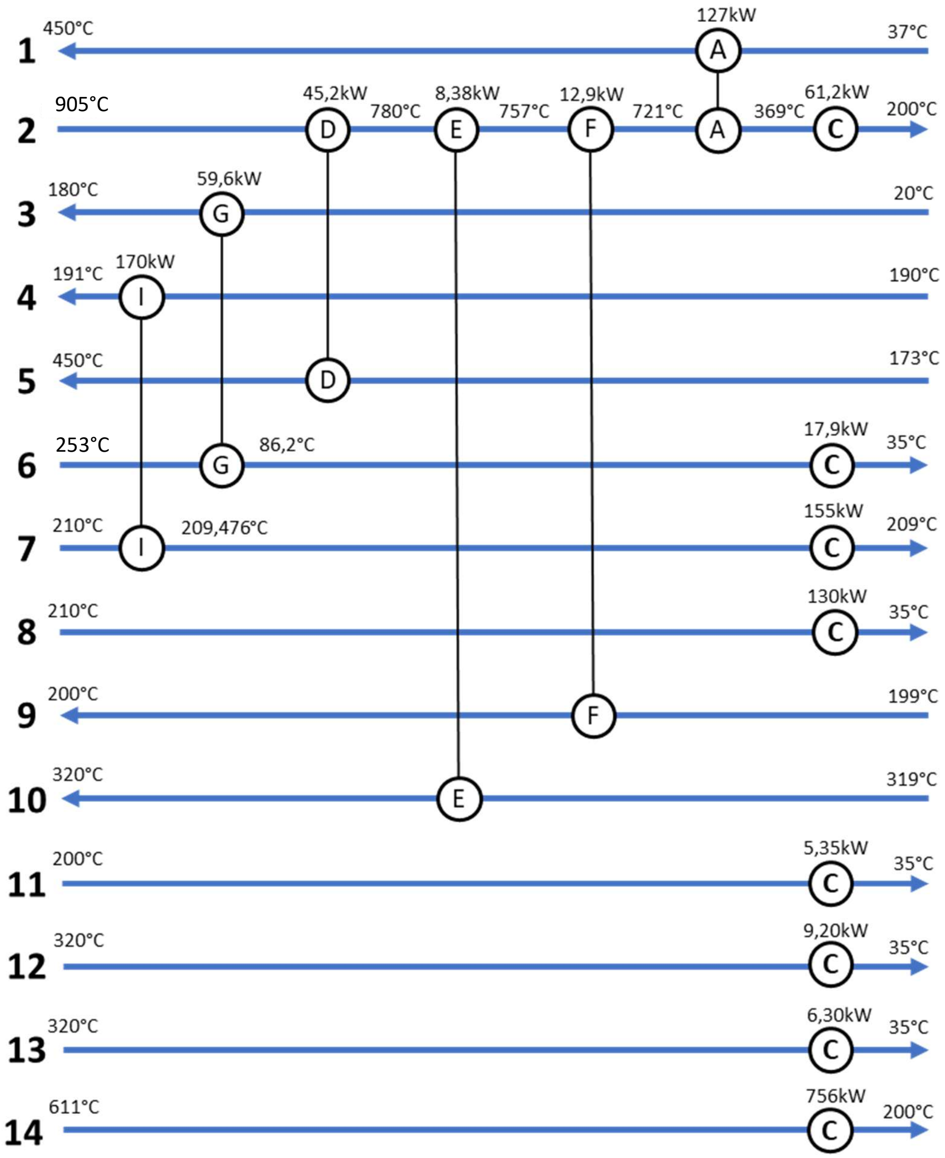

FIGURE 37 - HEAT EXCHANGERS SCHEME - CASE A WITH DIGESTATE

8.1.2 Case B

TABLE 25 - STREAMS FOR CASE B WITH DIGESTATE

Component	Stream	Typology	T_{in} [°C]	T_{out} [°C]	Thermal power [kW]	Gc_p [kW/K]
Air pre-heater	1	Cold	37.0	450	158.9	0.3847
Flue gas cooler	2	Hot	955	200	342.6	0.4538
Economizer	3	Cold	20	180	58.84	0.3678
Steam generator	4	Cold	190	191	166.6	166.6
Steam superheater	5	Cold	173	450	44.34	0.1601
Intercooler	6	Hot	262	35	77.88	0.3431
FTS reactor cooler	7	Hot	210	209	402.4	402.4
FTS products cooler	8	Hot	210	35	151.3	0.8646
Flash tank MT	9	Cold	199	200	16.69	16.69
Flash tank HT	10	Cold	319	320	10.00	10.00
Light products cooler	11	Hot	200	35	7.541	0.04570
Middle products cooler	12	Hot	320	35	10.66	0.03740
Heavy products cooler	13	Hot	320	35	7.913	0.02776
TG discharge cooler	14	Hot	615	100	431.1	0.8371

Heat required at high temperature: 0 kW

Cool required at low temperature: 976.0 kW

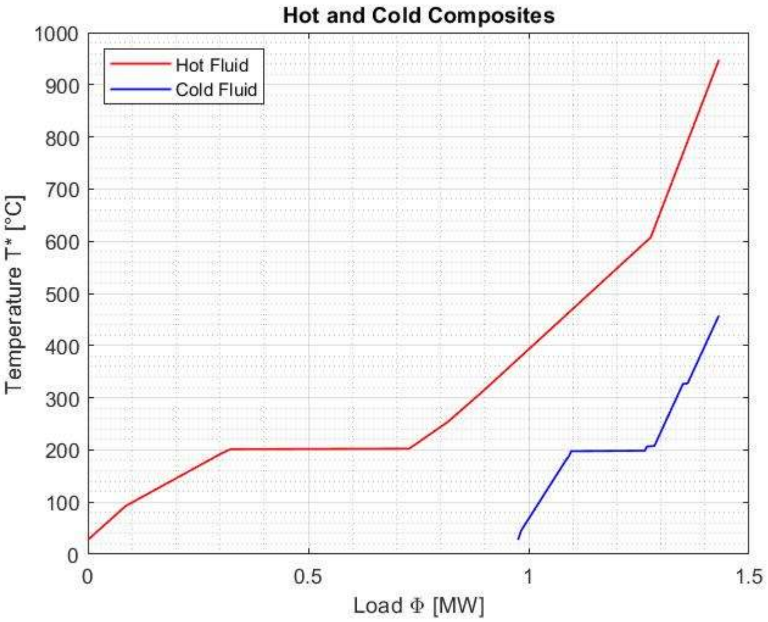

FIGURE 38 - COMPOSITE CURVE FOR CASE B WITH DIGESTATE

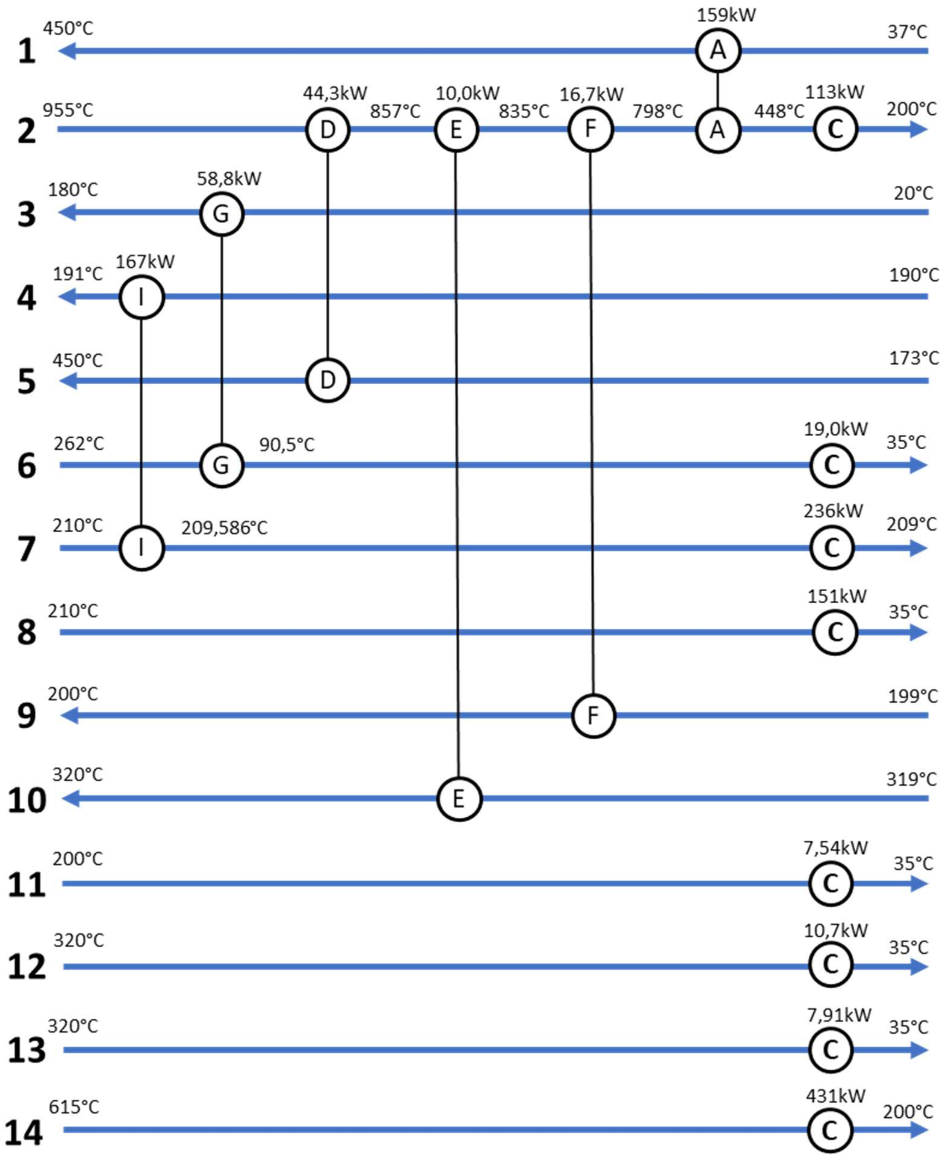

FIGURE 39 - HEAT EXCHANGERS SCHEME - CASE B WITH DIGESTATE

8.1.3 Case C

TABLE 26 - STREAMS FOR CASE C WITH DIGESTATE

Component	Stream	Typology	T_{in} [°C]	T_{out} [°C]	Thermal power [kW]	Gc_p [kW/K]
Air pre-heater	1	Cold	37.0	450	196.2	0.4751
Flue gas cooler	2	Hot	955	200	436.5	0.5781
Economizer	3	Cold	20	180	57.82	0.3614
Steam generator	4	Cold	190	191	163.7	163.7
Steam superheater	5	Cold	173	450	43.57	0.1573
Intercooler	6	Hot	265	35	102.3	0.4448
FTS reactor cooler	7	Hot	210	209	515.1	515.1
FTS products cooler	8	Hot	210	35	198.7	1.1354
Flash tank MT	9	Cold	199	200	20.93	20.93
Flash tank HT	10	Cold	319	320	13.09	13.09
Light products cooler	11	Hot	200	35	9.042	0.05480
Middle products cooler	12	Hot	320	35	14.16	0.04968
Heavy products cooler	13	Hot	320	35	10.10	0.03544

Heat required at high temperature: 0 kW

Cool required at low temperature: 790.6 kW

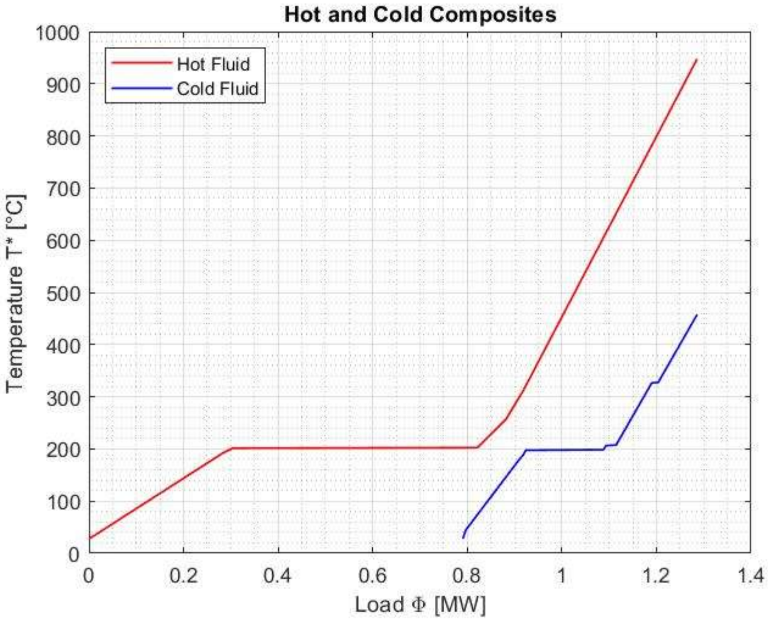

FIGURE 40 - COMPOSITE CURVE FOR CASE C WITH DIGESTATE

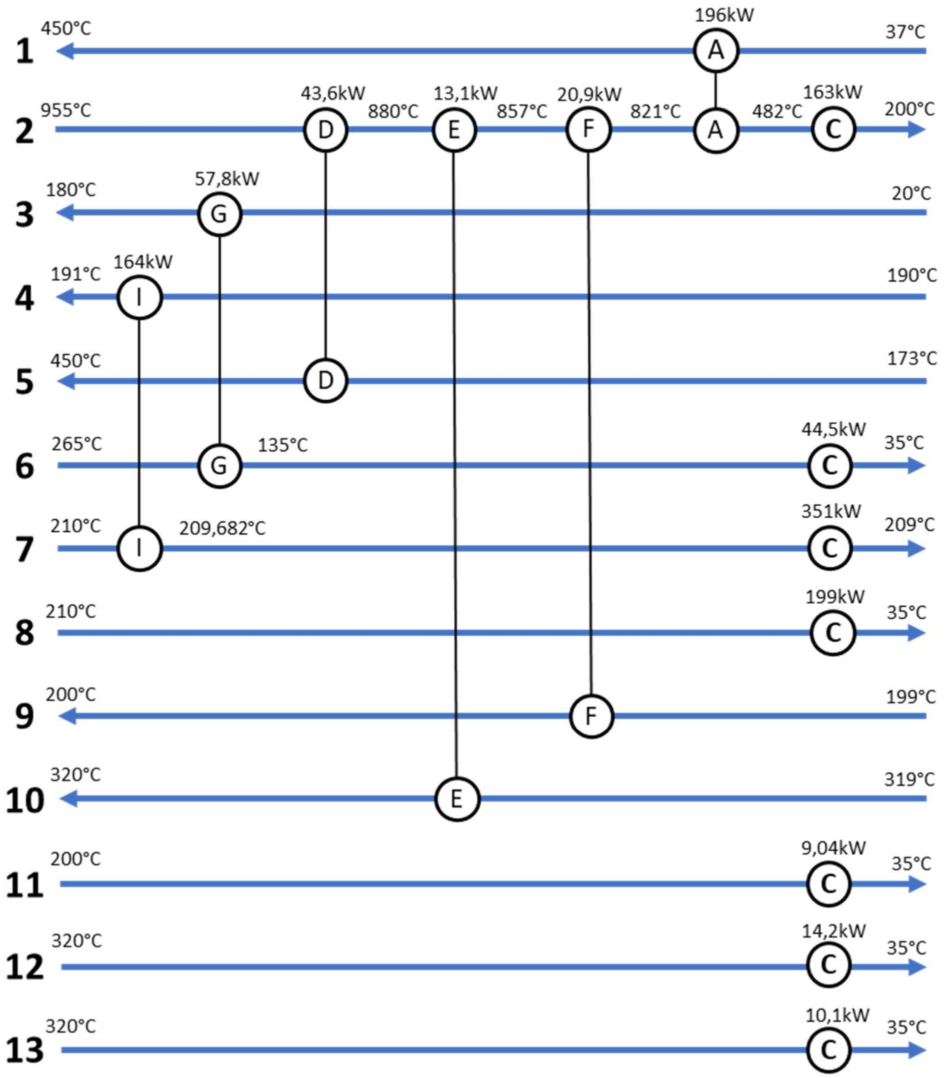

FIGURE 41 - HEAT EXCHANGERS SCHEME - CASE C WITH DIGESTATE

8.1.4 Case C with steam production

The production of steam is 872.9 kg/h. It could be higher than that, but it became necessary to split the streams and increase the number of heat exchanger. The way proposed is the simplest method to enhance the thermal recovery, which is anyway quite high. It is necessary to notice that the heat exchanger *K* is not a real heat exchanger because it is connected to the production of steam necessary to the FTS reactor cooling. Finally, the cooler on the steam 2 can be avoided because sending flue gases to the stack with a temperature of 200°C or 210°C does not make any difference.

TABLE 27 - STREAMS FOR CASE C WITH DIGESTATE AND STEAM PRODUCTION

Component	Stream	Typology	T_{in} [°C]	T_{out} [°C]	Thermal power [kW]	Gc_p [kW/K]
Air pre-heater	1	Cold	37.0	450	196.2	0.4751
Flue gas cooler	2	Hot	955	200	436.5	0.5781
Economizer	3	Cold	20	180	57.82	0.3614
Steam generator	4	Cold	190	191	163.7	163.7
Steam superheater	5	Cold	173	450	43.57	0.1573
Intercooler	6	Hot	265	35	102.3	0.4448
FTS reactor cooler	7	Hot	210	209	515.1	515.1
FTS products cooler	8	Hot	210	35	198.7	1.1354
Flash tank MT	9	Cold	199	200	20.93	20.93
Flash tank HT	10	Cold	319	320	13.09	13.09
Light products cooler	11	Hot	200	35	9.042	0.05480
Middle products cooler	12	Hot	320	35	14.16	0.04968
Heavy products cooler	13	Hot	320	35	10.10	0.03544
Economizer 2	14	Cold	20	180	179.6	1.123
Steam generator 2	15	Cold	190	191	508.4	508.4

Heat required at high temperature: 0 kW

Cool required at low temperature: 102.6 kW

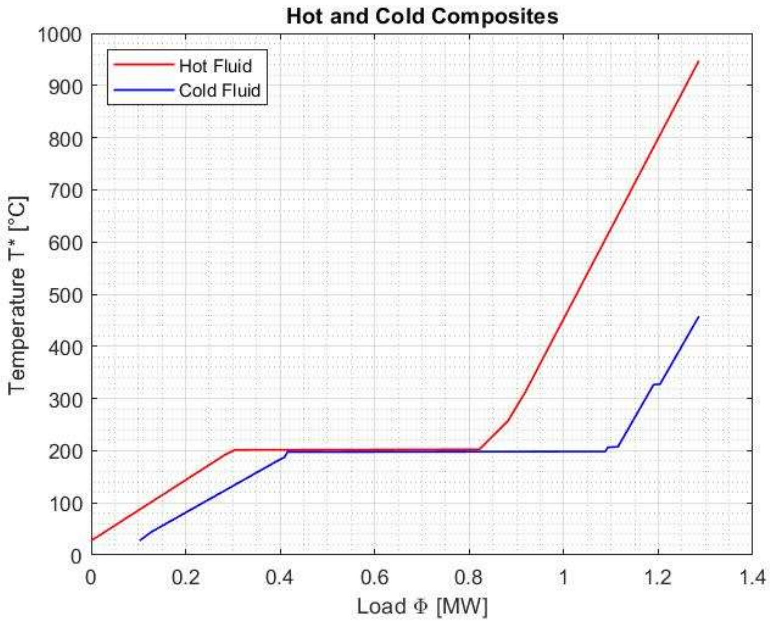

FIGURE 42 - COMPOSITE CURVE FOR CASE C WITH DIGESTATE AND STEAM PRODUCTION

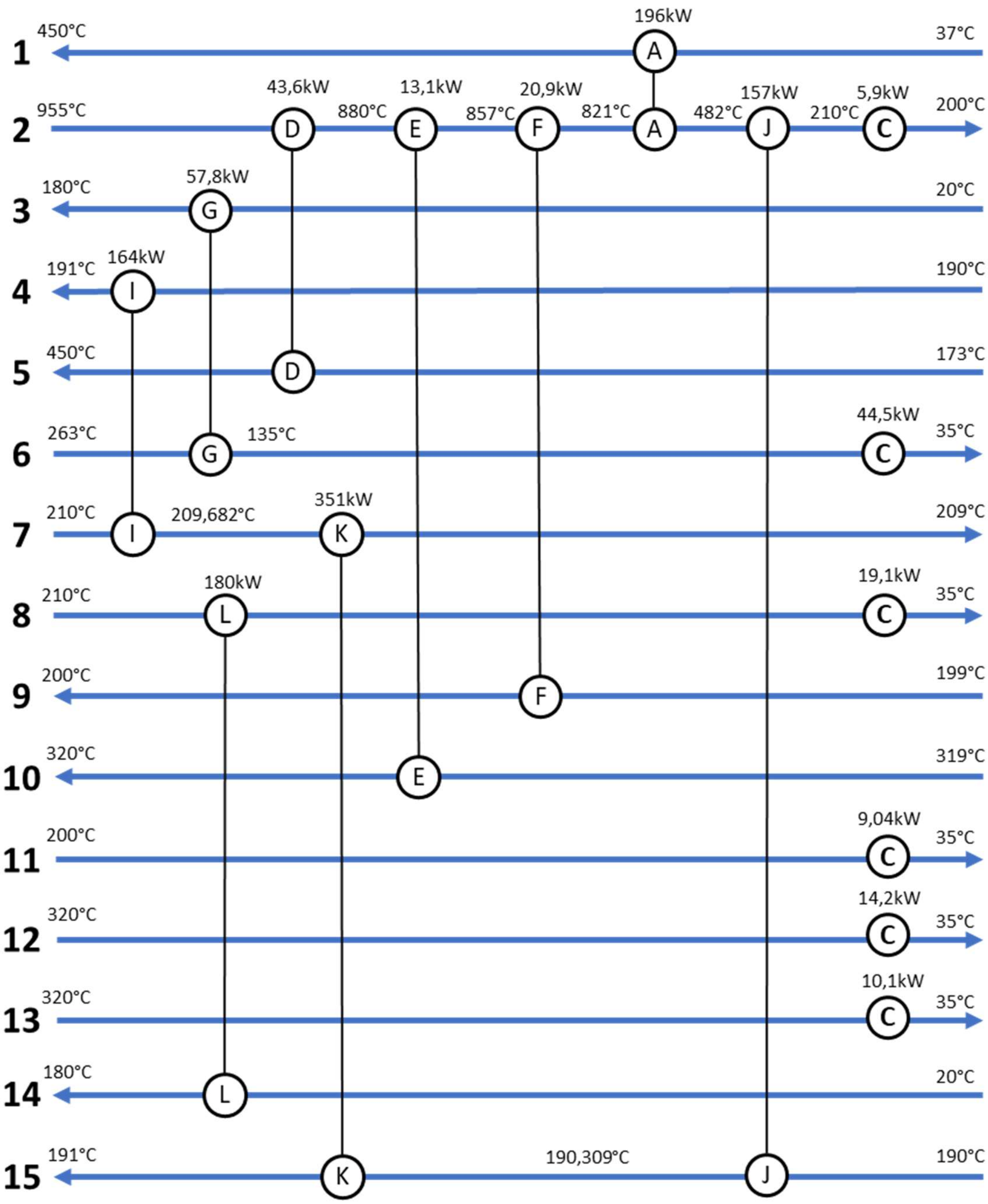

FIGURE 43 - HEAT EXCHANGERS SCHEME - CASE C WITH DIGESTATE AND STEAM PRODUCTION

8.2 Woody biomass

8.2.1 Case A

TABLE 28 - STREAMS FOR CASE A WITH PINE WOOD

Component	Stream	Typology	T_{in} [°C]	T_{out} [°C]	Thermal power [kW]	Gc_p [kW/K]
Air pre-heater	1	Cold	37.0	450	136.7	0.3310
Flue gas cooler	2	Hot	905	200	273.9	0.3885
Economizer	3	Cold	20	180	42.83	0.2677
Steam generator	4	Cold	190	191	121.3	121.3
Steam superheater	5	Cold	173	450	32.28	0.1165
Intercooler	6	Hot	252	35	67.68	0.3119
FTS reactor cooler	7	Hot	210	209	296.7	296.7
FTS products cooler	8	Hot	210	35	117.9	0.6737
Flash tank MT	9	Cold	199	200	11.87	11.87
Flash tank HT	10	Cold	319	320	7.640	7.640
Light products cooler	11	Hot	200	35	4.951	0.03001
Middle products cooler	12	Hot	320	35	8.360	0.02933
Heavy products cooler	13	Hot	320	35	5.776	0.02027
TG discharge cooler	14	Hot	616	100	708.0	1.372

Heat required at high temperature: 0 kW

Cool required at low temperature: 1.131 kW

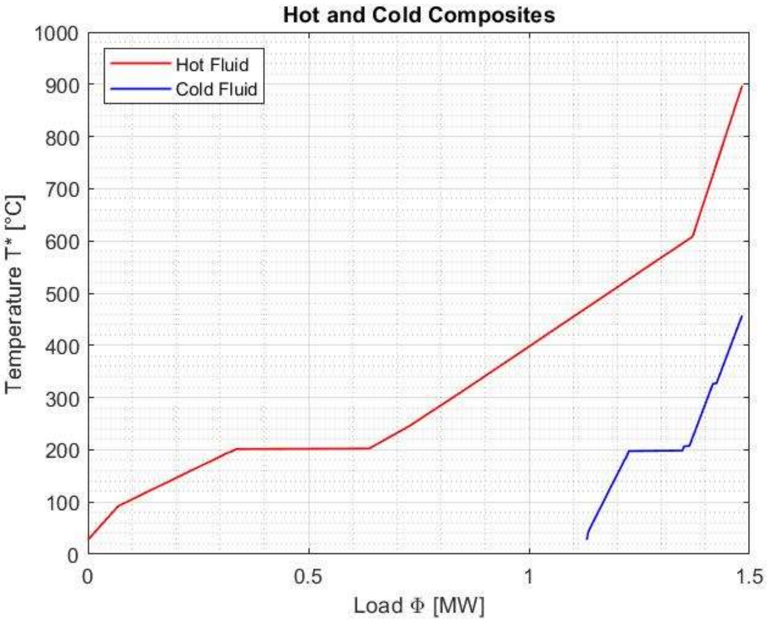

FIGURE 44 - COMPOSITE CURVE FOR CASE A WITH PINE WOOD

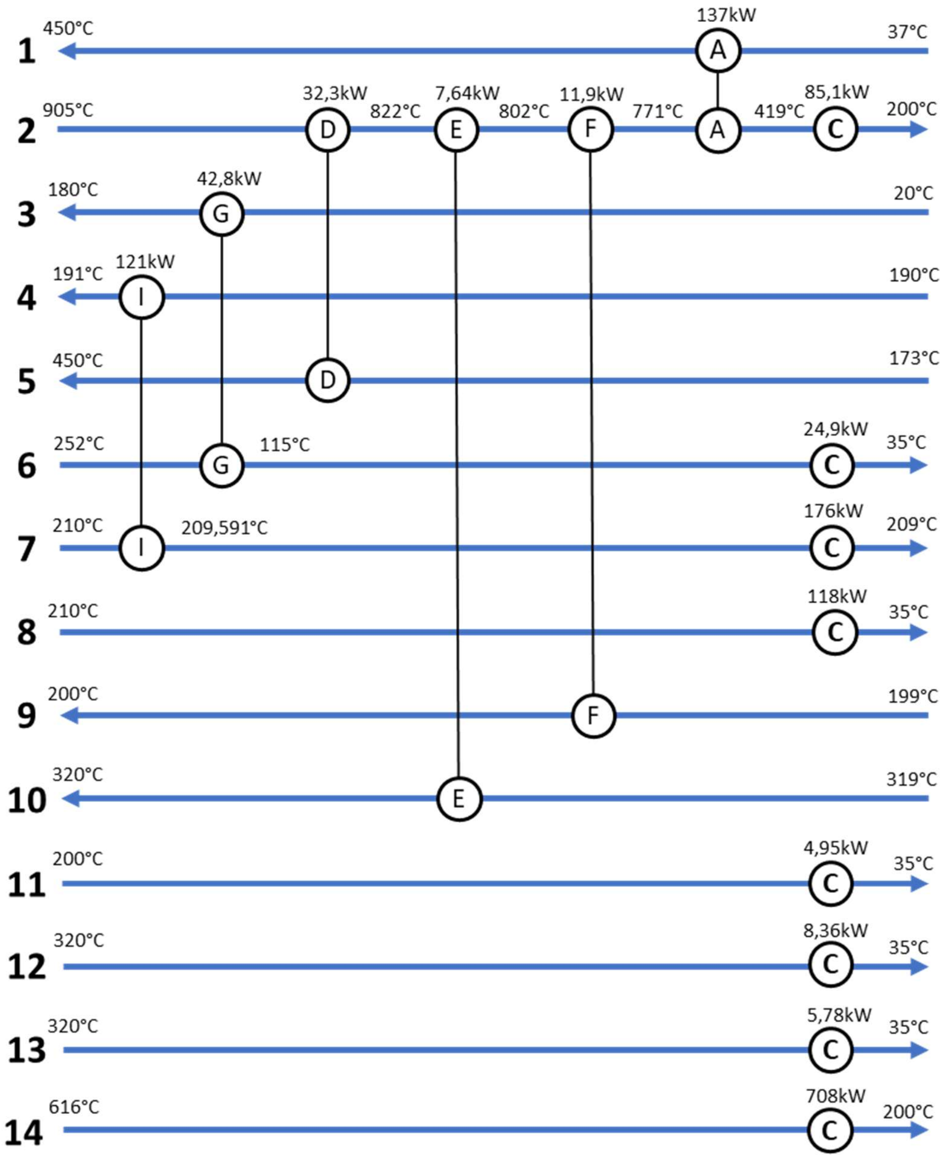

FIGURE 45 - HEAT EXCHANGERS SCHEME - CASE A WITH PINE WOOD

8.2.2 Case B

Table 29 - Streams for case B with pine wood

Component	Stream	Typology	T_{in} [°C]	T_{out} [°C]	Thermal power [kW]	Gc_p [kW/K]
Air pre-heater	1	Cold	37.0	450	167.0	0.4044
Flue gas cooler	2	Hot	955	200	360.0	0.4768
Economizer	3	Cold	20	180	39.91	0.2494
Steam generator	4	Cold	190	191	113.0	113.0
Steam superheater	5	Cold	173	450	30.08	0.1086
Intercooler	6	Hot	261	35	70.65	0.3126
FTS reactor cooler	7	Hot	210	209	369.9	369.9
FTS products cooler	8	Hot	210	35	138.4	0.7909
Flash tank MT	9	Cold	199	200	15.45	15.45
Flash tank HT	10	Cold	319	320	9.134	9.134
Light products cooler	11	Hot	200	35	7.072	0.04286
Middle products cooler	12	Hot	320	35	9.685	0.03398
Heavy products cooler	13	Hot	320	35	7.291	0.02558
TG discharge cooler	14	Hot	618	100	400.6	0.7734

Heat required at high temperature: 0 kW

Cool required at low temperature: 989.0 kW

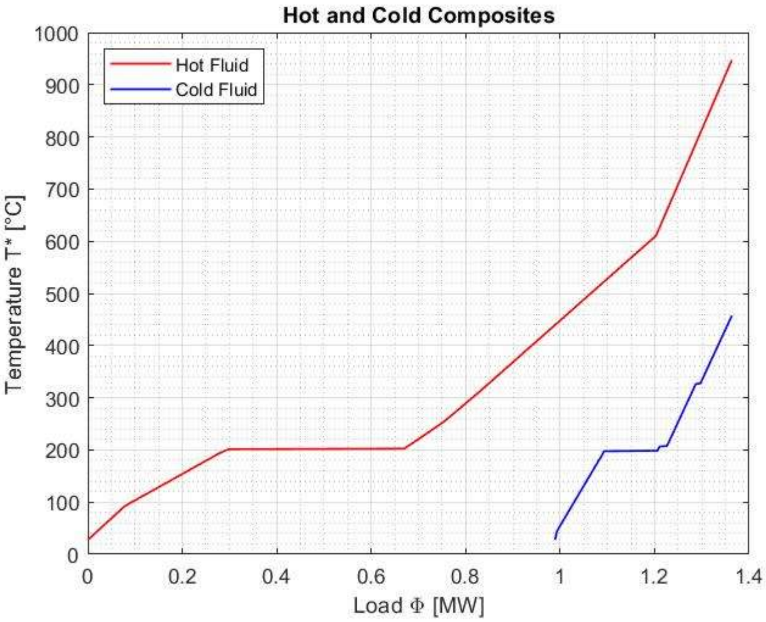

Figure 46 - Composite curve for case B with pine wood

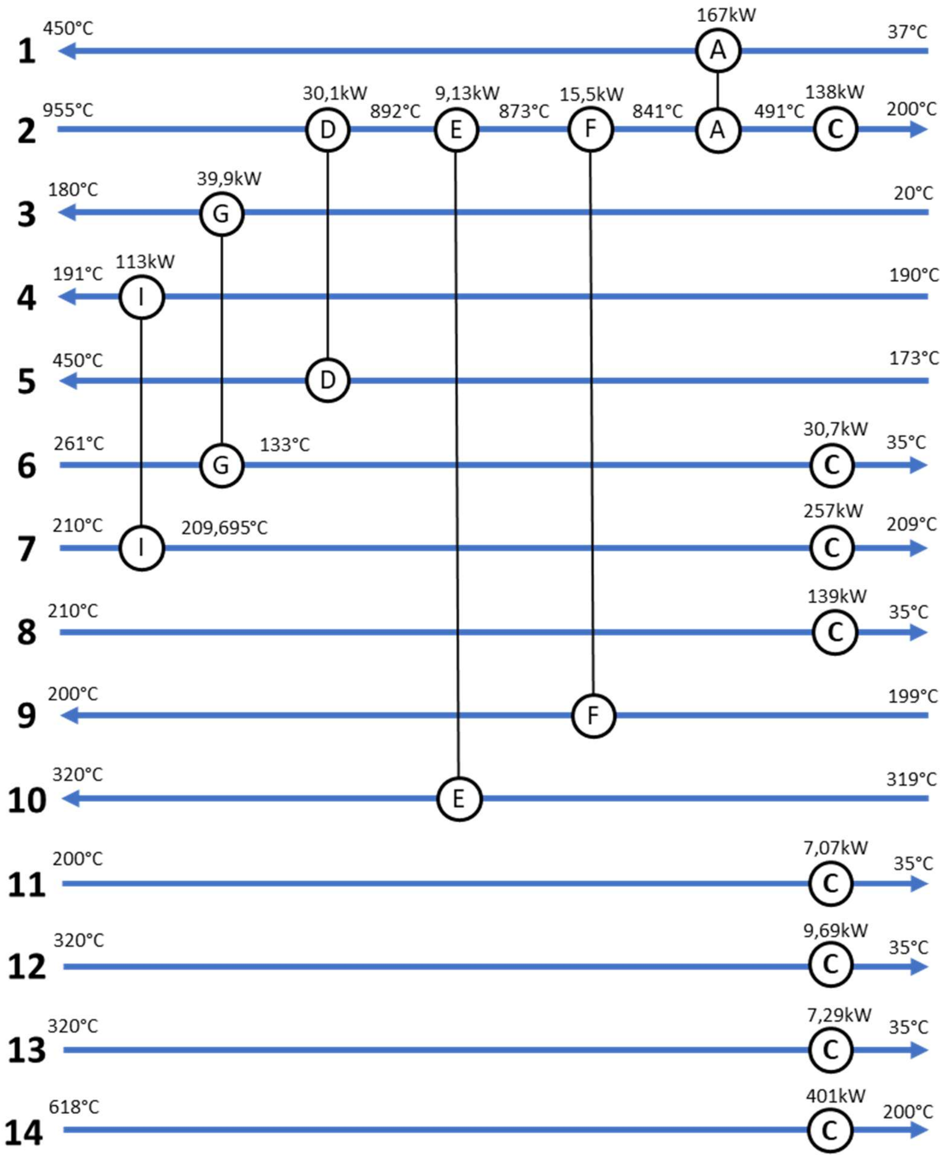

FIGURE 47 - HEAT EXCHANGERS SCHEME - CASE B WITH PINE WOOD

8.2.3 Case C

TABLE 30 - STREAMS FOR CASE C WITH PINE WOOD

Component	Stream	Typology	T_{in} [°C]	T_{out} [°C]	Thermal power [kW]	Gc_p [kW/K]
Air pre-heater	1	Cold	37.0	450	201.3	0.4874
Flue gas cooler	2	Hot	955	200	442.2	0.5857
Economizer	3	Cold	20	180	39.10	0.2444
Steam generator	4	Cold	190	191	110.7	110.7
Steam superheater	5	Cold	173	450	29.46	0.1064
Intercooler	6	Hot	263	35	89.53	0.3927
FTS reactor cooler	7	Hot	210	209	476.7	476.7
FTS products cooler	8	Hot	210	35	180.1	1.029
Flash tank MT	9	Cold	199	200	19.75	19.75
Flash tank HT	10	Cold	319	320	11.88	11.88
Light products cooler	11	Hot	200	35	8.890	0.05388
Middle products cooler	12	Hot	320	35	12.66	0.04442
Heavy products cooler	13	Hot	320	35	9.389	0.03294

Heat required at high temperature: 0 kW

Cool required at low temperature: 807.3 kW

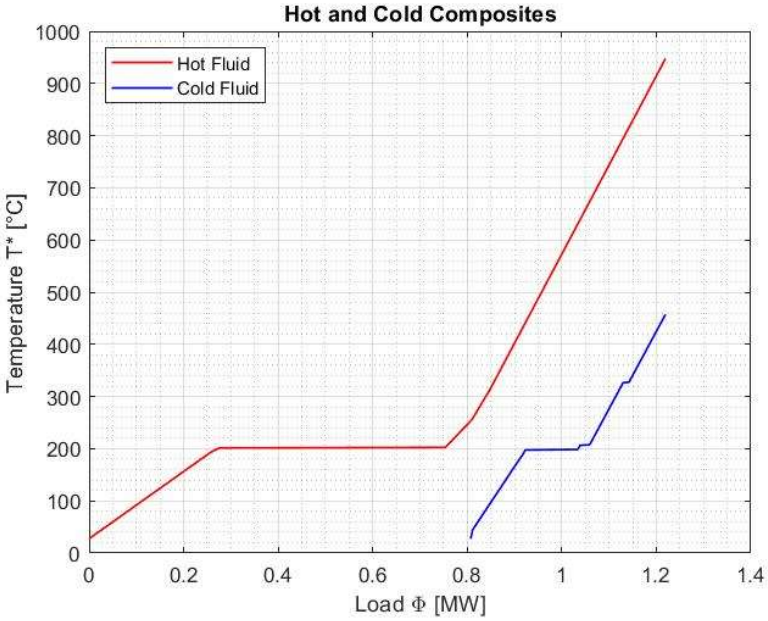

FIGURE 48 - COMPOSITE CURVE FOR CASE C WITH PINE WOOD

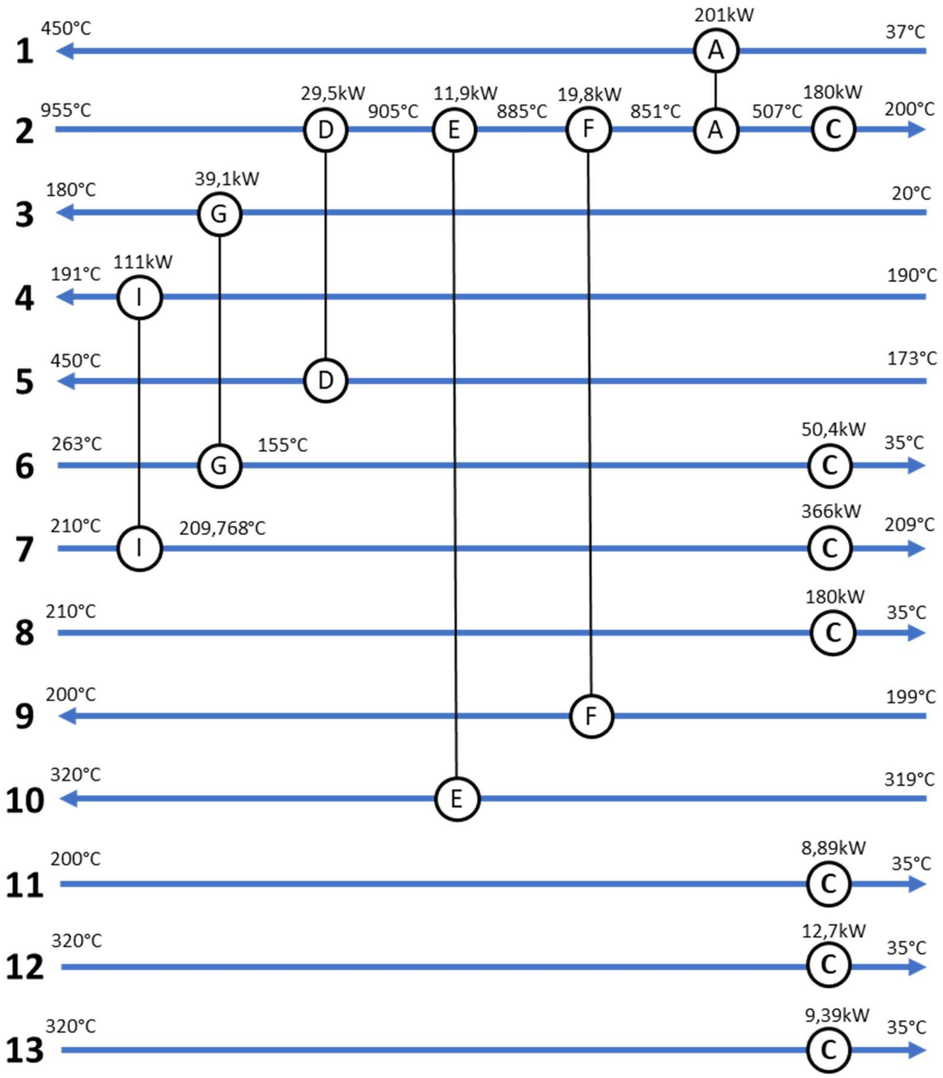

FIGURE 49 - HEAT EXCHANGERS SCHEME - CASE C WITH PINE WOOD

8.2.4 Case C with steam production

The production of steam is 875.2 kg/h. The case is similar to the one analyzed with the digestate. The only difference is the absence of a cooler in on the steam 8. Since the plant is the same for digestate and woody biomass, the cooler is supposed to be used in both cases. This is useful also for a simpler management of the plant.

TABLE 31 - STREAMS FOR CASE C WITH PINE WOOD AND STEAM PRODUCTION

Component	Stream	Typology	T_{in} [°C]	T_{out} [°C]	Thermal power [kW]	Gc_p [kW/K]
Air pre-heater	1	Cold	37.0	450	201.3	0.4874
Flue gas cooler	2	Hot	955	200	442.2	0.5857
Economizer	3	Cold	20	180	39.10	0.2444
Steam generator	4	Cold	190	191	110.7	110.7
Steam superheater	5	Cold	173	450	29.46	0.1064
Intercooler	6	Hot	263	35	89.53	0.3927
FTS reactor cooler	7	Hot	210	209	476.7	476.7
FTS products cooler	8	Hot	210	35	180.1	1.029
Flash tank MT	9	Cold	199	200	19.75	19.75
Flash tank HT	10	Cold	319	320	11.88	11.88
Light products cooler	11	Hot	200	35	8.890	0.05388
Middle products cooler	12	Hot	320	35	12.66	0.04442
Heavy products cooler	13	Hot	320	35	9.389	0.03294
Economizer 2	14	Cold	20	180	180.1	1.126
Steam generator 2	15	Cold	190	191	509.9	509.9

Heat required at high temperature: 0 kW

Cool required at low temperature: 117.3 kW

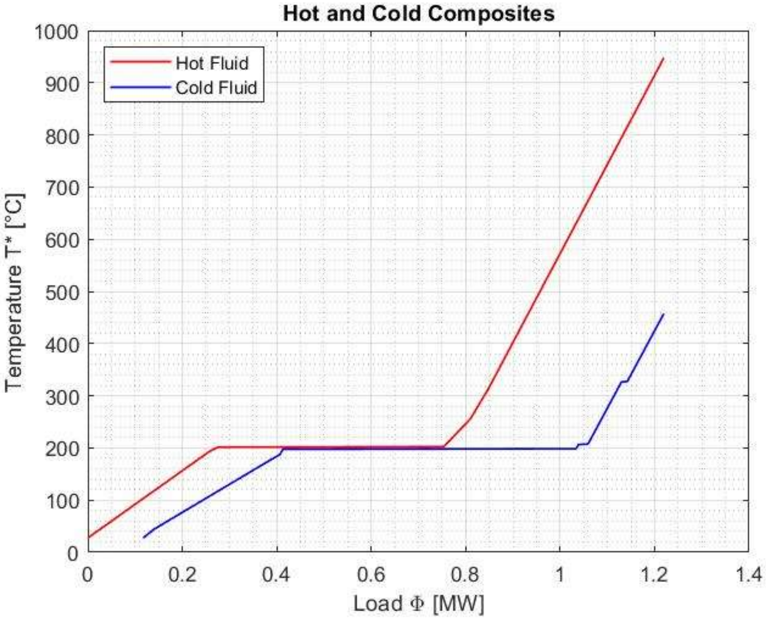

FIGURE 50 - COMPOSITE CURVE FOR CASE C WITH PINE WOOD AND STEAM PRODUCTION

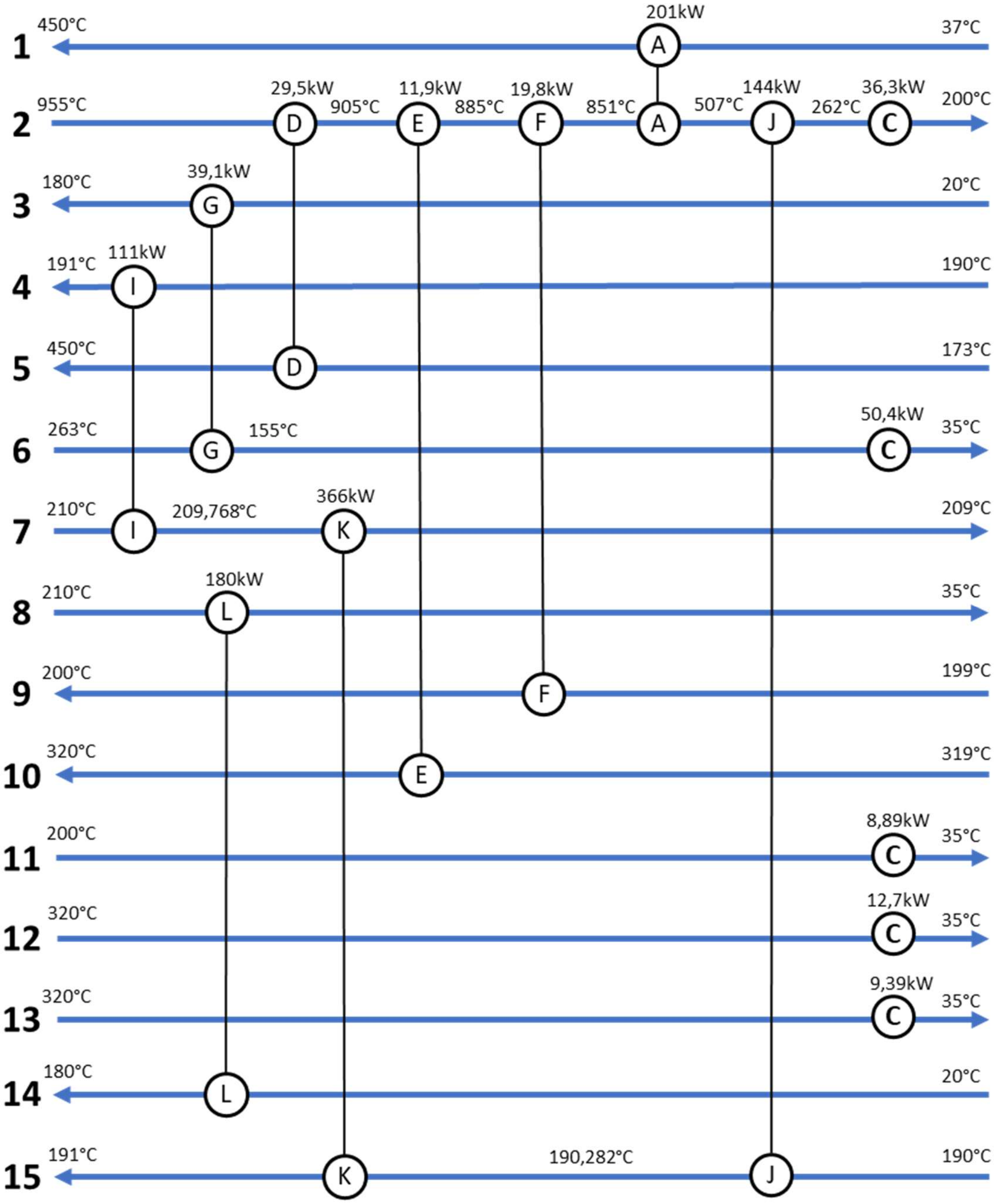

FIGURE 51 - HEAT EXCHANGERS SCHEME - CASE C WITH PINE WOOD AND STEAM PRODUCTION

8.3 Comments

The configuration of the thermal exchange grid is the same for the digestate and wood, unless for the cases 4 with steam production.

In all the cases where the gas turbine is present, the heat from flue gases is not used. So, it is possible to avoid a heat recovery unit. The exhausts are clean, since the fuel is gaseous and there is no sulfur nor nitrogen compounds. In addition, the temperatures reached in the combustor are low and it is possible to neglect nitrogen oxides formation. So, the cleaning system can be avoided and the flue gases can be vented in the atmosphere.

It is possible to consider the use of an internal combustion engine in substitution of the gas turbine: for small power it can have better performance and lower cost, moreover it is a very mature technology and available for every size of power, from flew kilowatts to several megawatts. Although, it cannot produce high-temperature heat, but with a CHP system it is possible to recover low-temperature heat to feed a district heating and/or for the digester needs.

Lastly, the stream 2 has to be cooled down because the flue gases are produced by a combustion of a solid containing sulfur and ash, so several pollutants can be found on the stack. The aim of this work is not to perform an analysis on the flue gas produced by a DFBG. So, since it was supposed that the char are made of 100% of carbon and ash, only a bag filter is necessary to respect the regulation on pollutants emission (sulfur and nitrogen compounds are considered negligible in the flue gas). Anyways, the possible condensation of the humidity present in the flue gases has to be avoided. So, the flue gases are cooled down just up to reach temperatures compatible with the working ones of the bag filters (200°C is supposed a good temperature for a polytetrafluorethylene filter).

8.3.1 Thermal recovery comparison

The heat wasted, that is not recovered, is not influenced by the type of feeding (digestate or pine wood). The cases C have the lower loss and this surely affects the global efficiency. *Figure 52* **– Cooling request in all the cases analyzed** shows in all the cases analyzed the fraction of the thermal power that is lost in heat exchanger. It is not taken into account the possible electric energy needed for the power balance[1].

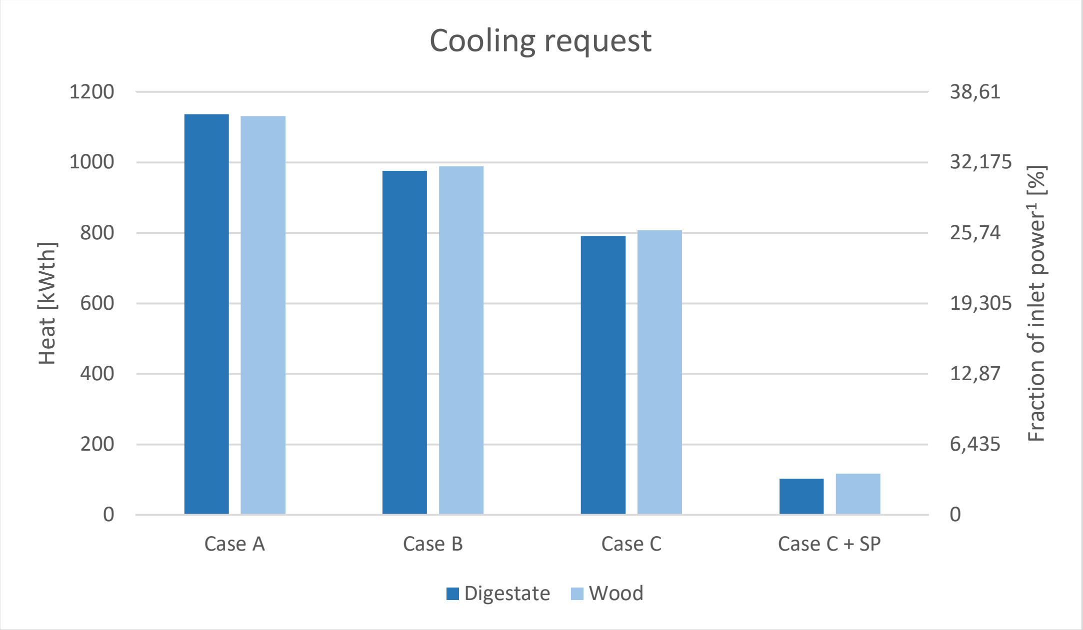

FIGURE 52 – COOLING REQUEST IN ALL THE CASES ANALYZED

Part III

9. Results

Before to show the results, it is necessary to fix some parameters in order to have systems working in the same conditions. The gasification temperature, the recirculation fraction of the off-gas and the ratio H_2/CO are kept constant varying the quantity of steam injected in the gasifier (S/B ratio). This latter value cannot be exact the same for each simulation and it requests a tolerance. For the program, it is fixed at 1% of the objective value (e.g. if H_2/CO=2, the tolerance is 0.02).

The syncrude production, together with its cuts, is an important parameter to understand the performance of the plant. In the Table 32 **- Final results for digestate gasification** and Table 33 **- Final results for woody biomass gasification**, these are reported together with the efficiencies, the electric power produced or demanded and the carbon dioxide emissions.

Lastly, the specific carbon dioxide emissions are done considering only the syncrude production, so no CO_2 is attributed to the electric energy consumed by the plant.

9.1 Useful formulae

Below, a brief recap on the formulae used in the results presentation is reported. First of all, the (26) and (27) show the syncrude production and the global efficiency. If the production of electric energy is zero, the two values are equal.

$$\eta_{syncrude} = \frac{LHV_{syncrude}\dot{m}_{syncrude}}{LHV_{biomass}\dot{m}_{biomass} + P_{el,bought}} \tag{26}$$

$$\eta_{glob} = \frac{LHV_{syncrude}\dot{m}_{syncrude} + P_{el,produced}}{LHV_{biomass}\dot{m}_{biomass} + P_{el,bought}} \tag{27}$$

Where $P_{el,produced}$ is the electric power produced by the plant, while $P_{el,bough}$ is the demand of external power.

For the calculation of the syncrude LHV, the paper of Stempien et al. [121] has been taken as reference. The LHV of paraffins and olefins are calculated separately.

$$LHV_{paraffins,m} = \sum_n \left[(608.44n + 213.31)x_{n,paraf}\right] \tag{28}$$

$$LHV_{olefins,m} = \sum_n \left[(604.93n + 113.83)x_{n,olef}\right] \tag{29}$$

Where *n* is the number of carbon atoms in the molecule and x_n is the molar yield in the syncrude. The LHVs reported are on molar basis, to transform these into mass basis, it is enough to multiply by the average molar weight of the syncrude molecues:

$$LHV_{paraffins}\left[{}^{MJ}/_{kg}\right] = LHV_{paraffins,m}\left[{}^{MJ}/_{mol}\right] \cdot \overline{MM}_{paraf} \tag{30}$$

$$\overline{MM}_{paraf} = \sum_n \left(x_{n,paraf} \cdot MM_n\right) \tag{31}$$

For olefins is analogous. Finally:

$$LHV_{syncrude} = LHV_{paraffins} + LHV_{olefins} \quad \textbf{(32)}$$

It has to be specified that the LHV of paraffins and olefins is on the total mass. So, if the fraction of the olefins is very small, also the $LHV_{olefins}$ found with these formulae is small.

9.2 Digestate

TABLE 32 - FINAL RESULTS FOR DIGESTATE GASIFICATION

Parameter	Case A	Case B	Case C	Case C + SP
T_g [°C]	850	900	900	900
Recirculation [-]	0.800	0.900	0.900	0.900
H_2/CO [-]	2.0	2.0	2.0	2.0
S/B [-]	0.442	0.436	0.430	0.430
Syncrude [kg/h]	92.4	117	148	148
Nafta [kg/h]	28.0	39.5	47.3	47.3
Middle [kg/h]	33.9	39.3	52.2	52.2
Waxes [kg/h]	30.4	38.2	48.7	48.7
P_{el} [kW]	+ 98.9	- 17.9	- 219	- 219
$\eta_{syncrude}$ [%]	36.3	45.7	54.5	54.5
η_{glob} [%]	39.5	45.7	54.5	70.9[1]
CO_2 emitted [kg/h]	842	764	657	657
CO_2 specific [kg/kg$_{syncrude}$]	9.11	6.53	4.44	4.44

[1] Considering only the heat available in the steam condensation, not for the subcooling of the water. The consumption of the feed pump is negligible.

The syncrude production grows from case A to case C. This happens for two factors: first the internal recirculation of the FTS reactor increases the conversion of hydrogen and carbon monoxide. Second, the gasification temperature optimization increases the syngas quality and quantity, as it is shown in *6.1.3 Validation*. In addition, the recirculation to the gasifier for case C, increases the amount of useful syngas. In the better case, about the 15% of the digestate gross weight is converted into syncrude.

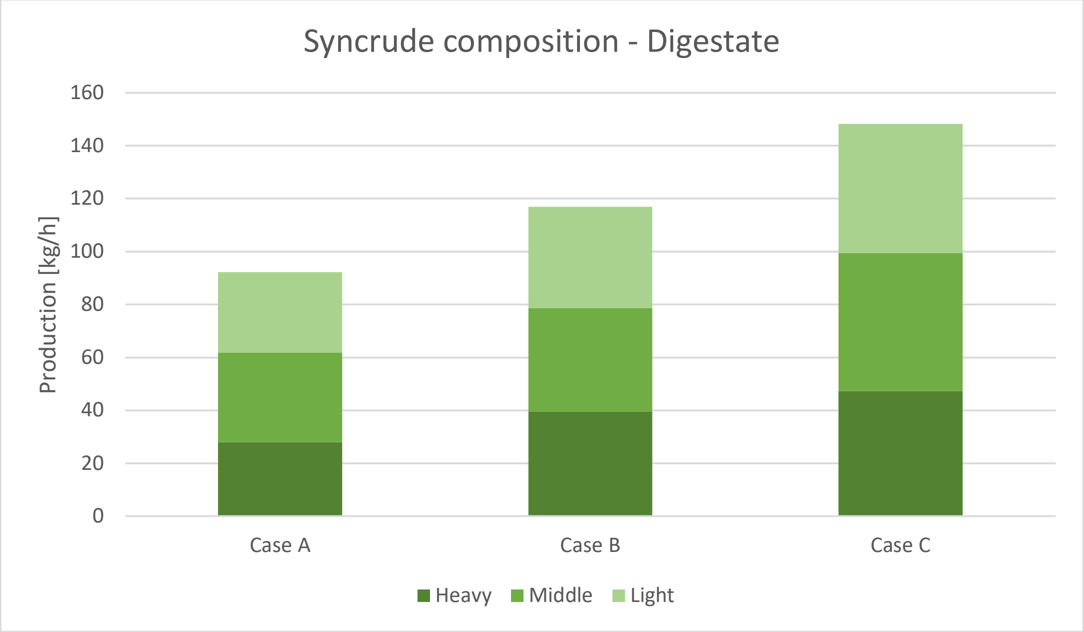

FIGURE 53 - SYNCRUDE COMPOSITION AND PRODUCTION FOR DIGESTATE GASIFICATION

9.3 Woody biomass

TABLE 33 - FINAL RESULTS FOR WOODY BIOMASS GASIFICATION

Parameter	Case A	Case B	Case C	Case C + SP
T_g [°C]	850	900	900	900
Recirculation [-]	0.800	0.900	0.900	0.900
H_2/CO [-]	2.0	2.0	2.0	2.0
S/B [-]	0.605	0.581	0.574	0.574
Syncrude [kg/h]	84.6	108	139	139
Nafta [kg/h]	25.9	37.0	46.5	46.5
Middle [kg/h]	30.8	35.7	46.7	46.7
Waxes [kg/h]	27.9	35.2	45.3	45.3
P_{el} [kW]	95.6	- 15.7	- 194	- 194
$\eta_{syncrude}$ [%]	33.2	42.2	51.3	51.3
η_{glob} [%]	36.3	42.2	51.3	67.7[1]
CO_2 emitted [kg/h]	830	757	653	653
CO_2 specific [$kg/kg_{syncrude}$]	9.81	7.01	4.69	4.69

[1] Considering only the heat available in the steam condensation, not for the subcooling of the water. The consumption of the feed pump is neglected.

The results are similar to the case with digestate gasification: the case A has the lower production while the case C is the best.

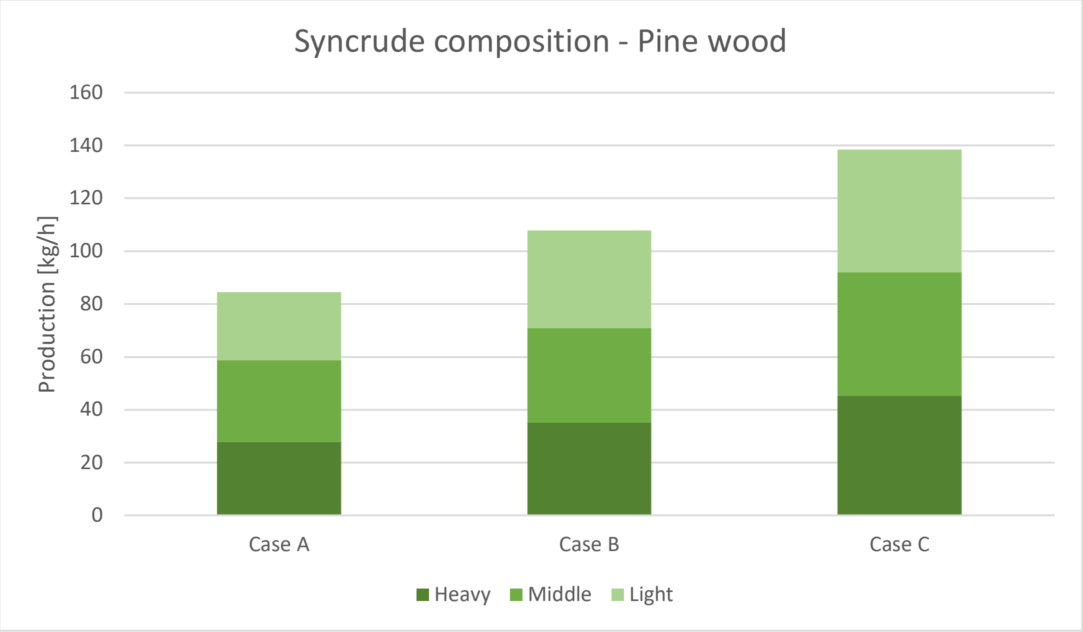

FIGURE 54 - SYNCRUDE COMPOSITION AND PRODUCTION FOR WOODY BIOMASS GASIFICATION

9.4 Discussion

The syncrude production using digestate or pine wood as feedstock biomass, is quite similar for both cases. The high amount of ash in the digestate does not affect the production as the biomass humidity does. As anticipated, the digestate used in this work has a humidity of 10%, respect to the 20% of the pine wood considered. The paper of Doherty et al. [23] shows how the water content in the biomass affects the efficiency and the productivity.

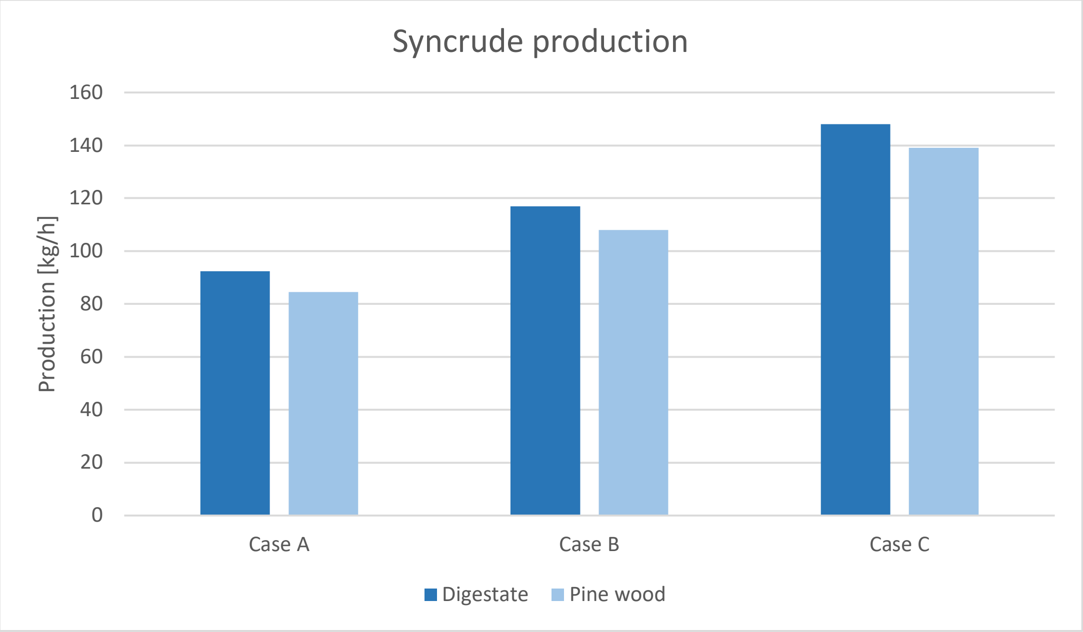

FIGURE 55 - SYNCRUDE PRODUCTION COMPARISON

To better understand the effect of the humidity on the syncrude production and on the efficiency, a sensitivity analysis on the as received biomass water content is performed. With the water content growth, the production drops down quickly: using a biomass with a moisture content of 10% or 20% the production decrease of about 15% (data extracted from the case B fed with digestate).

Considering the ideal case, where the biomass is completely dried, whole the water, needed to hold the H_2/CO ratio constant at 2, enters the gasifier as steam and at relatively high temperature. However, if a big part of the water enters together with the biomass (e.g. 30% of moisture), it requests large amount of energy to evaporate. This energy comes from the char combustion instead coming from the thermal recovery, so the efficiency drops down.

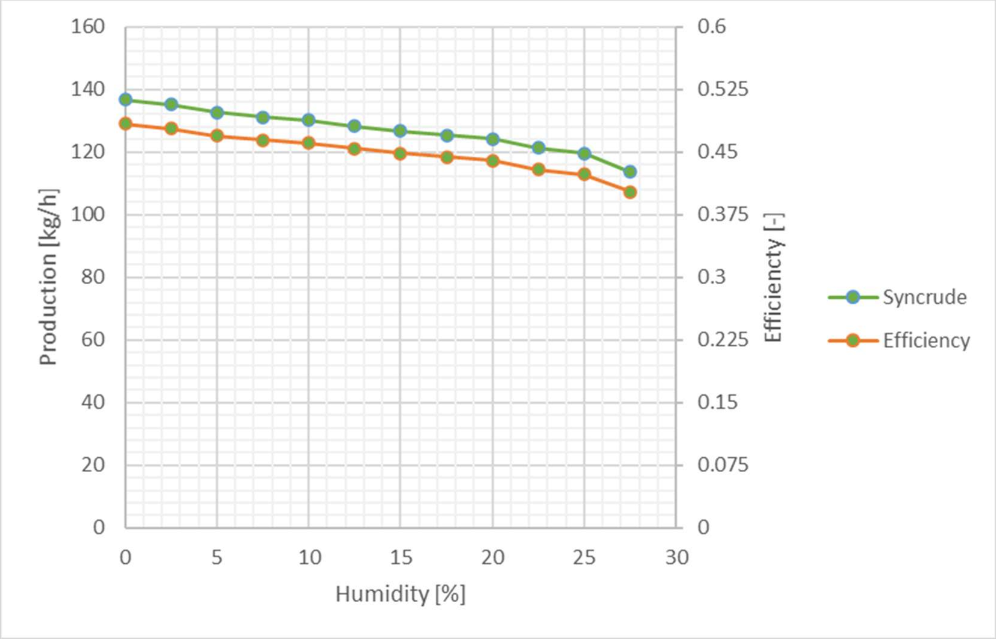

FIGURE 56 - SENSITIVITY ANALYSIS ON THE WATER CONTENT OF THE DIGESTATE IN THE CASE B

The emissions of carbon dioxide have an inverse behavior with respect to the syncrude production. The reduction from the case A to the case B is due to the higher temperature of T_g, it increases the CO yield instead the CO_2, as it is shown in the sensitivity analysis in *6.1.3 Validation*. In case C, the recirculation of the hydrocarbons to the gasifier leads to lower emission. Another effect is the increasing in the syncrude production, provides a reduction of the specific emissions by fixation of more CO_2 material in the syncrude and lower afterburn material to the combustor/power generation unit.

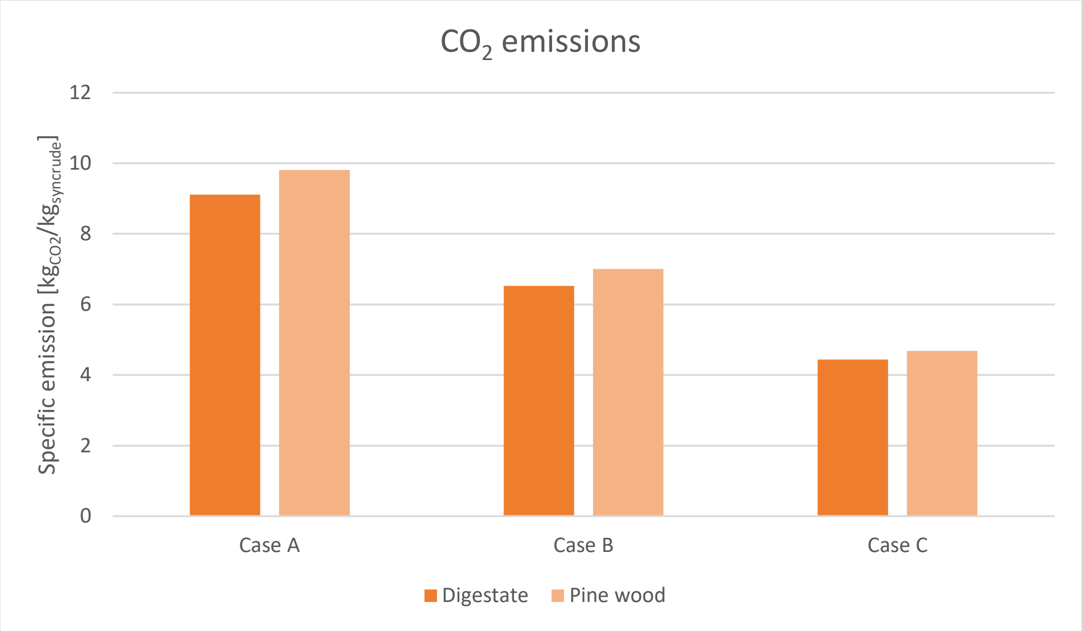

FIGURE 57 - CO_2 EMISSION COMPARISON

Supposing that the carbon dioxide removed from the syngas is stored in a geological deposit or converted in some useful products, the emission of the plant is lower than what are reported above.

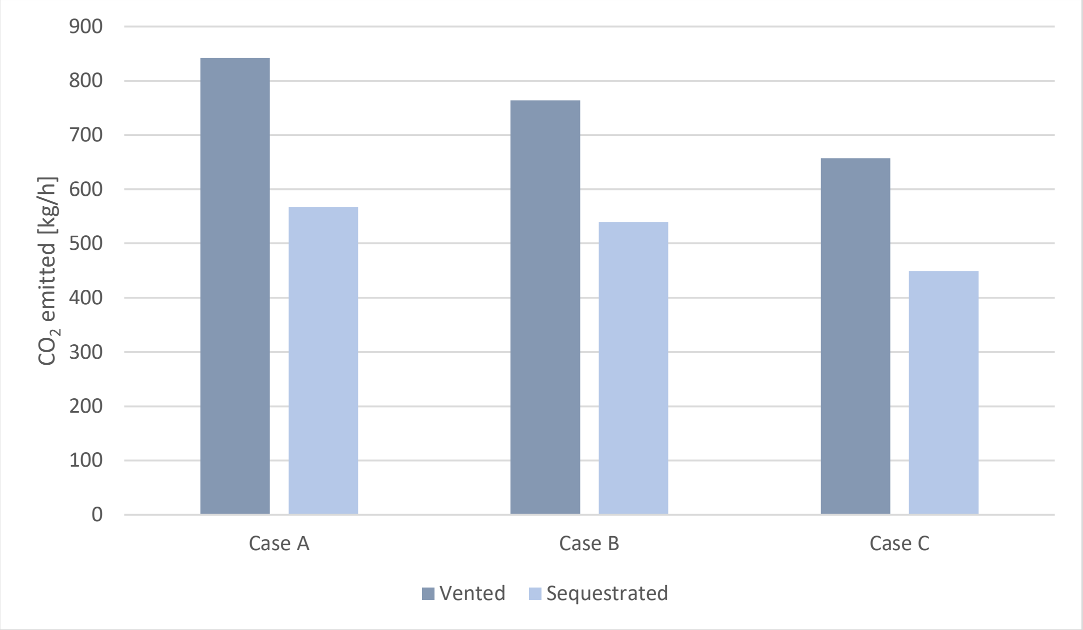

FIGURE 58 - CARBON DIOXIDE EMISSION WITH PSA STREAM VENTED AND GEOLOGICAL STORED

9.5 Mass balance

Aspen Plus provides a mass balance analysis: a summary is reported anyway in *Table 34* **- Mass balance** and *Table 35* **- Mass balance summary table - pine wood**, which show the main inlet and outlet flows. To a better understand the stream of each item, the following figures reporting only the name of the important ones.

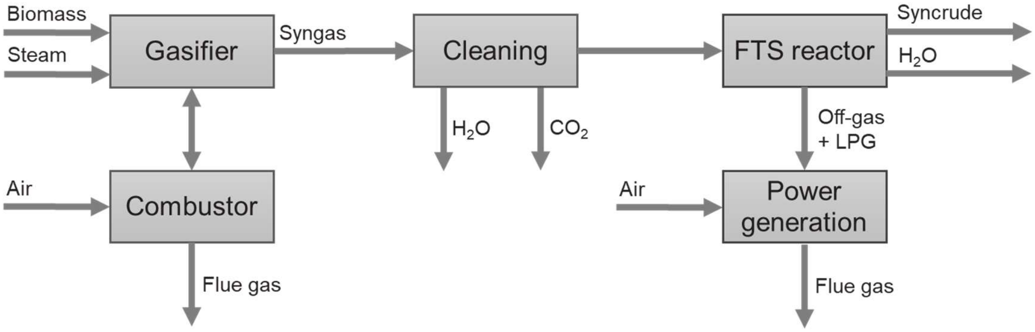

FIGURE 59 - CASE A AND B - MASS BALANCE

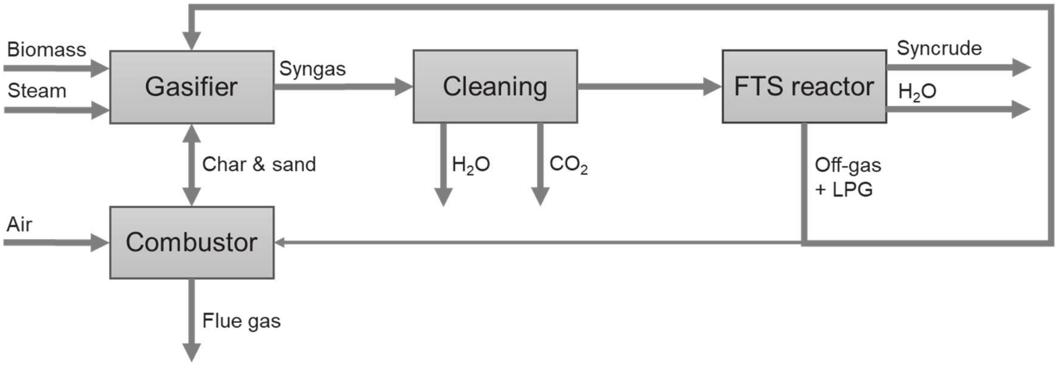

FIGURE 60 - CASE C - MASS BALANCE

TABLE 34 - MASS BALANCE SUMMARY TABLE - DIGESTATE

Stream	Way	Case A [kg/h]	Case B [kg/h]	Case C [kg/h]
Biomass a.r.	In	979	979	979
Water inlet	In	291	286	281
Air combustor	In	1060	1330	1640
Air GT	In	4650	2600	-
Flue gas combustor	Out	1150	1430	1790
Flue gas GT	Out	4800	2700	-
Syngas from gasifier	Out	917	892	1040
Off-gas + LPG	Out	151	106	210
Syncrude	Out	92.4	117	148
FTS water	Out	139	172	221
Cleaning water balance	Out	240	252	229
PSA CO_2 outlet	Out	274	224	208
Global water balance	-	**+ 87.6**	**+ 138**	**+ 169**

TABLE 35 - MASS BALANCE SUMMARY TABLE - PINE WOOD

Stream	Way	Case A [kg/h]	Case B [kg/h]	Case C [kg/h]
Biomass a.r.	In	733	733	733
Water inlet	In	208	194	190
Air combustor	In	1140	1390	1680
Air GT	In	4327	2426	-
Flue gas combustor	Out	1230	1510	1820
Flue gas GT	Out	4451	2507	-
Syngas from gasifier	Out	856	823	899
Off-gas + LPG	Out	124	81.3	116
Syncrude	Out	84.6	108	139
FTS water	Out	127	158	204
Cleaning water balance	Out	261	263	238
PSA CO_2 outlet	Out	258	210	198
Global water balance	-	**+ 180**	**+ 227**	**+ 253**

The water balance is always positive, so the plant produces more water than what it needs for the gasification and the syngas conditioning.

9.6 Energy balance

A thermal balance was already performed in *Pinch analysis*. In this section, the electric energy balance is reported.

TABLE 36 - ENERGY BALANCE - DIGESTATE

Stream/component	Way	Case A [kW]	Case B [kW]	Case C [kW]
Air blower	In	5.34	6.66	8.23
Water pump	In	0.12	0.12	0.12
LP compressor	In	76.6	79.9	105
HP compressor	In	50.2	54.5	74.5
PSA system	In	41.1	33.6	31.2
Gas turbine	Out	272	157	-
Balance	-	**98.6**	**- 17.8**	**- 219**

TABLE 37 - ENERGY BALANCE - PINE WOOD

Stream/component	Way	Case A [kW]	Case B [kW]	Case C [kW]
Air blower	In	5.73	7.00	8.43
Water pump	In	0.09	0.08	0.08
LP compressor	In	69.3	72.5	91.6
HP compressor	In	45.2	49.2	64.7
PSA system	In	38.7	31.5	29.7
Gas turbine	Out	254	144	-
Balance	-	**95.0**	**- 16.3**	**- 194**

9.7 Carbon efficiency

A carbon balance is performed in order to understand the plant ability to convert it into products. The streams that contain carbon are: the PSA, the GT and the gasifier discharge plus the input biomass stream. The residual carbon contained in the ash and water discharged is negligible.

TABLE 38 - CARBON EFFICIENCY - DIGESTATE

Carbon stream from	Case A	Case B	Case C
Biomass [mol/s]	7.17	7.17	7.17
PSA discharge [mol/s]	- 1.73	- 1.42	- 1.36
GT discharge [mol/s]	- 1.63	- 0.966	- 0.723
Combustor [mol/s]	- 1.95	- 2.44	- 2.58
Carbon efficiency	**25.9%**	**32.7%**	**35.0%**

TABLE 39 - CARBON EFFICIENCY - PINE WOOD

Stream	Case A	Case B	Case C
Biomass [mol/s]	6.94	6.94	6.94
PSA discharge [mol/s]	- 1.63	- 1.33	- 1.28
GT discharge [mol/s]	- 1.52	- 0.894	- 0.660
Gasifier discharge [mol/s]	- 2.10	- 2.56	- 2.66
Carbon efficiency	**24.4%**	**31.1%**	**33.7%**

As expected, the carbon conversion efficiencies reflect the thermal ones: the cases C has the highest value. These results are consistent with respect to Hillestad et al. [3].

10. Economic assessment

The economic analysis allows the quantification of the initial expenditure for the commissioning and the costs for the plant operation. The aim of this section is to get the final levelized cost of the products in order to compare it with the market value. If the costs are equal or lower, the plant is sustainable; if the costs are higher, the plant needs some statal incentives to work or it needs to find some way to decrease the costs. At the end, it is possible to select the best of the four configurations keeping into account not only the efficiency but also the economic performances.

10.1 Capital investment

Capital investment is the total amount of money that it is necessary to pay to physical realize the plant. Inside this value there are several factors:

- Total equipment cost of purchase and installation
- Cost of the land
- Site preparation cost
- Cost of building, contingency and plant engineering
- Project development and licenses cost
- Commissioning cost

$$C_{inv} = \left[\sum_i C_{PI,i}\right] \cdot \left(1 + f_{land} + f_{site} + f_{building}\right) \cdot \left(1 + f_{cont} + f_{eng}\right) \cdot \left(1 + f_{dev} + f_{com}\right) \qquad \textbf{(33)}$$

Where:

$$C_{PI} = C_{P_b I_b} \cdot \frac{I}{I_b} \qquad \textbf{(34)}$$

See the *Table 40* **- Factors for CAPEX estimation** for the reference of each factor.

Table 40 - Factors for CAPEX estimation

Symbol	Name	Value [3]
C_{PI}	Cost of purchase and installation	-
f_{land}	Cost of the land	0.2
f_{site}	Site preparation cost	0.1
$f_{building}$	Cost of building	0.1
f_{cont}	Cost of contingency	0.2
f_{eng}	Cost of engineering	0.1
f_{dev}	Project development and licenses cost	0.03
f_{com}	Commissioning cost	0.1

I and I_b are the CEPCI index (Chemical Engineering Plant Cost Index). This is a dimensionless number used to update the capital cost of an equipment at a certain year, keeping into account inflation and deflation. In particular, I_b is the CEPCI index at the reference year while the I at the current one.

10.2 Operating cost

$$C_{TOC} = C_F + C_{op,d} + C_{op,i} + C_{maint} \tag{35}$$

Where: (see *Table 41* - **Factors for OPEX cost estimation**)

TABLE 41 - FACTORS FOR OPEX COST ESTIMATION

Symbol	Name
C_{TOC}	Total operating cost
C_F	Cost of feedstock supply
$C_{op,d}$	Variable direct operational cost dependent on the annual processing feedstock
$C_{op,i}$	Fixed indirect cost for having a plant in activity
C_{maint}	Maintenance costs

$$C_F = \frac{M_F}{\rho_F} \cdot t_{prod} \cdot \left(c_{pr} + c_{tr,f} + L c_{tr,L}\right) \tag{36}$$

With:

$$L = 2\sqrt{\frac{M_F \cdot t_{prod}}{m_{F,S}}} \tag{37}$$

Where: (see *Table 42* **- Factors for transport cost estimation**)

TABLE 42 - FACTORS FOR TRANSPORT COST ESTIMATION

Symbol	Name
M_F	Feedstock mass flow rate
ρ_F	Feedstock density
t_{prod}	Annual production time
c_{pr}	Feedstock production cost (per volume unit)
$c_{tr,f}$	Fixed transport cost (per volume unit)
$c_{tr,L}$	Distance-dependent transport cost (per volume unit)
L	Transport distance
$m_{F,S}$	Feedstock availability for unit area

10.3 Costs estimation

The costs estimations of the equipment are found in other works. The more recent data has been preferred in order to have a more precisely framework of the today situation. The whole analysis is shown once for the case A with digestate, while, for all the other cases, just the most significant data are summarized in the tables.

10.3.1 Preliminary observations and hypothesis

A list of preliminary observations has to be done in order to clarify the next treatise.

1. All the costs are referred to 2019 due to the necessity to use the average yearly CEPCI that it is not already available for 2020.
2. The HRSG on the GT discharge is not considered in the economic analysis where it is not necessary (always except the case C with steam production).
3. The costs of disposal of the fluidized bed material are neglected.
4. The biomass is assumed ready-to-use, so no other equipment is required to the drying and/or the pelletizing.
5. The costs of disposal/sell of the Na_2S is neglected.
6. The plant is supposed to buy the whole fresh water and discharge completely the condensate.
7. To calculate the NaOH consumption, a 10% of excess is considered.
8. The digestate does not request transportation because it is produced on site.
9. Operating hours in one year: 7800h [3].
10. 100% of equity is employed.
11. Lifetime of the plant is 25 years [3].
12. The costs related to the cooling fluids (water and/or air) are neglected.
13. Costs of land and site are not included because a plant for the biogas production is supposed to already exist, so it is not necessary to purchase and prepared the site.
14. The FTS catalyst is substituted every 3 years and it costs 1% of the total investment cost [122].

Some values are reported on foreign currency, so since the conversion is variable, the conversion factors are fixed and showed in the *Table 43* **- Foreign currency conversion**.

TABLE 43 - FOREIGN CURRENCY CONVERSION

Currency	Conversion
EU/USD	0.8975
EU/SEK	0.1000

To conclude, it is necessary to remember that this analysis of the final costs of production is an estimation. For this reason, the values found are affected by an error of about ±30%.

10.3.2 Case A – Digestate

First, the equipment costs (total equipment purchase cost, TPEC) have to be calculated using the **(34)** then the total CAPEX (also called TIC) using the **(33)**. The results are shown in the *Table 44* **- Equipment cost estimation** and in the *Table 45* **- Costs of the single section**.

TABLE 44 - EQUIPMENT COST ESTIMATION

Equipment	Base cost [k€]	Ref. year	Base size	Unit	Scale factor	Ref.	Final cost [k€$_{2019}$]
FT reactor	20’100	2015	310	MWth	0.7	[1]	426
DFBG	5’800	2010	500	ton/day	0.6	[61]	1’020
LP compressor	490	2014	413	kW	0.68	[112]	164
HP compressor	490	2014	413	kW	0.68	[112]	123
Cyclone syngas	50.0	2014	1	m3/s	0.7	[112]	22.8
Gas turbine	8’470	2014	25	MWe	0.7	[112]	376
Guard bed	20.0	2014	8	m3/s	1	[112]	0.513

Water pump	100	2014	10	m3/s	0.36	[112]	1.54
Wet scrubber	3’000	2008	12	m3/s	0.7	[111]	241
Venturi scrubber	4’090	2002	9	m3/s	0.7	[68]	585
Bag filters	1’900	2002	12.1	m3/s	0.65	[2]	222
Tar cracker	3’600	2002	34.2	m3/s	0.7	[2]	202
PSA	28.0	2007	17.07	kmol/h	0.6	[123]	40.1
HX D	130	2015	150	kW	0.78	[97]	55.0
HX E	130	2015	150	kW	0.78	[97]	14.8
HX F	130	2015	150	kW	0.78	[97]	20.7
HX G	130	2015	150	kW	0.78	[97]	68.3
HX I	130	2015	150	kW	0.78	[97]	155
HX C2	130	2015	150	kW	1.78	[97]	28.4
HX C6	130	2015	150	kW	0.78	[97]	26.7
HX C7	130	2015	150	kW	0.78	[97]	144
HX C8	130	2015	150	kW	0.78	[97]	125
HX C11	130	2015	150	kW	0.78	[97]	10.4
HX C12	130	2015	150	kW	0.78	[97]	15.9
HX C13	130	2015	150	kW	0.78	[97]	11.8

TABLE 45 - COSTS OF THE SINGLE SECTIONS

Section	**Cost [k€]**
Gasifier	1’250
C&C	1’500
FTS	426
Total heat exchangers	676
Other BOP	378
TEPC	**4’104**
TIC	**6'632**

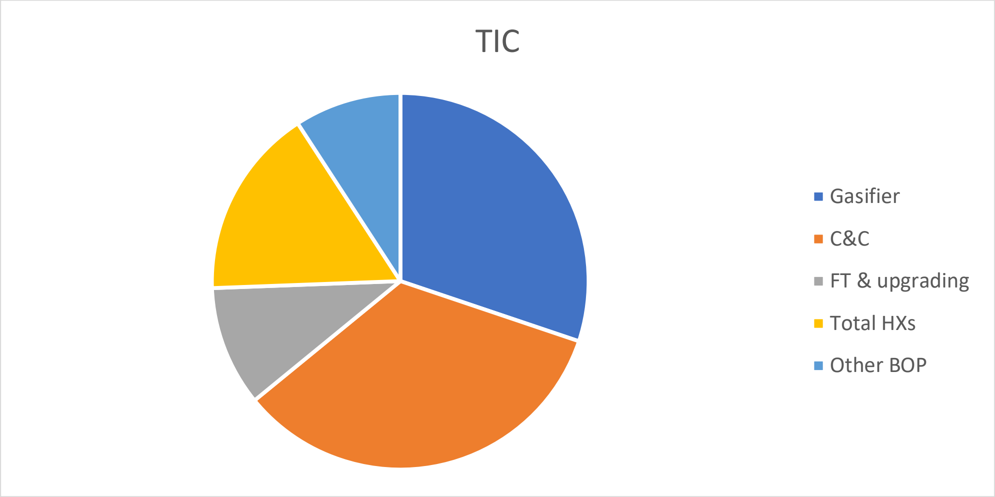

FIGURE 61 - DISTRIBUTION OF THE TIC

The total expenditure is about 6.6 million of euro. It means about 6M€ of investment for 1MWth of FTS syncrude produced. In the *Figure 61* **- Distribution of the TIC**, the impact of the different sections is shown. The gasifier and the syngas cleaning and conditioning sections are the most expensive. A possible way to reduce the global cost is to find a way to remove the sulfur compounds in an alternative mode or together with ammonia and hydrochloric acid avoiding one scrubber. The best option is to remove it in the digester for the biogas production.

To estimate the OPEX, it is necessary to know all the variable costs, such as the cost of ash disposal, the solvent for the sulfur removal or the water consumption. The *Table 46* **- Data from the plant** reports all the interesting steams and parameters. For the olivine consumption, the data from Dutta et al. [61] are employed: it estimates the total amount of the material as 27 times the dry biomass consumed by the plant in 1 hour. Each day (24h), the 7.2% is removed together with the ash and it has to be replaced.

TABLE 46 - DATA FROM THE PLANT

Item	Value	Unit
Feedstock mass flow	0.9789	ton/h
Ash flow	0.2819	ton/h
Electric energy	0.0989	MW
Transport	0.00	km
NaOH consumption	21.1	kg/h
Wastewater	0.379	m3/h
Fresh water	0.291	m3/h
Syncrude production	92.4	kg/h
Naphtha	28.0	kg/h
Diesel	33.9	kg/h
Waxes	30.4	kg/h
Fresh olivine	0.0714	ton/h

In the *Table 47* **– Miscellaneous costs of the plant**, all the items composing the OPEX are reported. The FTS catalyst has to be replaced completely every 3 years and it costs the 1% of the TIC [122].

TABLE 47 – MISCELLANEOUS COSTS OF THE PLANT

Item	Value	Unit	Reference
Cost of biomass	30.0	€/ton	[89]
Ash disposal	35.9	€/ton	[3]
Electric energy (buy)	156[3]	€/MWh	[124]
Electric energy (sold)	136.6[1]	€/MWh	[112]
Cost of transport	0.00	€/ton	
NaOH cost	400	€/ton	[125]
Wastewater	2.50	€/m3	[112]
Fresh water	2.00	€/m3	[112]
Operator (one)	63’443	€/y	
Labor	2%	of TPEC	[3]
Maintenance	2%	of TIC	[3]
Insurance & taxes	2%	of TIC	[3]
Administration & services	1%	of TIC	[3]
Naphtha	0.310	€/l	[3]
Diesel	1.04	€/l	[3]

Waxes	2.00	€/kg	[3]
Average cost of syncrude	1.271[2]	€/kg	
Olivine	155.2	€/ton	[61]
FTS catalyst replacement	1%[4]	of TIC	[122]

[1] Germany tariff for electric energy production from biomass for a power generation lower that 150kW.

[2] Average cost of syncrude calculated with a density of 0.8 for the diesel-kerosene fractions and 0.7 for the naphtha one.

[3] Average German tariff for industrial energy.

[4] Replacement every 3 years [122].

At least one operator has to be in the plant during the regular operations. This means 21 shifts per week, so 5 operators have to be employed.

TABLE 48 - PLANT OPERATIONAL COSTS

Name	Value
Cost of biomass	229'063 €
Ash disposal	78'943 €
Cost of transport	- €
Electric energy	- €
NaOH cost	65'832 €
Olivine	86'375 €
Wastewater	7'391 €
Fresh water	4'540 €
Operators	317'215 €
Labor	82'087 €
Maintenance	132'645 €
Insurance & taxes	132'645 €
Administration & services	66'322 €
TOC	**1'225'102 €**

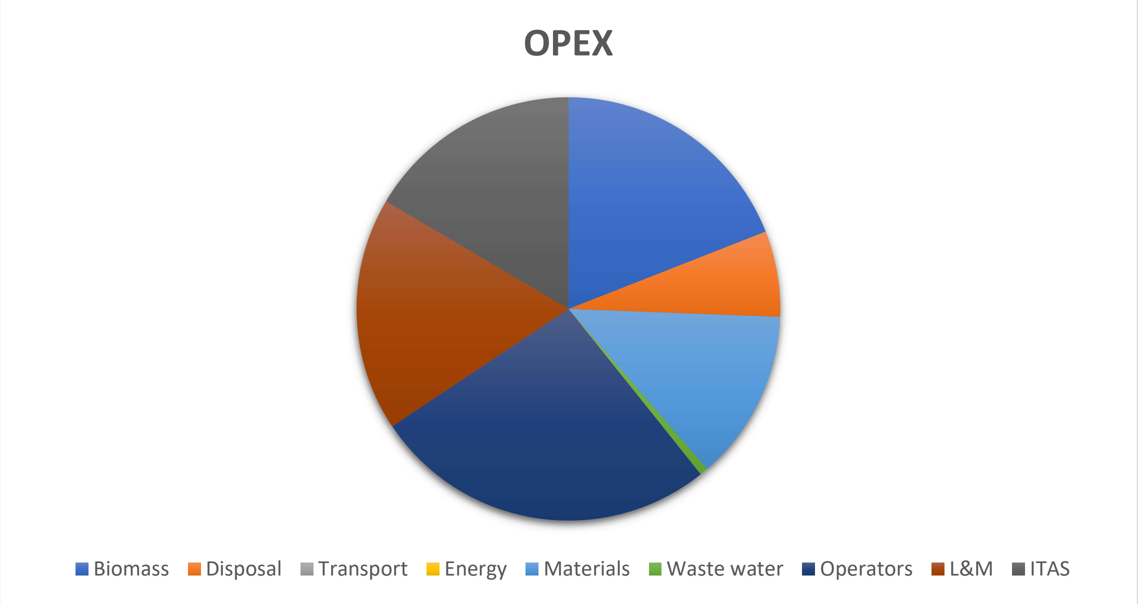

FIGURE 62 - DISTRIBUTION OF THE OPEX

In the *Figure 62* **- Distribution of the OPEX**, L&M means labor and maintenance, while ITAS is insurance, taxes, administration and services cost. A large amount of the expenditure is attributed to the cost of operators.

In this case A, an excess of electric energy is generated, the plant has two revenues: the income from the electric energy sold (with incentives due to the renewable character of the biomass used) and from the syncrude (which is the aim of the work). In the other cases, the electric energy is another expenditure: the calculation is still the same, but the value becomes negative.

In this analysis, the two value of interest are the cost of syncrude and waxes. So, when the first is calculating, only the electric energy is sold, while for the heavy hydrocarbons (waxes), also the naphtha and the middle distillate are sold at the market value.

TABLE 49 - REVENUES ESTIMATION

Revenue	Value
Electric energy	105'376 €
Naphtha	96'720 €
Middle	343'746 €
TR	**545'842 €**

The net present cost (NPC), the levelized cost of syncrude (LCOS) and the levelized cost of waxes (LCOW) are calculated using the formulae reported below:

$$NPC_{sync} = CAPEX + \sum_{j=1}^{n} \left(\frac{OPEX}{(1+d)^j} \right) \quad \textbf{(38)}$$

$$NPC_{waxes} = CAPEX + \sum_{j=1}^{n} \left(\frac{OPEX - TR}{(1+d)^j} \right) \quad \textbf{(39]}$$

$$LCOS = \frac{NPC_{sync}}{\sum_{j=1}^{n} \frac{m}{(1+d)^j}} \quad \textbf{(40)}$$

$$LCOW = \frac{NPC_{waxes}}{\sum_{j=1}^{n} \frac{m}{(1+d)^j}} \quad \textbf{(41)}$$

$$d = \frac{d' - ir}{1 + ir} \quad \textbf{(42)}$$

Where TR is the total revenues, d is the real rate of discount (RRD), d' is the nominal discount rate (NDR), ir is the inflation rate and m is the total quantity of syncrude produced in one year.

TABLE 50 – LCOS & LCOW ESTIMATION

Financial data	Value
Plant lifetime	25 years
Dept share	0%
Equity share	100%
Real rate of discount (d)	4.90% [126]
NPC_{sync}	22'788'539 €

NPC_{waxes}	16'517'936 €
LCOS	**2.221 €/kg**
LCOW	**4.893 €/kg**

10.3.3 Summary – Digestate

In this section, the most important data from the economic analysis are summarized in the tables below. For the comments about the calculation, see the previous section.

TABLE 51 - SUMMARY COSTS OF SINGLE SECTIONS - DIGESTATE

Section	Case A	Case B	Case C	Case C + SP
Gasifier	1'607 k€	1'633 k€	1'322 k€	1'322 k€
C&C	1'478 k€	1'428 k€	1'834 k€	1'834 k€
FTS	425.7 k€	502.1 k€	593.4 k€	593.4 k€
Total heat exchangers	676.3 k€	815.8 k€	1'041 k€	1'348 k€
Other BOP	377.7 k€	257.3 k€	1.53 k€	1.53 k€
TEPC	**4'125 k€**	**4'314 k€**	**4'637 k€**	**4'944 k€**
TIC	**6'665 k€**	**6'971 k€**	**7'493 k€**	**7'989 k€**

TABLE 52 - SUMMARY DATA FROM THE PLANT - DIGESTATE

Item	Case A	Case B	Case C	Case C + SP	Unit
Feedstock mass flow	0.9789	0.9789	0.9789	0.9789	ton/h
Ash flow	0.2819	0.2819	0.2819	0.2819	ton/h
Electric energy	0.0989	-0.0176	-0.219	-0.219	MW
Transport	0.00	0.00	0.00	0.00	km
NaOH consumption	21.1	21.1	21.1	21.1	kg/h
Wastewater	0.379	0.424	0.450	0.450	m3/h
Fresh water	0.291	0.286	0.281	0.281	m3/h
Syncrude production	92.4	117	148	148	kg/h
Naphtha	28.0	39.5	47.3	47.3	kg/h
Diesel	33.9	39.3	52.2	52.2	kg/h
Waxes	30.4	38.2	48.7	48.7	kg/h
Olivine	0.0714	0.0714	0.0714	0.0714	ton/h

TABLE 53 - SUMMARY OPEX COSTS - DIGESTATE

Item	Case A	Case B	Case C	Case C + SP
Cost of biomass	229'063 €	229'063 €	229'063 €	229'063 €
Ash disposal	98'926 €	98'926 €	98'926 €	98'926 €
Cost of transport	0.00 €	0.00 €	0.00 €	0.00 €
NaOH cost	65'832 €	65'832 €	65'832 €	65'832 €
Wastewater	7'391 €	8'268 €	8'775 €	8'775 €
Fresh water	4'540 €	4'462 €	4'384 €	4'384 €
Olivine	86'375 €	86'375 €	86'375 €	86'375 €
Operators (5)	317'215 €	317'215 €	317'215 €	317'215 €
Labor	82'496 €	86'280 €	92'744 €	98'886 €

Maintenance	133'306 €	139'419 €	149'864 €	159'790 €
Insurance & taxes	133'306 €	139'419 €	149'864 €	159'790 €
Administration & services	66'653 €	69'710 €	74'932 €	79'895 €
TOC	**1'225'102 €**	**1'244'968 €**	**1'277'974 €**	**1'308'930 €**

TABLE 54 - SUMMARY REVENUE ESTIMATION - DIGESTATE

Revenue	Case A	Case B	Case C	Case C + SP
Electric energy	105'376 €	-21'416 €	-266'479 €	-266'479 €
Steam production	0.00 €	0.00 €	0.00 €	174'982 €
Naphtha	96'720 €	136'444 €	163'388 €	163'388 €
Middle	343'746 €	398'502 €	529'308 €	529'308 €
TR	**545'842 €**	**513'531 €**	**426'217 €**	**601'198 €**

TABLE 55 - SUMMARY LCOS AND LCOW ESTIMATION - DIGESTATE

Financial data	Case A	Case B	Case C	Case C + SP
NPC_{sync}	22'789 k€	25'190 k€	29'686 k€	28'145 k€
NPC_{waxes}	16'518 k€	17'575 k€	19'824 k€	18'284 k€
LCOS	**2.221 €**	**1.939 €**	**1.806 €**	**1.713 €**
LCOW	**4.893 €**	**4.143 €**	**3.666 €**	**3.381 €**

10.3.4 Sensitivity analysis – Digestate

To understand what parameters are the most critical for the final cost of production, some sensitivity analyses are performed. These are done on the case C with steam production and only with the digestate, being the most performing and promising configuration.

10.3.4.1 Biomass cost

A sensitivity on the digestate cost is the first performed. The European Commission report above-mentioned [89] shows a reasonable digestate price of 5-30€/ton. In the present work, the upper limit was taken into account; however, for the sensitivity analysis, a negative price of -35.7€/ton is taken as lower limit. It represents the case where the digestate is not used and it is disposed in landfill becoming a cost (this is an option evaluated in the EC report). 50€/ton was taken as a reasonable high price for the upper limit.

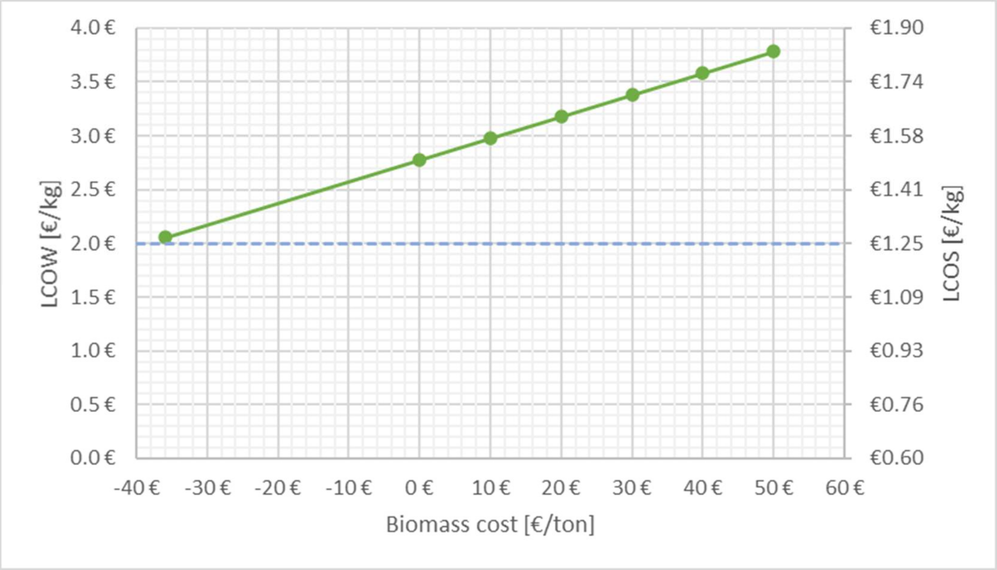

FIGURE 63 - SENSITIVITY ON BIOMASS COST. THE DOTTED BLUE LINE REPRESENTS THE MARKET VALUE OF THE WAXES [97].

The light blue dotted line represents the market value of waxes (2€/kg [97]), the point where the green and the light blue lines cut across each other is called break-even point. Here the plant is able to repay the whole expenditure during its life generating the profit expected in the analysis. The light blue line works only with the LCOW, it has no meaning with the LCOS.

Remembering the uncertainties that affect this kind of analysis, it is possible that the plant is sustainable if the digestate has no other uses unless the disposal in landfill. In this case, if the company would keep the middle distillate for its machineries uses, supposing that it is interesting only in savings (the NDR becomes equal to 0%), the levelized cost is about 0.65€/l. Supposing that the digestate has a value of zero and the plant has a double size, the cost becomes 0.61€/l. This is comparable with the work of Snehesh et al. [8] which shows a fuel price between 0.52€/l and 0.70€/l.

10.3.4.2 Electric energy cost

The case C requests a non-negligible amount of electric energy and this is responsible for about the 20% of the OPEX in the case of LCOS estimation. An investigation on the cost variation is performed: 40€/MWh is assumed as lower limit, which is a reasonable low value for the energy coming from an onshore wind farm. The upper limit is 180€/MWh which is a 15% more than the Germany average industrial price including tax [124].

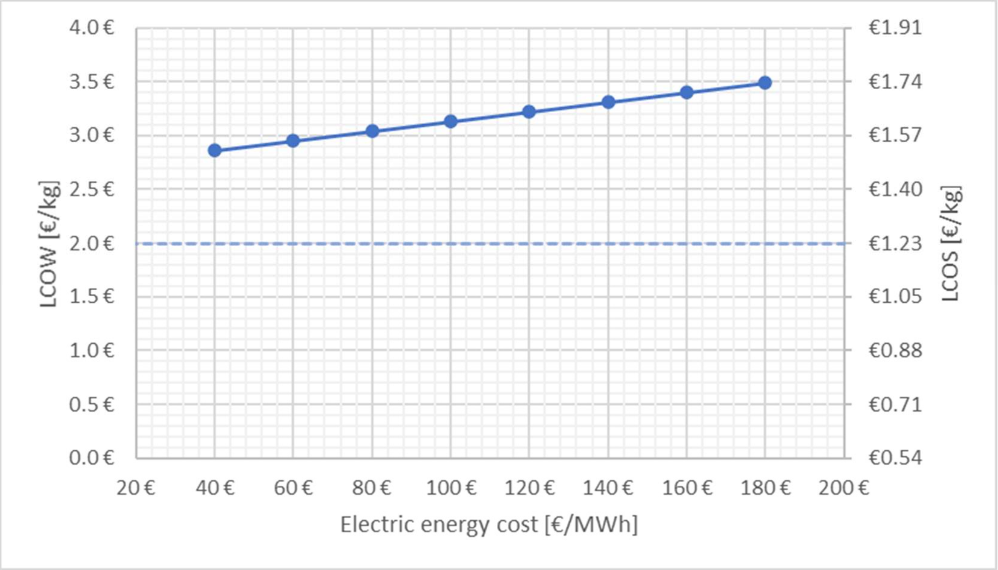

FIGURE 64 - SENSITIVITY ON ELECTRIC ENERGY COST. THE DOTTED BLUE LINE REPRESENTS THE MARKET VALUE OF THE WAXES [97].

The LCOS and LCOW are less sensible at the electric energy cost variation with respect to the digestate one, even though the wide range of prices. It means that the improvement to save power or to reduce its costs could be not so effective.

10.3.4.3 Biomass and electric energy costs

It is useful to understand the behavior of the plant varying the biomass and the electric energy costs together. The only case where the LCOW is below the market value (it means that the plant is able to make a profit) is in case of avoid the disposal of the digestate and with a low price of the electric energy.

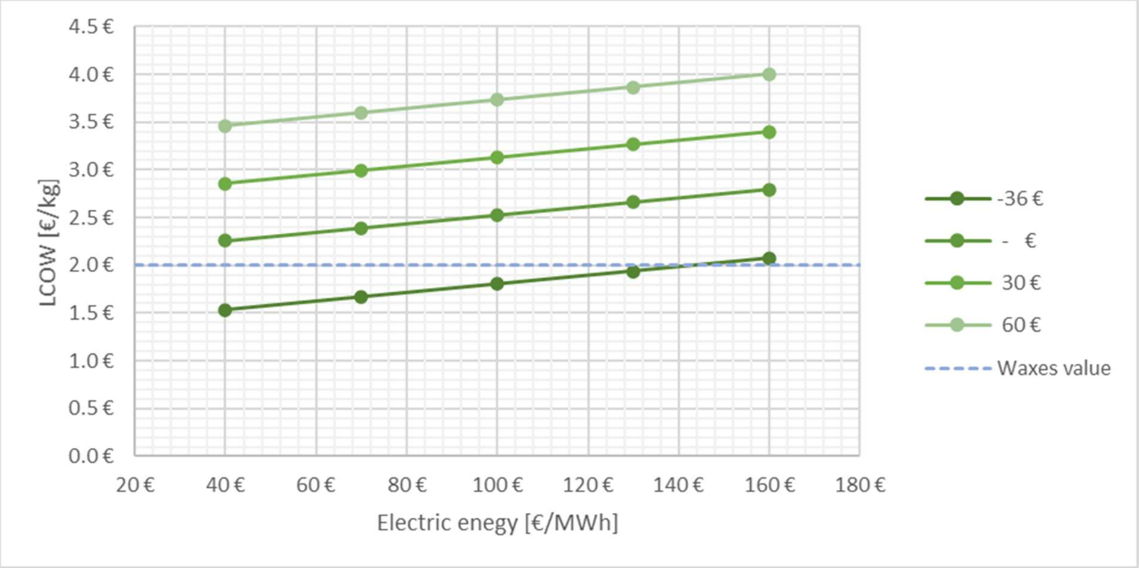

FIGURE 65 - SENSITIVITY ON BIOMASS AND ELECTRIC ENERGY COSTS. THE DOTTED BLUE LINE REPRESENTS THE MARKET VALUE OF THE WAXES [97].

10.3.4.4 Steam cost

The production of steam adds one revenue which lets to decrease the LCOx. The low pressure steam has a base cost of 25.7€/ton [112], but if it is sold to an industry, it can save CO_2 emission in addition to save fuel. In a scenario where a carbon tax subsists, the *green* steam can increase its value. On the other hand, if there is no possibility to sell steam but only the heat to a district heating grid, the value decrease. The range employed ranged from 10€/ton to 40€/ton.

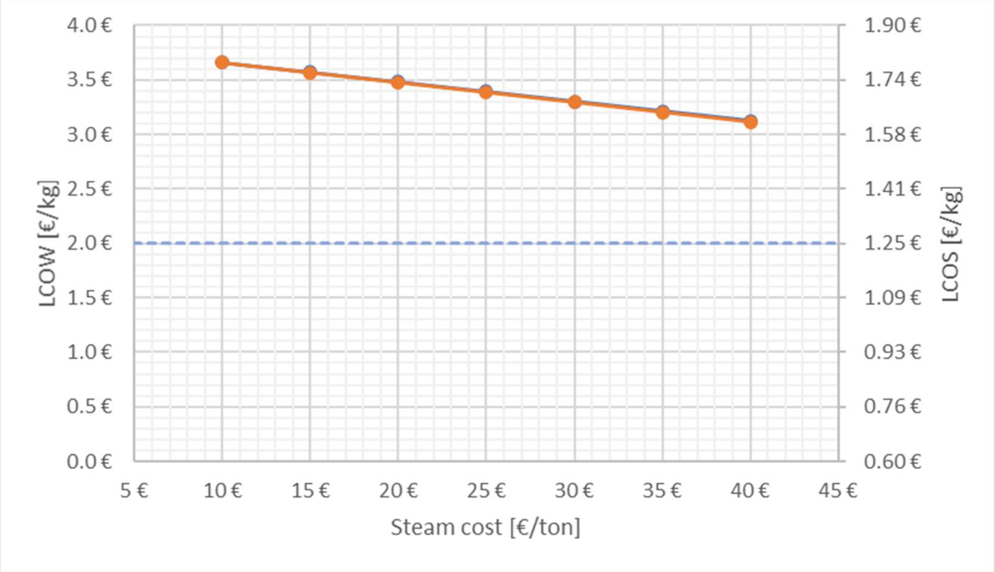

FIGURE 66 - SENSITIVITY ON STEAM COST. THE DOTTED BLUE LINE REPRESENTS THE MARKET VALUE OF THE WAXES [97].

10.3.4.5 Plant size

Generally, increasing the size, the costs of production are reduced. In this case, the plant was kept small to be feed to an anaerobic digestor. Supposing to have several digesters near the plant (to neglect the transport costs), the analysis is performed. The limits in this case are about one order of magnitude more and less of the nominal size. Further projection can be affected to a high error due to the exiting the limit of variation in the equipment costs evaluation. As expected, smaller sizes are critical for the economy, while larger plant can reach the break-even point.

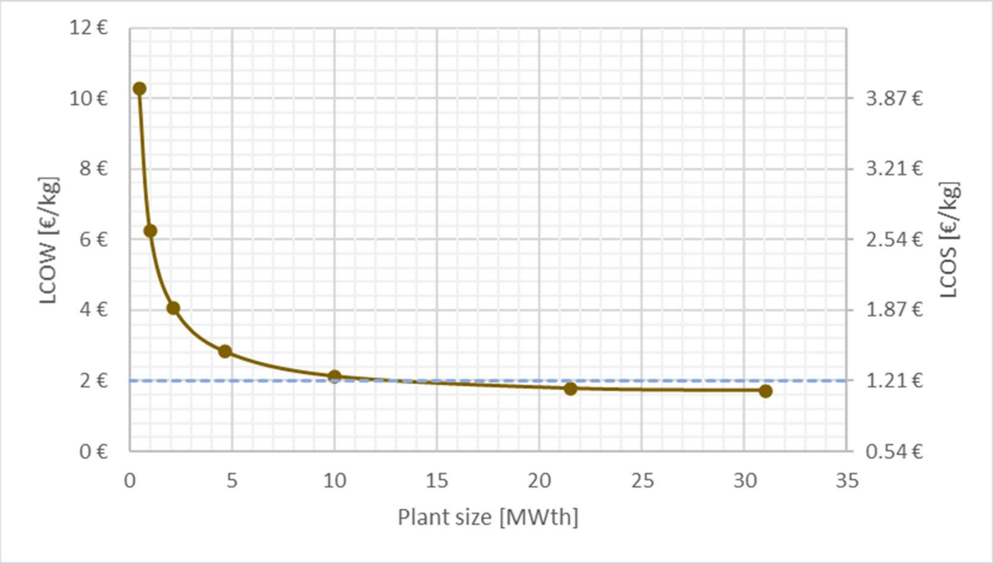

FIGURE 67 - SENSITIVITY ON PLANT SIZE**.** THE DOTTED BLUE LINE REPRESENTS THE MARKET VALUE OF THE WAXES [97].

10.3.4.6 Nominal discount rate

The analysis on the nominal discount rate variation is useful because it shows if the plant is sustainable obtaining a lower profit. In the economic analysis, the nominal discount rate was fixed at 7% and it was found that the plant is not sustainable. The Figure 68 **- Sensitivity on the nominal plant size. The dotted blue line represents the market value of the waxes [97].** shows that the plant cannot work generating no profit in any case of waxes production. However, it can generate middle distillate at a cost of about 1.55€/l when the NDR is zero.

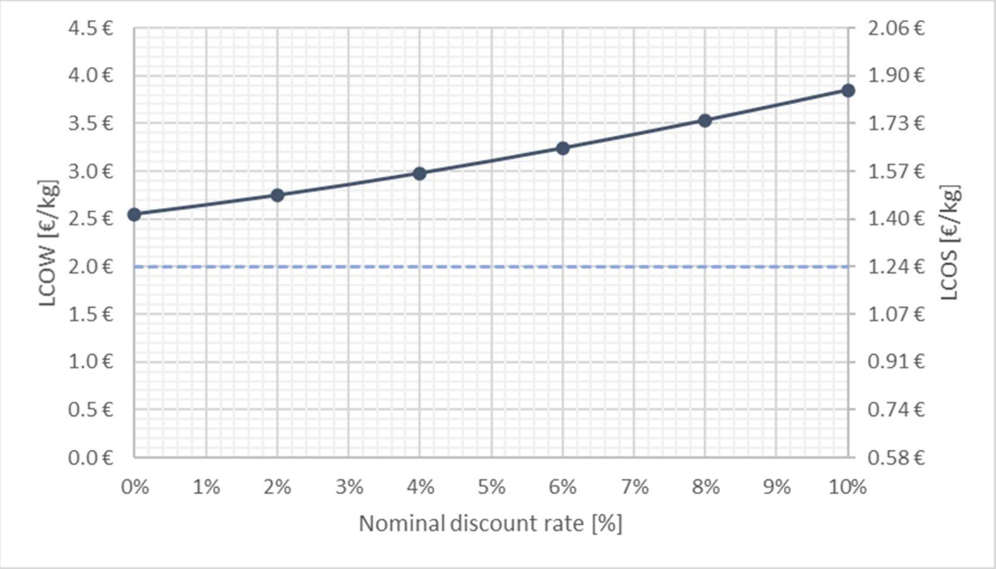

FIGURE 68 - SENSITIVITY ON THE NOMINAL PLANT SIZE. THE DOTTED BLUE LINE REPRESENTS THE MARKET VALUE OF THE WAXES [97].

10.3.5 Summary – Woody biomass

A summary of the result is reported as it had been done for the cases with digestate.

TABLE 56 - SUMMARY COSTS OF SINGLE SECTIONS – PINE WOOD

Section	Case A	Case B	Case C	Case C + SP
Gasifier	1'567 k€	1'592 k€	1'230 k€	1'230 k€
C&C	1'596 k€	1'554 k€	2'009 k€	2'009 k€
FTS	400.0 k€	473.1 k€	542.2 k€	542.2 k€
Total heat exchangers	643.6 k€	792.4 k€	997.1 k€	950.9 k€
Other BOP	360.2 k€	242.4 k€	1.33 k€	1.33 k€
TEPC	**4'160 k€**	**4'361 k€**	**4'634 k€**	**4'588 k€**
TIC	**6'723 k€**	**7'048 k€**	**7'488 k€**	**7'414 k€**

TABLE 57 - SUMMARY DATA FROM THE PLANT – PINE WOOD

Item	Case A	Case B	Case C	Case C + SP	Unit
Feedstock mass flow	0.7731	0.7731	0.7731	0.7731	ton/h
Ash flow	0.00680	0.00680	0.00680	0.00680	ton/h
Electric energy	0.0956	-0.0157	-0.194	-0.194	MW
Transport	49.1	49.1	49.1	49.1	km
NaOH consumption	0.403	0.403	0.403	0.403	kg/h
Wastewater	0.388	0.421	0.442	0.442	m3/h
Fresh water	0.208	0.194	0.190	0.190	m3/h
Syncrude production	84.6	108	139	139	kg/h
Naphtha	25.9	37.0	46.5	46.5	kg/h
Diesel	30.8	35.7	46.7	46.7	kg/h
Waxes	27.9	35.2	45.3	45.3	kg/h
Olivine	0.0501	0.0501	0.0501	0.0501	ton/h

TABLE 58 - SUMMARY OPEX COSTS – PINE WOOD

Item	Case A	Case B	Case C	Case C + SP
Cost of biomass	587'264 €	587'264 €	587'264 €	587'264 €
Ash disposal	15'930 €	15'930 €	15'930 €	15'930 €
Cost of transport	72'331 €	72'331 €	72'331 €	72'331 €
NaOH cost	1'258 €	1'258 €	1'258 €	1'258 €
Wastewater	7'566 €	8'210 €	8'619 €	8'619 €
Fresh water	3'245 €	3'026 €	2'964 €	2'964 €
Olivine	60'629 €	60'629 €	60'629 €	60'629 €
Operators (5)	317'215 €	317'215 €	317'215 €	317'215 €
Labor	83'210 €	87'229 €	92'683 €	91'760 €
Maintenance	134'458 €	140'953 €	149'767 €	148'275 €
Insurance & taxes	134'458 €	140'953 €	149'767 €	148'275 €
Administration & services	67'229 €	70'477 €	74'884 €	74'137 €
TOC	**1'484'793 €**	**1'505'474 €**	**1'533'311 €**	**1'528'656 €**

TABLE 59 - SUMMARY REVENUE ESTIMATION – PINE WOOD

Revenue	Case A	Case B	Case C	Case C + SP
Electric energy	101'860 €	-19'104 €	-236'059 €	-236'059 €
Steam production	0.00	0.00	0.00	174'982 €
Naphtha	89'466 €	127'809 €	160'624 €	160'624 €
Middle	312'312 €	361'998 €	473'538 €	473'538 €
TR	**503'638 €**	**470'703 €**	**398'103 €**	**573'546 €**

TABLE 60 - SUMMARY LCOS AND LCOW ESTIMATION – PINE WOOD

Financial data	Case A	Case B	Case C	Case C + SP
NPC_{sync}	26'595 k€	28'945 k€	32'883 k€	30'242 k€
NPC_{waxes}	20'875 k€	21'972 k€	23'855 k€	21'214 k€
LCOS	**2.831 €**	**2.414 €**	**2.130 €**	**1.959 €**
LCOW	**6.738 €**	**5.621 €**	**4.742 €**	**4.217 €**

10.4 Results and comments

A recap is done in order to highlight the most important results of the economic analysis. At the beginning of the work, it was supposed that the use of a digestate was more economic than a woody biomass one, so also the levelized cost of products should be lower. This was not obvious and the whole treatise was focused on quantify the differences between the two scenarios. At the end of the work, the results show that the thesis is confirmed: the syncrude and waxes produced using the digestate have a cost of production lower than using wood. The *Table 61* **- Summary of cases C plus steam production** shows the differences between the main parameters that made up the LCOS and LCOW. The CAPEX is higher for the digestate, this is due to the higher syngas mass flow and the higher production. On the other hand, the OPEX is lower due to the lower cost of the fuel. In addition, the revenues are higher due to the higher producibility of the plant.

TABLE 61 - SUMMARY OF CASES C PLUS STEAM PRODUCTION

Cases C+SP	Digestate	Woody biomass
CAPEX	7'989 k€	7'414 k€
OPEX	1'309 k€	1'529 k€
Revenues (w/o waxes)	601.1 k€	573.5 k€
LCOS	1.713 €/kg	1.959 €/kg
LCOW	3.381 €/kg	4.217 €/kg

The two graphs below (*Figure 69* **- LCOS comparison through the different cases and fuel used** and *Figure 70* **– LCOW comparison through the different cases and fuel used**) show the differences in levelized costs between the use of digestate and wood in all the cases. This analysis is an estimation and it has an error of about 30%, for this reason the error bars are reported. In no case the costs are lower or at least equal to the market value. For the waxes, it can be about 2€/kg as reported by Herz et al. [97] while the cost found in this work is between 2.37 and 4.40 €/kg in the best case scenario. So, the plant cannot be economically sustainable as it is without incentives. An even worst situation subsists for the syncrude: in the 2010s, the crude price (Brent) ranged between 20 and 125$/barrel [127] on the international market, it means between about 0.78 and 0.12 €/kg. These values are far away from the 1.20-2.23€/kg obtained for the syncrude of this work. Although, the syncrude is not equal to the natural oil: for instance, it has no traces of sulfur and aromatic compounds. This synthetic oil can have a higher value respect to the regular crude.

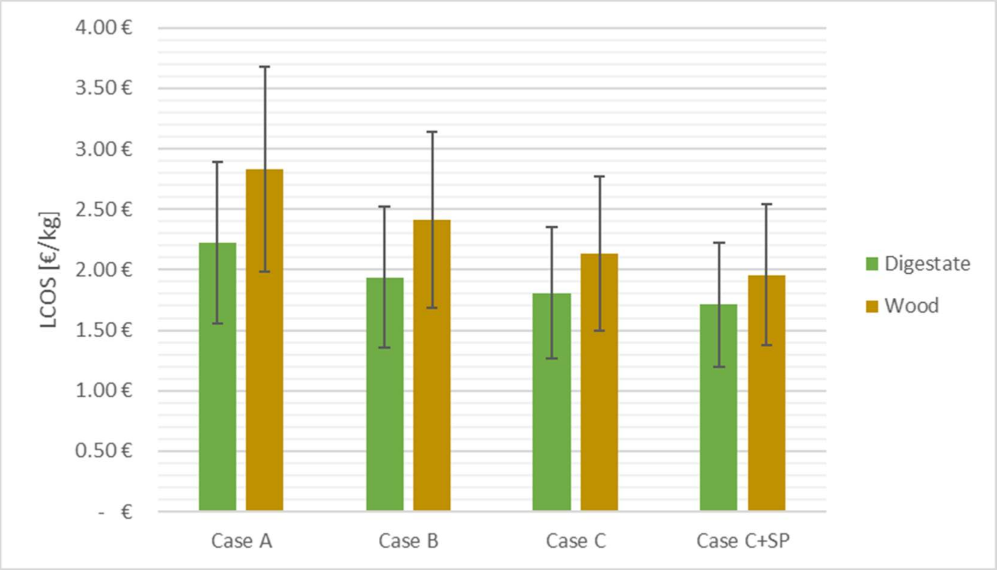

FIGURE 69 - LCOS COMPARISON THROUGH THE DIFFERENT CASES AND FUEL USED

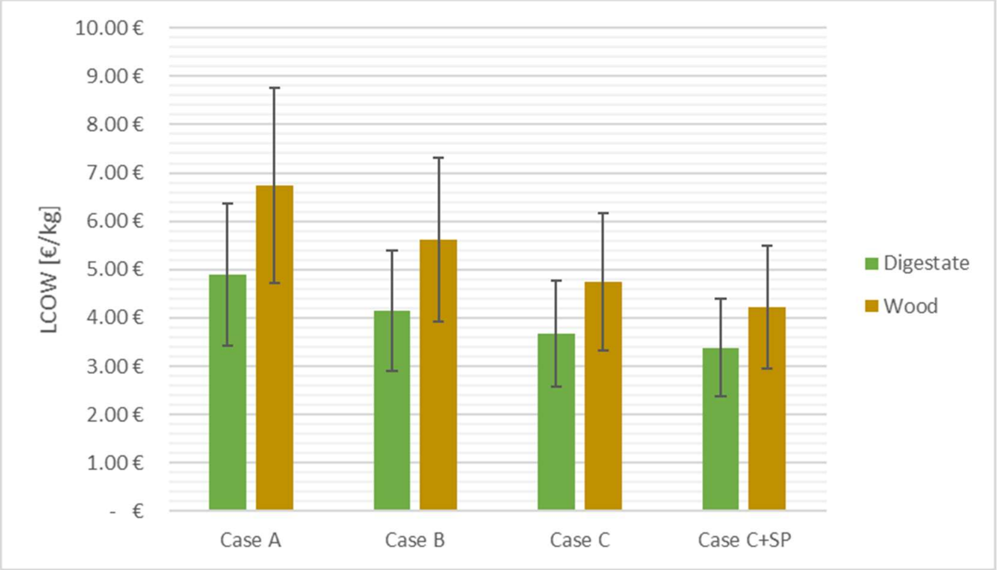

FIGURE 70 – LCOW COMPARISON THROUGH THE DIFFERENT CASES AND FUEL USED

11. Conclusions

11.1 Comparison with other works

In the present work, results of productivities, efficiencies and production costs are found for two types of biomass under three different configurations. It is important to have a comparison with other works treating similar plants. The *Table 62* **- Comparison table of the performances of several works*Errore. L'origine riferimento non è stata trovata.*** reports several articles and distinguishing the size of the gasifiers. In the section *Choice of the biomass*, the papers are already presented in *Table 10* **- BTX plants**. Here, those of interest producing FTS fuels are presented.

The units for the final cost are different and there is not any possibility to refer them to the same unit without approximation. On the other hand, in the present work, it is possible to calculate the cost on weight, volume or energy basis and it is done for a better comprehension of the comparison.

TABLE 62 - COMPARISON TABLE OF THE PERFORMANCES OF SEVERAL WORKS

#	**Authors**	**Size [MW_{th}]**	**Production [$kg_{syncrude}/ton_{biomass}$]**	**Final Product**	**Final cost**	**Syncrude efficiency [%]**	**Ref.**
1	**Tagomori et al.**	750	144-152[1,4]	FT diesel	38.3-40.5 $\$_{2019}$/GJ[2]	n.a.	[1]
2	**Trippe et al.**	1000	n.a.	FT gasoline	1.58-1.6 €$_{2013}$/kg[3]	38.1-38.7[3]	[73]
3	**Hamelinck et al.**	400	n.a.	FT diesel	13€$_{2003}$/GJ	42	[2]
4	**Tijmensen et al.**	100	n.a.	FT fuels and power	16€$_{2001}$/GJ	n.a.	[72]
5	**Im-orb et al.**	393	n.a.	FT fuels	n.a.	16.5$_{max}$	[4]
6	**Swanson et al.**	350[2]	n.a.	FT fuels	39.8 $\$_{2007}$/GJ[4]	49.7[5]	[55]
7	**Prins et al.**	210	151	FT fuels and power	n.a.	36.5	[67]
8	**Spyrakis et al.**	4.8[2]	113$_{max}$[8]	FT fuels	n.a.	28.7$_{max}$	[70]
9	**Rafati et al.**	400	n.a.	FT fuels	29 $\$_{2016}$/GJ	43.0[6]	[68]
10	**Hillestad et al.**	435	n.a.	FT fuels	2.6 €$_{2017}$/L[5,7]	53	[3]
11	**Tuomi et al.**	100	n.a.	FT fuels	n.a.	49.0[4]	[74]
12	**Snehesh et al.**	4.9	137-240	FT fuels and power	0.582-0.781 $\$_{2016}$/L	30.6-53.5	[8]
13	**Dietrich et al.**	400	n.a.	FT fuels	2.43 €$_{2016}$/kg	36.3	[59]
14	**Present work (digestate)**	3.11	94.4-151	FT fuels/wax	1.71-2.22 €/kg 38.8-50.3 €/GJ	36.3-54.5	-
15	**Present work (wood)**	3.11	115-190	FT fuels/wax	1.96-2.83 €/kg 44.4-64.2 €/GJ	33.2-51.3	-

[1] With pine and eucalyptus respectively.

[2] attributed to diesel.

[3] depending on the gasifier pressure

[4] calculated
[5] estimated
[6] using cobalt catalyst
[7] of biodiesel
[8] on dry biomass

In the *Figure 71* **- Syncrude production efficiency comparison**, the syncrude production efficiency is shown. Some papers report a minimum and a maximum value due to the different configuration investigated, as it is done in the present work. The graph shows these differences. Where the bar is total dark is because the authors specified only the best efficiency and where the bar is total light is because the authors investigate just one case.

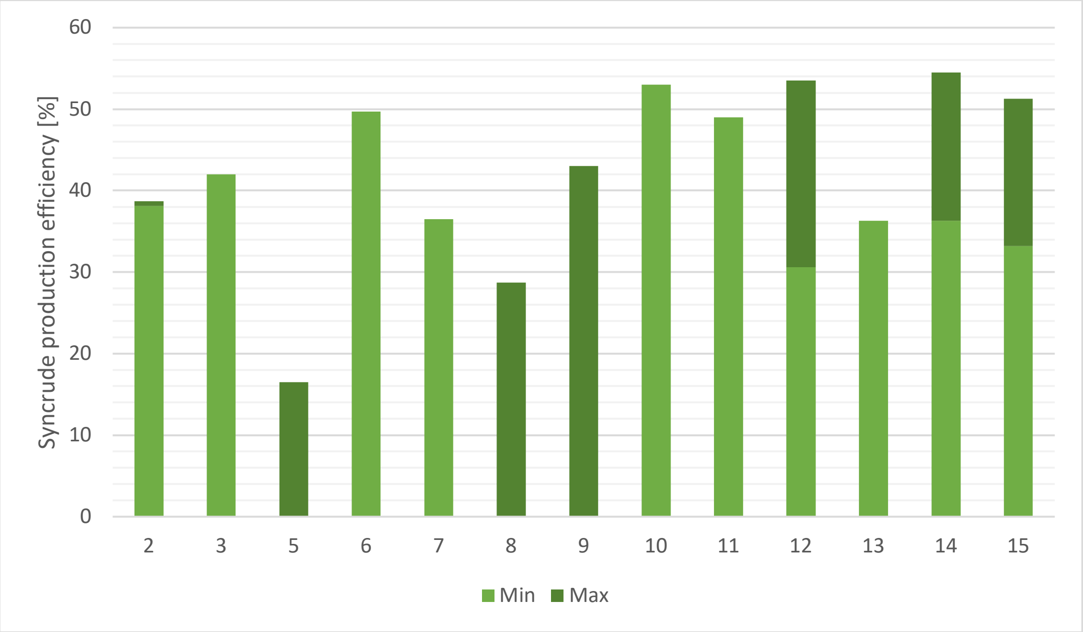

FIGURE 71 - SYNCRUDE PRODUCTION EFFICIENCY COMPARISON

It is possible to see that the present work has efficiencies comparable to the cases reported. However, small plants might have a lower efficiency, so the plant presented would have low performance. Therefore, an analysis about the relationship between efficiency and size is performed. The graph in *Figure 72* **– Relationship between efficiency and plant size** shows that the efficiency has no relation with the plant size, so it means that a small plant can have the same efficiency of a huge plant or even better.

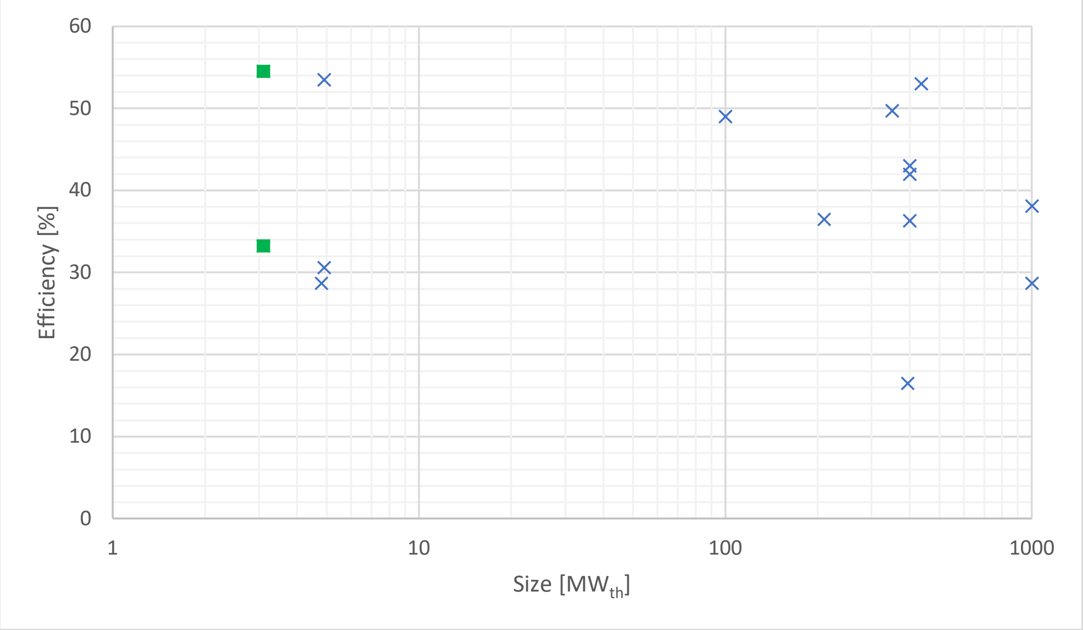

FIGURE 72 – RELATIONSHIP BETWEEN EFFICIENCY AND PLANT SIZE AGAINST LITERATURE WORKS PRESENTED IN TABLE 62. THE GREEN SQUARES REPRESENT THE EFFICIENCIES FOUND IN THIS WORK.

Only flew papers declare the syncrude production with respect to the feedstock biomass. In all the cases the production is referred to the as received biomass (only the number 8 is modified respect to the *Table 62* - **Comparison table of the performances of several works** supposing a 10% of moisture). The results of the present work are in between the best and the worst case. However, these data cannot represent very well the performance because there are many differences due to the moisture and ash contents.

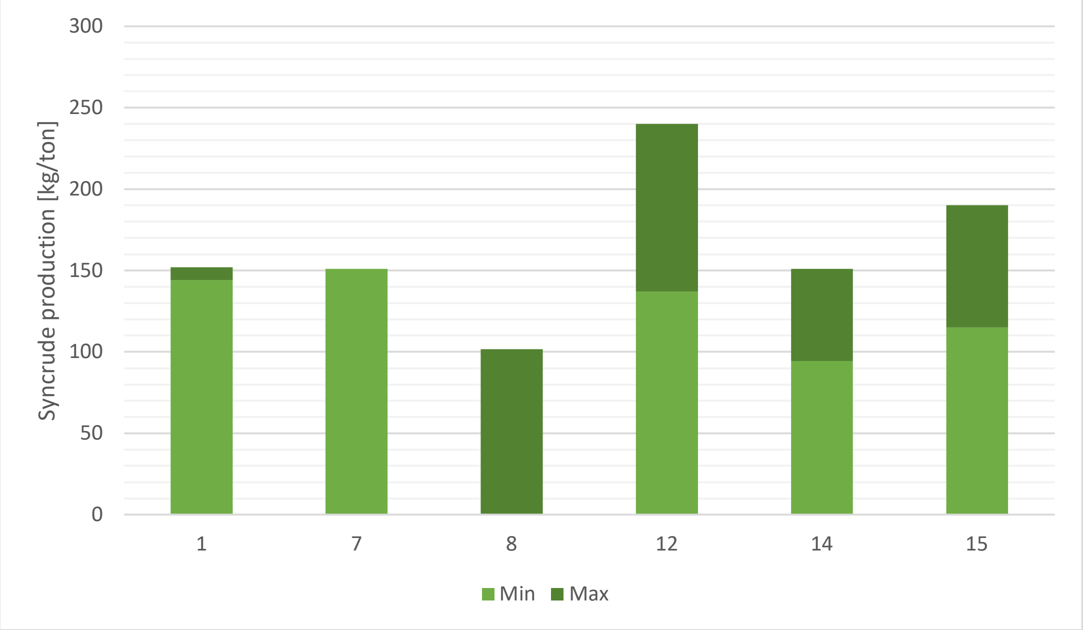

FIGURE 73 – SPECIFIC SYNCRUDE PRODUCTION COMPARISON

The case of the economic evaluation is different with respect to the efficiency: sure enough, the cost of the syncrude produced in the present work is higher than all the others. This is probably due to the small size of the plant that are not common in the production of synthetic fuel/chemicals. As it is showed in the *10.3.4.5 Plant size*, increasing the dimension of the plant reduces the production cost.

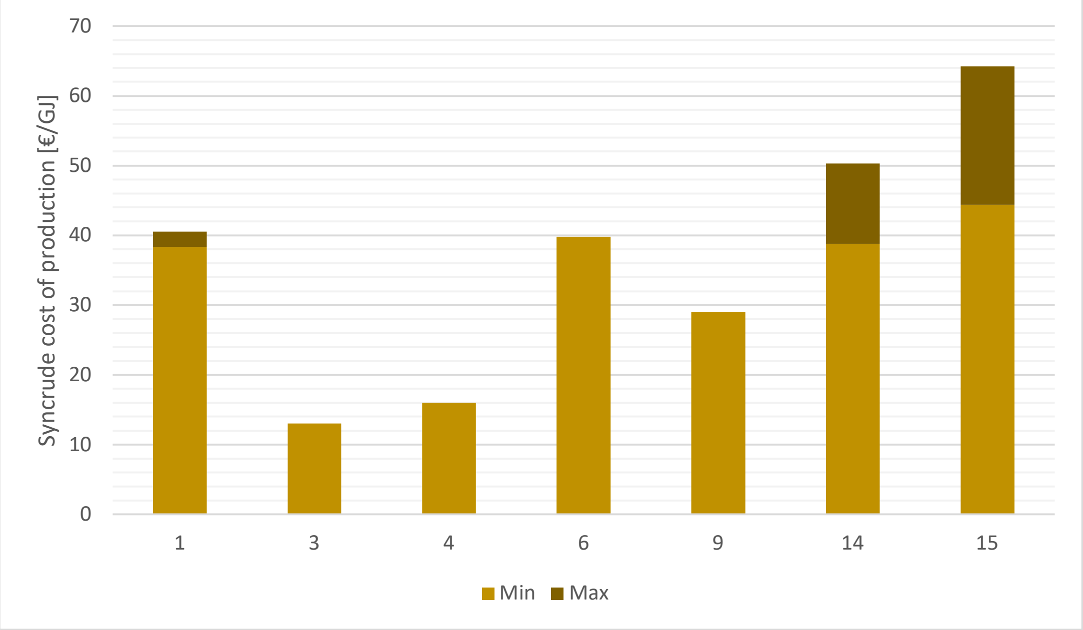

FIGURE 74 – SYNCRUDE PRODUCTION COST COMPARISON

The cost of waxes on energy basis is about 0.31€/kWh for the case C with steam production. This value is comparable with Herz et al. [128] which have found a cost of production of 0.38€/kWh in the case of electric energy price equal to the one used in this work.

11.2 Future developments

During the work development, some ideas to improve the system came up. Here, these are reported and briefly explained.

11.2.1 Thermal recovery

The plant generates more heat than what it is necessary for its internal use. So, to increase the efficiency, it would be studied the feasibility to a higher level of preheating of the air and the steam. It has been seen that the temperature of the combustion air is very important for the efficiency of the whole plant. For instance, increasing the air pre-heating temperature from 450°C to 650°C the syncrude production grows of 4.2%, while using the same data for the steam superheating, the increasing is about 1.4%. Furthermore, it is possible to investigate a drying system for the biomass in order to recover a low temperature heat or a system for the torrefaction of the feedstock biomass. These latter requests a temperature of about 200°C, but since there is the possibility to produce a large amount of medium temperature heat, it can improve the global efficiency and enhance the productivity.

11.2.2 Generation of electric energy

The produced steam from the heat recovery system can be used in a steam turbine to produce energy and increase the green-energy sold or to reduce the energy bought. Herz et al. [97] use a steam turbine to produce less than 25kW$_{el}$ in a 1MW$_{th}$ biogas-to-liquid plant. The main problem with a micro steam-turbine system is the economic feasibility and it has to be further investigated. Another aspect is the large amount of energy from the FTS reactor, which has a temperature of about 200°C. The alternatives can be two:

- ORC can be employed as substitute of the steam cycle.
- The steam can be injected in the GT in order to increase the mass flow rate.

11.2.3 Integration with an electrolyte cell/H_2 stream

The system produces a carbon dioxide flux, which can be vented in the atmosphere, stored or used in some applications (see the paper of Jarvis and Samsatli [129]). The latter is the most interesting because it can transform a waste into a useful product. Below, some ideas are reported and briefly explained.

- Carbon dioxide can be used in an electrolyte cell, such as solid oxide electrolyzer cell (SOEC), together with steam to convert the CO_2 and H_2O into CO, H_2 and O_2. In this way another syngas stream can be produced and used to increase the flow rate in the FTS reactor. The advantages are several: first of all, the carbon dioxide emissions are reduced, then the productivity is increased. On the other hand, there is the necessity to buy external electric energy, which can have a high cost. It is better to foresee a photovoltaic park or a wind farm in order to convert that energy into green fuels. Moreover, it is a technique to store renewable energy.
- Since solid oxide electrolyzer cells are not a commercially mature technology, it is possible to produce hydrogen with an alkaline cell. The H_2 is mixed with the CO_2 in a reverse-WGS reactor, in this way a syngas is produced converting the carbon dioxide in monoxide. This concept is similar to the work of Hillestad et al. [3] and Dietrich et al. [59].
- A variation of the previews point is to inject the H_2 directly in the gasifier together with the CO_2. The high temperature and the catalytic sand (olivine) inside the reactor can do the same work of the RWGS reactor. This has to be investigated.

In all the cases, a further study on the system tolerance to partial load has to be investigate: when renewable sources have a low production, the system works with a reduce flow rate and that can affect the efficiency and the productivity of the whole plant.

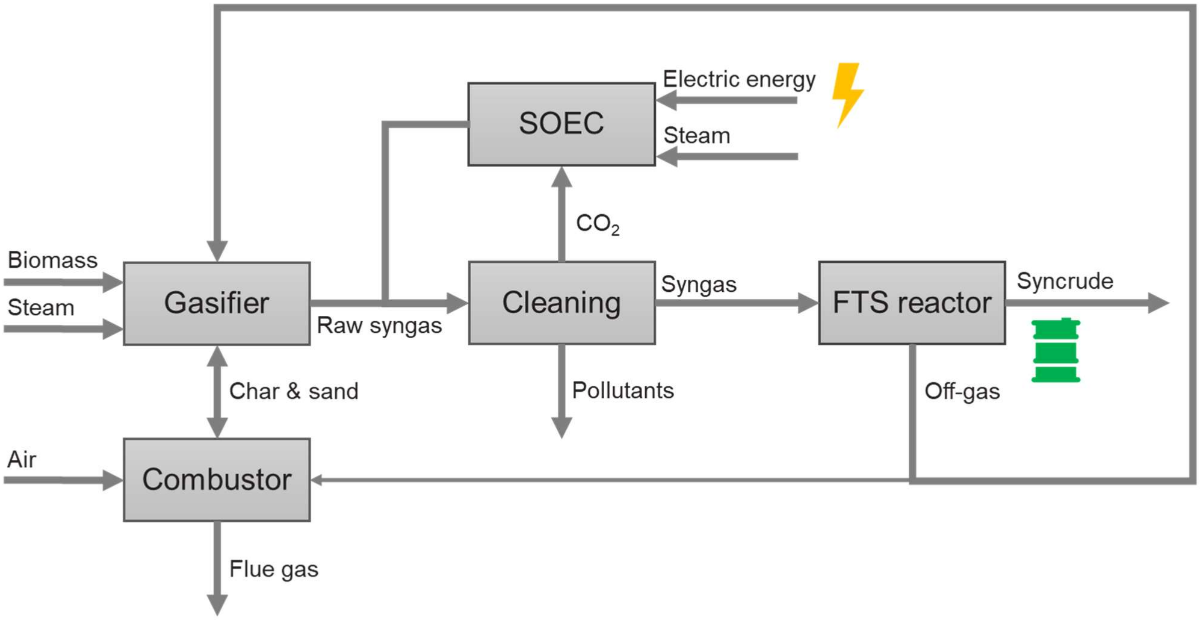

FIGURE 75 - POSSIBLE INTEGRATION OF THE PLANT WITH A SOEC

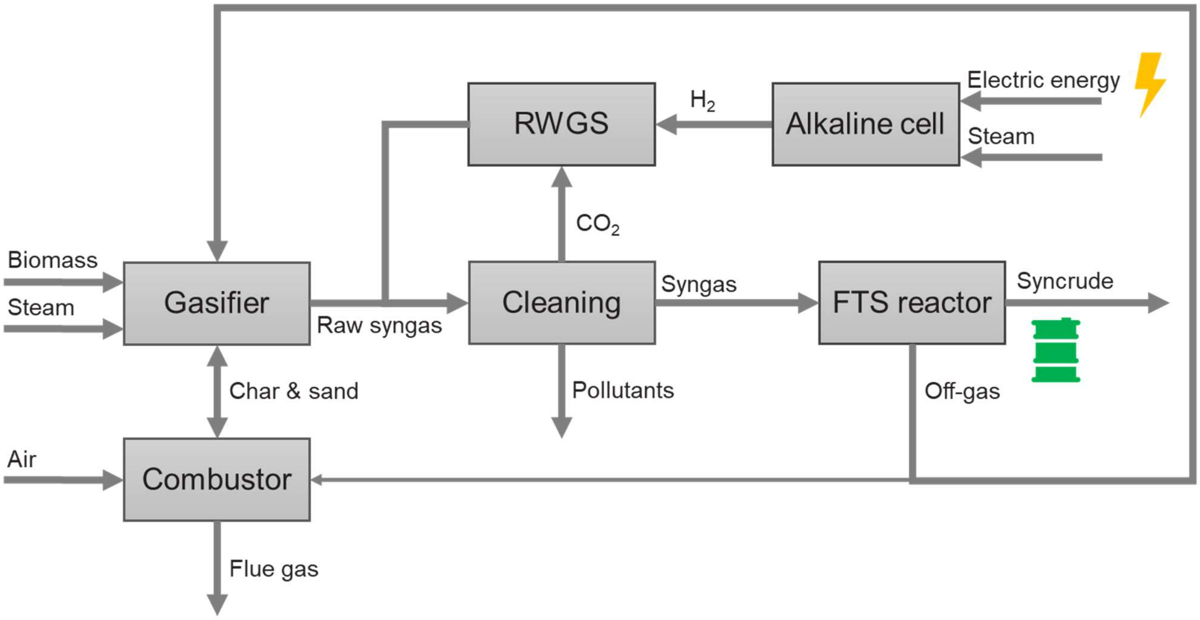

FIGURE 76 - POSSIBLE INTEGRATION OF THE PLANT WITH AN ALKALINE CELL FOR HYDROGEN PRODUCTION

11.2.4 Energy storage

Since the FTS reactor produces LPG fraction, it can be condensed, removed from the off-gas and stored. When the grid increases its demand of energy, the fuel can be used in a gas turbine or in an ICE. This system finds a good place in a scenario with a high penetration of renewable energy sources such as photovoltaic or wind energy. Sure enough, these are not constant and can undergo to large variation during the day. A storage system able to a fast star-up as a green-LPG-fed ICE can satisfy the demand.

This system can be integrated in all the other improvements above presented.

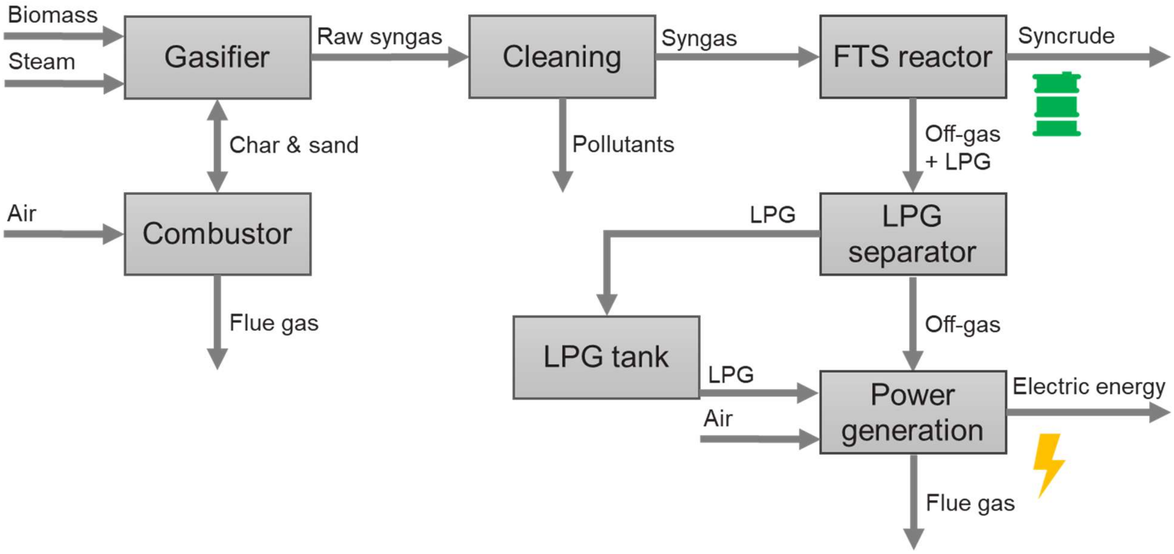

FIGURE 77 - POSSIBLE INTEGRATION OF THE PLANT WITH AN LPG STORAGE SYSTEM

11.3 Final comments

In this work, an alternative way to produce hydrocarbons from a biomass was presented. It was shown that it is technologically feasible to produce a syncrude starting from a non-conventional biomass as the digestate. The different types of biomass do not change so much the efficiency of the plant, which is more sensible to the pre-treatment such as the drying process. About 33% to 55% of the energy consumed by the plant is converted into hydrocarbons. This result is comparable to the ones found on literature. Moreover, a certain amount of energy can be recovered in the form of heat or electric energy. In this way, the global efficiency can reach the 71%.

A digestate has a lower quality with respect to the conventional woody biomass because it contains higher quantities of sulfur, chlorine and ash. However, the one used has a lower content of water and this can affect the efficiency more than all the other parameters. In the best cases analyzed, the syncrude production efficiency is 55% using the digestate and 51% using the pine wood.

The higher consumption of sodium hydroxide for the sulfur removal and the large amount of ash produced increase the OPEX, but the savings produced by the lower price of the biomass are able to make the operational costs lower that the ones when pine wood is used. Globally, the LCOS and LCOW range from 1.71€/kg to 2.83€/kg and from 3.38€/kg to 6.74€/kg respectively. This is higher that the costs found in literature, this is due to the small capacity of the plant compared to the others. A solution to decrease the LCOx is to enlarge the size, as shown in section *10.3.4.5 Plant* size. However, it would be possible to adopt this solution where there are several digesters closed each other, such as in a wastewater treatment plant (WWTP) or in a very large farm or in a OFMSW collection point. In addition, further developments and integrations shown in *11.2 Future* developments, can improve the production and decrease the cost. However, some of those could not be economical feasible in a short time, such as the case involving fuel cells, which are still expensive.

The work has shown how the conversion of a biomass into a fuel can be possible also in small plants. There is still a lot of work to do in order to reduce the costs and to make this syncrude competitive. For instance, the addition of hydrogen can increase the carbon conversion and yield of the final production, the thermal recovery or the production of electric energy can increase the global efficiency and the revenues. All of these can lead to a reduction of the costs of production, making more convenient and sustainable the distributed production of fuels and chemicals.

Another solution can be the internal use of the products: if the company needs fuel for the heating during the winter season, a storage system for the naphtha produced can be evaluated. In this way, the light hydrocarbons are not sold, but it is a saving for the company itself. The same can be done for the middle distillate which are made of diesel and kerosene: these can power engines and machineries. In this scenario, the aim is not to get a profit but to reduce the annual expenditure, so the rate of return can be set to zero with a consequent reduction of the product price. In addition, it can reduce the environmental impact of the company and bring reputational benefits.

12. Bibliography

[1] I. S. Tagomori, P. R. R. Rochedo, and A. Szklo, “Techno-economic and georeferenced analysis of forestry residues-based Fischer-Tropsch diesel with carbon capture in Brazil,” *Biomass Bioenergy*, vol. 123, pp. 134–148, Apr. 2019, doi: 10.1016/j.biombioe.2019.02.018.

[2] C. Hamelinck, A. Faaij, H. Denuil, and H. Boerrigter, “Production of FT transportation fuels from biomass; technical options, process analysis and optimisation, and development potential,” *Energy*, vol. 29, no. 11, pp. 1743–1771, Sep. 2004, doi: 10.1016/j.energy.2004.01.002.

[3] M. Hillestad *et al.*, “Improving carbon efficiency and profitability of the biomass to liquid process with hydrogen from renewable power,” *Fuel*, vol. 234, pp. 1431–1451, Dec. 2018, doi: 10.1016/j.fuel.2018.08.004.

[4] K. Im-orb, L. Simasatitkul, and A. Arpornwichanop, “Techno-economic analysis of the biomass gasification and Fischer–Tropsch integrated process with off-gas recirculation,” *Energy*, vol. 94, pp. 483–496, Jan. 2016, doi: 10.1016/j.energy.2015.11.012.

[5] D. Barisano *et al.*, “HYDROGEN PRODUCTION FROM BIOMASS VIA GASIFICATION PROCESS: THE RESULTS OF THE EU UNIfHY PROJECT,” p. 8, 2017.

[6] C. T. Chang, M. Costa, M. La Villetta, A. Macaluso, D. Piazzullo, and L. Vanoli, “Thermo-economic analyses of a Taiwanese combined CHP system fuelled with syngas from rice husk gasification,” *Energy*, vol. 167, pp. 766–780, Jan. 2019, doi: 10.1016/j.energy.2018.11.012.

[7] Y.-D. Kim *et al.*, “Fischer–tropsch diesel production and evaluation as alternative automotive fuel in pilot-scale integrated biomass-to-liquid process,” *Appl. Energy*, vol. 180, pp. 301–312, Oct. 2016, doi: 10.1016/j.apenergy.2016.07.095.

[8] A. S. Snehesh, H. S. Mukunda, S. Mahapatra, and S. Dasappa, “Fischer-Tropsch route for the conversion of biomass to liquid fuels - Technical and economic analysis,” *Energy*, vol. 130, pp. 182–191, Jul. 2017, doi: 10.1016/j.energy.2017.04.101.

[9] “Cambridge Dictionary.” https://dictionary.cambridge.org/it/dizionario/inglese/biomass.

[10] “Key World Energy Statistics 2019,” p. 81.

[11] B. Mola-Yudego *et al.*, “Wood biomass potentials for energy in northern Europe: Forest or plantations?,” *Biomass Bioenergy*, vol. 106, pp. 95–103, Nov. 2017, doi: 10.1016/j.biombioe.2017.08.021.

[12] “L’Unione europea e le foreste,” *Parlamento europeo*. https://www.europarl.europa.eu/factsheets/it/sheet/105/l-unione-europea-e-le-foreste.

[13] A. Schuck, “Compilation of a Calibrated European Forest Map Derived from NOAA-AVHRR Data.” European Forest Institute, 2002.

[14] V. B. Veljković *et al.*, “Biodiesel production from corn oil: A review,” *Renew. Sustain. Energy Rev.*, vol. 91, pp. 531–548, Aug. 2018, doi: 10.1016/j.rser.2018.04.024.

[15] S. H. Mohd Azhar *et al.*, “Yeasts in sustainable bioethanol production: A review,” *Biochem. Biophys. Rep.*, vol. 10, pp. 52–61, Jul. 2017, doi: 10.1016/j.bbrep.2017.03.003.

[16] A. T. Sipra, N. Gao, and H. Sarwar, “Municipal solid waste (MSW) pyrolysis for bio-fuel production: A review of effects of MSW components and catalysts,” *Fuel Process. Technol.*, vol. 175, pp. 131–147, Jun. 2018, doi: 10.1016/j.fuproc.2018.02.012.

[17] C. Higman, “Gasification processes and synthesis gas treatment technologies for carbon dioxide (C 0 2) capture,” p. 37.

[18] K. Göransson, U. Söderlind, J. He, and W. Zhang, “Review of syngas production via biomass DFBGs,” *Renew. Sustain. Energy Rev.*, vol. 15, no. 1, pp. 482–492, Jan. 2011, doi: 10.1016/j.rser.2010.09.032.

[19] “L’Italia e l’autarchia,” *Treccani.it*. http://www.treccani.it/enciclopedia/l-italia-e-l-autarchia_%28Il-Contributo-italiano-alla-storia-del-Pensiero:-Tecnica%29/.

[20] “Fascismo e autarchia,” *Fondazionemicheletti.eu*. https://www.fondazionemicheletti.eu/public/contents/26-lezioni-novecento/allegati/file/04_07_Autarchia.pdf.

[21] C. Higman, “State of the Gasification Industry: Worldwide Gasification Database 2014 Update,” p. 22.

[22] C. Freda, F. Nanna, A. Villone, D. Barisano, S. Brandani, and G. Cornacchia, “Air gasification of digestate and its co-gasification with residual biomass in a pilot scale rotary kiln,” *Int. J. Energy Environ. Eng.*, vol. 10, no. 3, pp. 335–346, Sep. 2019, doi: 10.1007/s40095-019-0310-3.

[23] W. Doherty, A. Reynolds, and D. Kennedy, “Aspen Plus Simulation of Biomass Gasification in a Steam Blown Dual Fluidised Bed,” p. 10, 2013.

[24] P. Guo *et al.*, “Gasification Reactivity and Physicochemical Properties of the Chars from Raw and Torrefied Wood, Grape Marc, and Macroalgae,” *Energy Fuels*, vol. 31, no. 3, pp. 2246–2259, Mar. 2017, doi: 10.1021/acs.energyfuels.6b02215.

[25] S. A. Opatokun, V. Strezov, and T. Kan, “Product based evaluation of pyrolysis of food waste and its digestate,” *Energy*, vol. 92, pp. 349–354, Dec. 2015, doi: 10.1016/j.energy.2015.02.098.

[26] M. S. Eikeland, R. K. Thapa, and B. M. Halvorsen, “Aspen Plus Simulation of Biomass Gasification with Known Reaction Kinetic,” Nov. 2015, pp. 149–156, doi: 10.3384/ecp15119149.

[27] M. Fernandez-Lopez, J. Pedroche, J. L. Valverde, and L. Sanchez-Silva, “Simulation of the gasification of animal wastes in a dual gasifier using Aspen Plus®,” *Energy Convers. Manag.*, vol. 140, pp. 211–217, May 2017, doi: 10.1016/j.enconman.2017.03.008.

[28] M. H. Rahman, L. Daniel, U. Shah, X. Bi, J. R. Grace, and C. J. Lim, “Estimation of solids circulation rate and char transfer rate from gasifier to combustor in a dual fluidized-bed pilot plant for biomass steam gasification,” *Particuology*, vol. 46, pp. 22–29, Oct. 2019, doi: 10.1016/j.partic.2019.03.004.

[29] M. B. Nikoo and N. Mahinpey, “Simulation of biomass gasification in fluidized bed reactor using ASPEN PLUS,” *Biomass Bioenergy*, vol. 32, no. 12, pp. 1245–1254, Dec. 2008, doi: 10.1016/j.biombioe.2008.02.020.

[30] R. Timsina, R. K. Thapa, and M. S. Eikeland, “Aspen Plus simulation of biomass gasification for different types of biomass,” Jan. 2020, pp. 151–157, doi: 10.3384/ecp20170151.

[31] P. Kaushal, T. Pröll, and H. Hofbauer, “Model development and validation: Co-combustion of residual char, gases and volatile fuels in the fast fluidized combustion chamber of a dual fluidized bed biomass gasifier,” *Fuel*, vol. 86, no. 17–18, pp. 2687–2695, Dec. 2007, doi: 10.1016/j.fuel.2007.03.032.

[32] U. Arena, “Process and technological aspects of municipal solid waste gasification. A review,” *Waste Manag.*, vol. 32, no. 4, pp. 625–639, Apr. 2012, doi: 10.1016/j.wasman.2011.09.025.

[33] D. Barisano *et al.*, “Steam/oxygen biomass gasification at pilot scale in an internally circulating bubbling fluidized bed reactor,” *Fuel Process. Technol.*, vol. 141, pp. 74–81, Jan. 2016, doi: 10.1016/j.fuproc.2015.06.008.

[34] F. Gallucci *et al.*, “Influence of Oxidant Agent on Syngas Composition: Gasification of Hazelnut Shells through an Updraft Reactor,” *Energies*, vol. 13, no. 1, p. 102, Dec. 2019, doi: 10.3390/en13010102.

[35] L. P. R. Pala, Q. Wang, G. Kolb, and V. Hessel, “Steam gasification of biomass with subsequent syngas adjustment using shift reaction for syngas production: An Aspen Plus model,” *Renew. Energy*, vol. 101, pp. 484–492, Feb. 2017, doi: 10.1016/j.renene.2016.08.069.

[36] R. Ø. Gadsbøll, Z. Sárossy, L. Jørgensen, J. Ahrenfeldt, and U. B. Henriksen, “Oxygen-blown operation of the TwoStage Viking gasifier,” *Energy*, vol. 158, pp. 495–503, Sep. 2018, doi: 10.1016/j.energy.2018.06.071.

[37] P. Basu, “Design of Biomass Gasifiers,” in *Biomass Gasification, Pyrolysis and Torrefaction*, Elsevier, 2018, pp. 263–329.

[38] R. Warnecke, “Gasi®cation of biomass: comparison of ®xed bed and ¯uidized bed gasi®er,” *Biomass Bioenergy*, p. 9, 2000.

[39] J. K. Neathery, “Chapter 4. Biomass Gasification,” in *Energy and Environment Series*, M. Crocker, Ed. Cambridge: Royal Society of Chemistry, 2010, pp. 67–94.

[40] P. Basu, “Gasification Theory,” in *Biomass Gasification, Pyrolysis and Torrefaction*, Elsevier, 2018, pp. 211–262.

[41] S. Rapagnà, K. Gallucci, and P. U. Foscolo, “Olivine, dolomite and ceramic filters in one vessel to produce clean gas from biomass,” *Waste Manag.*, vol. 71, pp. 792–800, Jan. 2018, doi: 10.1016/j.wasman.2017.07.038.

[42] M. Lapuerta, J. J. Hernández, A. Pazo, and J. López, “Gasification and co-gasification of biomass wastes: Effect of the biomass origin and the gasifier operating conditions,” *Fuel Process. Technol.*, vol. 89, no. 9, pp. 828–837, Sep. 2008, doi: 10.1016/j.fuproc.2008.02.001.

[43] C. Pfeifer, S. Koppatz, and H. Hofbauer, “Steam gasification of various feedstocks at a dual fluidised bed gasifier: Impacts of operation conditions and bed materials,” *Biomass Convers. Biorefinery*, vol. 1, no. 1, pp. 39–53, Mar. 2011, doi: 10.1007/s13399-011-0007-1.

[44] J. C. Schmid, T. Pröll, H. Kitzler, C. Pfeifer, and H. Hofbauer, “Cold flow model investigations of the countercurrent flow of a dual circulating fluidized bed gasifier,” *Biomass Convers. Biorefinery*, vol. 2, no. 3, pp. 229–244, Sep. 2012, doi: 10.1007/s13399-012-0035-5.

[45] A. A. Khan, W. de Jong, P. J. Jansens, and H. Spliethoff, “Biomass combustion in fluidized bed boilers: Potential problems and remedies,” *Fuel Process. Technol.*, vol. 90, no. 1, pp. 21–50, Jan. 2009, doi: 10.1016/j.fuproc.2008.07.012.

[46] F. Fischer, H. TRoPsCH, and O. Muleeim-On-The-Buhr, “UNITED STATES PATENT OFFICE,” p. 3.

[47] R. G. dos Santos and A. C. Alencar, “Biomass-derived syngas production via gasification process and its catalytic conversion into fuels by Fischer Tropsch synthesis: A review,” *Int. J. Hydrog. Energy*, p. S0360319919327090, Aug. 2019, doi: 10.1016/j.ijhydene.2019.07.133.

[48] M. J. Overett, R. O. Hill, and J. R. Moss, “Organometallic chemistry and surface science: mechanistic models for the Fischer–Tropsch synthesis,” *Coord. Chem. Rev.*, vol. 206–207, pp. 581–605, Sep. 2000, doi: 10.1016/S0010-8545(00)00249-6.

[49] G. Jacobs and B. H. Davis, “Chapter 5. Conversion of Biomass to Liquid Fuels and Chemicals via the Fischer–Tropsch Synthesis Route,” in *Energy and Environment Series*, M. Crocker, Ed. Cambridge: Royal Society of Chemistry, 2010, pp. 95–124.

[50] M. Panahi, E. Yasari, and A. Rafiee, “Multi-objective optimization of a gas-to-liquids (GTL) process with staged Fischer-Tropsch reactor,” *Energy Convers. Manag.*, vol. 163, pp. 239–249, May 2018, doi: 10.1016/j.enconman.2018.02.068.

[51] G. Cinti, A. Baldinelli, A. Di Michele, and U. Desideri, “Integration of Solid Oxide Electrolyzer and Fischer-Tropsch: A sustainable pathway for synthetic fuel,” *Appl. Energy*, vol. 162, pp. 308–320, Jan. 2016, doi: 10.1016/j.apenergy.2015.10.053.

[52] R. Luque, A. R. de la Osa, J. M. Campelo, A. A. Romero, J. L. Valverde, and P. Sanchez, “Design and development of catalysts for Biomass-To-Liquid-Fischer–Tropsch (BTL-FT) processes for biofuels production,” *Energy Env. Sci*, vol. 5, no. 1, pp. 5186–5202, 2012, doi: 10.1039/C1EE02238E.

[53] S. Zheng, Y. Liu, J. Li, and B. Shi, “Deuterium tracer study of pressure effect on product distribution in the cobalt-catalyzed Fischer–Tropsch synthesis,” *Appl. Catal. Gen.*, vol. 330, pp. 63–68, Oct. 2007, doi: 10.1016/j.apcata.2007.07.010.

[54] S. S. Ail and S. Dasappa, “Biomass to liquid transportation fuel via Fischer Tropsch synthesis – Technology review and current scenario,” *Renew. Sustain. Energy Rev.*, vol. 58, pp. 267–286, May 2016, doi: 10.1016/j.rser.2015.12.143.

[55] R. M. Swanson, A. Platon, J. A. Satrio, R. C. Brown, and D. D. Hsu, “Techno-Economic Analysis of Biofuels Production Based on Gasification,” NREL/TP-6A20-46587, 994017, Nov. 2010. doi: 10.2172/994017.

[56] R. Rauch, A. Kiennemann, and A. Sauciuc, “Fischer-Tropsch Synthesis to Biofuels (BtL Process),” in *The Role of Catalysis for the Sustainable Production of Bio-fuels and Bio-chemicals*, Elsevier, 2013, pp. 397–443.

[57] R. Luque, J. M. Campelo, and J. Clark, *Handbook of biofuels production*. Woodhead Publishing Limited, 2011.

[58] “Cobalt historical data,” *Investing.com*. https://www.investing.com/commodities/cobalt-historical-data.

[59] R.-U. Dietrich *et al.*, “Cost calculations for three different approaches of biofuel production using biomass, electricity and CO 2,” *Biomass Bioenergy*, vol. 111, pp. 165–173, Apr. 2018, doi: 10.1016/j.biombioe.2017.07.006.

[60] K. Dussan and R. F. D. Monaghan, "Integrated Thermal Conversion and Anaerobic Digestion for Sludge Management in Wastewater Treatment Plants," *Waste Biomass Valorization*, vol. 9, no. 1, pp. 65–85, Jan. 2018, doi: 10.1007/s12649-016-9812-x.

[61] A. Dutta *et al.*, "Process Design and Economics for Conversion of Lignocellulosic Biomass to Ethanol: Thermochemical Pathway by Indirect Gasification and Mixed Alcohol Synthesis," NREL/TP-5100-51400, 1015885, May 2011. doi: 10.2172/1015885.

[62] W. Elsner, M. Wysocki, P. Niegodajew, and R. Borecki, "Experimental and economic study of small-scale CHP installation equipped with downdraft gasifier and internal combustion engine," *Appl. Energy*, vol. 202, pp. 213–227, Sep. 2017, doi: 10.1016/j.apenergy.2017.05.148.

[63] J. Francois *et al.*, "Detailed process modeling of a wood gasification combined heat and power plant," *Biomass Bioenergy*, vol. 51, pp. 68–82, Apr. 2013, doi: 10.1016/j.biombioe.2013.01.004.

[64] N. C. Henao, E. E. S. Lora, D. M. Y. Maya, O. J. Venturini, and E. H. M. Franco, "Technical feasibility study of 200 kW gas microturbine coupled to a dual fluidized bed gasifier," *Biomass Bioenergy*, vol. 130, p. 105369, Nov. 2019, doi: 10.1016/j.biombioe.2019.105369.

[65] M. Martín and I. E. Grossmann, "Energy optimization of bioethanol production via gasification of switchgrass," *AIChE J.*, vol. 57, no. 12, pp. 3408–3428, Dec. 2011, doi: 10.1002/aic.12544.

[66] L. Menin, S. Vakalis, V. Benedetti, F. Patuzzi, and M. Baratieri, "Techno-economic assessment of an integrated biomass gasification, electrolysis, and syngas biomethanation process," *Biomass Convers. Biorefinery*, Feb. 2020, doi: 10.1007/s13399-020-00654-9.

[67] M. J. Prins, K. J. Ptasinski, and F. J. J. G. Janssen, "Exergetic optimisation of a production process of Fischer–Tropsch fuels from biomass," *Fuel Process. Technol.*, vol. 86, no. 4, pp. 375–389, Jan. 2005, doi: 10.1016/j.fuproc.2004.05.008.

[68] M. Rafati, L. Wang, D. C. Dayton, K. Schimmel, V. Kabadi, and A. Shahbazi, "Techno-economic analysis of production of Fischer-Tropsch liquids via biomass gasification: The effects of Fischer-Tropsch catalysts and natural gas co-feeding," *Energy Convers. Manag.*, vol. 133, pp. 153–166, Feb. 2017, doi: 10.1016/j.enconman.2016.11.051.

[69] Y. K. Salkuyeh, B. A. Saville, and H. L. MacLean, "Techno-economic analysis and life cycle assessment of hydrogen production from different biomass gasification processes," *Int. J. Hydrog. Energy*, vol. 43, no. 20, pp. 9514–9528, May 2018, doi: 10.1016/j.ijhydene.2018.04.024.

[70] S. Spyrakis, K. D. Panopoulos, and E. Kakaras, "Synthesis, Modeling and Exergy Analysis of Atmospheric Air Blown Biomass Gasification for Fischer-Tropsch Process," p. 6.

[71] H. Thunman, C. Gustavsson, A. Larsson, I. Gunnarsson, and F. Tengberg, "Economic assessment of advanced biofuel production via gasification using cost data from the GoBiGas plant," *Energy Sci. Eng.*, vol. 7, no. 1, pp. 217–229, Feb. 2019, doi: 10.1002/ese3.271.

[72] M. J. A. Tijmensen, A. P. C. Faaij, and C. N. Hamelinck, "Exploration of the possibilities for production of Fischer Tropsch liquids and power via biomass gasiÿcation," *Biomass Bioenergy*, p. 24, 2002.

[73] F. Trippe, M. Fröhling, F. Schultmann, R. Stahl, E. Henrich, and A. Dalai, "Comprehensive techno-economic assessment of dimethyl ether (DME) synthesis and Fischer–Tropsch synthesis as alternative process steps within biomass-to-liquid production," *Fuel Process. Technol.*, vol. 106, pp. 577–586, Feb. 2013, doi: 10.1016/j.fuproc.2012.09.029.

[74] S. Tuomi, E. Kurkela, I. Hannula, and C.-G. Berg, "The impact of biomass drying on the efficiency of a gasification plant co-producing Fischer-Tropsch fuels and heat – A conceptual investigation," *Biomass Bioenergy*, vol. 127, p. 105272, Aug. 2019, doi: 10.1016/j.biombioe.2019.105272.

[75] G. Venturi, "La sostenibilità dell'energia da biomassa, un tema complesso," *Qualenergia.it*, Apr. 16, 2020. https://www.qualenergia.it/articoli/la-sostenibilita-dellenergia-da-biomassa-un-tema-complesso/.

[76] G. Ferrari, "In Europa si tagliano sempre più alberi," *Focus*, Jul. 09, 2020. https://www.focus.it/ambiente/ecologia/in-europa-si-tagliano-sempre-piu-alberi.

[77] Q.-V. Bach, H.-R. Gye, and C.-J. Lee, "Process modeling for steam biomass gasification in a dual fluidized bed gasifier," in *Computer Aided Chemical Engineering*, vol. 44, Elsevier, 2018, pp. 343–348.

[78] W. L. Saw and S. Pang, “The influence of calcite loading on producer gas composition and tar concentration of radiata pine pellets in a dual fluidised bed steam gasifier,” *Fuel*, vol. 102, pp. 445–452, Dec. 2012, doi: 10.1016/j.fuel.2012.07.013.

[79] A. Chiodini, L. Bua, L. Carnelli, R. Zwart, B. Vreugdenhil, and M. Vocciante, “Enhancements in Biomass-to-Liquid processes: Gasification aiming at high hydrogen/carbon monoxide ratios for direct Fischer-Tropsch synthesis applications,” *Biomass Bioenergy*, vol. 106, pp. 104–114, Nov. 2017, doi: 10.1016/j.biombioe.2017.08.022.

[80] A. Colantoni, L. Longo, F. Gallucci, and D. Monarca, “Pyro-gasification of hazelnut pruning using a downdraft gasifier for concurrent production of syngas and biochar,” *Contemp. Eng. Sci.*, vol. 9, pp. 1339–1348, 2016, doi: 10.12988/ces.2016.68142.

[81] V. Marcantonio, E. Bocci, and D. Monarca, “Development of a Chemical Quasi-Equilibrium Model of Biomass Waste Gasification in a Fluidized-Bed Reactor by Using Aspen Plus,” *Energies*, vol. 13, no. 1, p. 53, Dec. 2019, doi: 10.3390/en13010053.

[82] Xiao, Wang, Zheng, Qin, and Zhou, “Catalytic Coal Gasification Process Simulation with Alkaline Organic Wastewater in a Fluidized Bed Reactor Using Aspen Plus,” *Energies*, vol. 12, no. 7, p. 1367, Apr. 2019, doi: 10.3390/en12071367.

[83] J. Neumann, S. Binder, A. Apfelbacher, J. R. Gasson, P. Ramírez García, and A. Hornung, “Production and characterization of a new quality pyrolysis oil, char and syngas from digestate – Introducing the thermo-catalytic reforming process,” *J. Anal. Appl. Pyrolysis*, vol. 113, pp. 137–142, May 2015, doi: 10.1016/j.jaap.2014.11.022.

[84] D. Wiśniewski, J. Gołaszewski, and A. Białowiec, “The pyrolysis and gasification of digestate from agricultural biogas plant / Piroliza i gazyfikacja pofermentu z biogazowni rolniczych,” *Arch. Environ. Prot.*, vol. 41, no. 3, pp. 70–75, Sep. 2015, doi: 10.1515/aep-2015-0032.

[85] N. Lacroix, D. R. Rousse, and R. Hausler, “Anaerobic digestion and gasification coupling for wastewater sludge treatment and recovery,” *Waste Manag. Res.*, vol. 32, no. 7, pp. 608–613, Jul. 2014, doi: 10.1177/0734242X14538308.

[86] N. Antoniou, F. Monlau, C. Sambusiti, E. Ficara, A. Barakat, and A. Zabaniotou, “Contribution to Circular Economy options of mixed agricultural wastes management: Coupling anaerobic digestion with gasification for enhanced energy and material recovery,” *J. Clean. Prod.*, vol. 209, pp. 505–514, Feb. 2019, doi: 10.1016/j.jclepro.2018.10.055.

[87] G. Chen, X. Guo, Z. Cheng, B. Yan, Z. Dan, and W. Ma, “Air gasification of biogas-derived digestate in a downdraft fixed bed gasifier,” *Waste Manag.*, vol. 69, pp. 162–169, Nov. 2017, doi: 10.1016/j.wasman.2017.08.001.

[88] D. Brown, J. Shi, and Y. Li, “Comparison of solid-state to liquid anaerobic digestion of lignocellulosic feedstocks for biogas production,” *Bioresour. Technol.*, vol. 124, pp. 379–386, Nov. 2012, doi: 10.1016/j.biortech.2012.08.051.

[89] Wood, “Digestate and compost as organic fertilisers – Risk assessment and risk management options,” Wood Environment & Infrastructure Solutions UK Limited, Feb. 2019.

[90] M. Marchese, E. Giglio, M. Santarelli, and A. Lanzini, “Energy performance of Power-to-Liquid applications integrating biogas upgrading, reverse water gas shift, solid oxide electrolysis and Fischer-Tropsch technologies,” *Energy Convers. Manag. X*, vol. 6, p. 100041, Apr. 2020, doi: 10.1016/j.ecmx.2020.100041.

[91] A. Blank and E. Hoffmann, “Upgrading of a co-digestion plant by implementation of a hydrolysis stage,” *Waste Manag. Res.*, vol. 29, no. 11, pp. 1145–1152, Nov. 2011, doi: 10.1177/0734242X11423954.

[92] M. Nacken, L. Ma, S. Heidenreich, F. Verpoort, and G. V. Baron, “Development of a catalytic ceramic foam for efficient tar reforming of a catalytic filter for hot gas cleaning of biomass-derived syngas,” *Appl. Catal. B Environ.*, vol. 125, pp. 111–119, Aug. 2012, doi: 10.1016/j.apcatb.2012.05.027.

[93] H. R. Sara, B. Enrico, V. Mauro, D. C. Andrea, and N. Vincenzo, “Techno-economic Analysis of Hydrogen Production Using Biomass Gasification -A Small Scale Power Plant Study,” *Energy Procedia*, vol. 101, pp. 806–813, Nov. 2016, doi: 10.1016/j.egypro.2016.11.102.

[94] L. F. de Diego *et al.*, “Tar abatement for clean syngas production during biomass gasification in a dual fluidized bed,” *Fuel Process. Technol.*, vol. 152, pp. 116–123, Nov. 2016, doi: 10.1016/j.fuproc.2016.05.042.

[95] S. Kraft, F. Kirnbauer, and H. Hofbauer, “CPFD simulations of an industrial-sized dual fluidized bed steam gasification system of biomass with 8 MW fuel input,” *Appl. Energy*, vol. 190, pp. 408–420, Mar. 2017, doi: 10.1016/j.apenergy.2016.12.113.

[96] B. Hernandez and M. Martin, “Optimization for biogas to chemicals via tri-reforming. Analysis of Fischer-Tropsch fuels from biogas,” *Energy Convers. Manag.*, vol. 174, pp. 998–1013, Oct. 2018, doi: 10.1016/j.enconman.2018.08.074.

[97] G. Herz, E. Reichelt, and M. Jahn, “Design and evaluation of a Fischer-Tropsch process for the production of waxes from biogas,” *Energy*, vol. 132, pp. 370–381, Aug. 2017, doi: 10.1016/j.energy.2017.05.102.

[98] P. J. Woolcock and R. C. Brown, “A review of cleaning technologies for biomass-derived syngas,” *Biomass Bioenergy*, vol. 52, pp. 54–84, May 2013, doi: 10.1016/j.biombioe.2013.02.036.

[99] M. Mayerhofer, P. Mitsakis, X. Meng, W. de Jong, H. Spliethoff, and M. Gaderer, “Influence of pressure, temperature and steam on tar and gas in allothermal fluidized bed gasification,” *Fuel*, vol. 99, pp. 204–209, Sep. 2012, doi: 10.1016/j.fuel.2012.04.022.

[100] “Tars: Composition and Characteristics,” *All power labs*. http://wiki.gekgasifier.com/w/page/6123830/Tars%3A%20Composition%20and%20Characteristics.

[101] J. Han and H. Kim, “The reduction and control technology of tar during biomass gasification/pyrolysis: An overview,” *Renew. Sustain. Energy Rev.*, vol. 12, no. 2, pp. 397–416, Feb. 2008, doi: 10.1016/j.rser.2006.07.015.

[102] M. W. Seo *et al.*, “Methanol absorption characteristics for the removal of H2S (hydrogen sulfide), COS (carbonyl sulfide) and CO2 (carbon dioxide) in a pilot-scale biomass-to-liquid process,” *Energy*, vol. 66, pp. 56–62, Mar. 2014, doi: 10.1016/j.energy.2013.08.038.

[103] X. Gamisans, “Gas pollutants removal in a single- and two-stage ejector–venturi scrubber,” *J. Hazard. Mater.*, vol. 90, no. 3, pp. 251–266, Mar. 2002, doi: 10.1016/S0304-3894(01)00352-1.

[104] W. J. Nock, M. Walker, R. Kapoor, and S. Heaven, “Modeling the Water Scrubbing Process and Energy Requirements for CO $_2$ Capture to Upgrade Biogas to Biomethane,” *Ind. Eng. Chem. Res.*, vol. 53, no. 32, pp. 12783–12792, Aug. 2014, doi: 10.1021/ie501280p.

[105] M. Asadullah, “Biomass gasification gas cleaning for downstream applications: A comparative critical review,” *Renew. Sustain. Energy Rev.*, vol. 40, pp. 118–132, Dec. 2014, doi: 10.1016/j.rser.2014.07.132.

[106] T. G. Kreutz, E. D. Larson, G. Liu, and R. H. Williams, “Fischer-Tropsch Fuels from Coal and Biomass,” p. 86.

[107] H. Ahn, M. Luberti, Z. Liu, and S. Brandani, “Process configuration studies of the amine capture process for coal-fired power plants,” *Int. J. Greenh. Gas Control*, vol. 16, pp. 29–40, Aug. 2013, doi: 10.1016/j.ijggc.2013.03.002.

[108] D. Aaron and C. Tsouris, “Separation of CO $_2$ from Flue Gas: A Review,” *Sep. Sci. Technol.*, vol. 40, no. 1–3, pp. 321–348, Jan. 2005, doi: 10.1081/SS-200042244.

[109] C. A. Grande, “Advances in Pressure Swing Adsorption for Gas Separation,” *ISRN Chem. Eng.*, vol. 2012, pp. 1–13, 2012, doi: 10.5402/2012/982934.

[110] L. Riboldi and O. Bolland, “Overview on Pressure Swing Adsorption (PSA) as CO2 Capture Technology: State-of-the-Art, Limits and Potentials,” *Energy Procedia*, vol. 114, pp. 2390–2400, Jul. 2017, doi: 10.1016/j.egypro.2017.03.1385.

[111] J. C. Meerman, M. M. J. Knoope, A. Ramírez, W. C. Turkenburg, and A. P. C. Faaij, “Technical and economic prospects of coal- and biomass-fired integrated gasification facilities equipped with CCS over time,” *Int. J. Greenh. Gas Control*, vol. 16, pp. 311–323, Aug. 2013, doi: 10.1016/j.ijggc.2013.01.051.

[112] F. G. Albrecht, D. H. König, N. Baucks, and R.-U. Dietrich, “A standardized methodology for the techno-economic evaluation of alternative fuels – A case study,” *Fuel*, vol. 194, pp. 511–526, Apr. 2017, doi: 10.1016/j.fuel.2016.12.003.

[113] S. A. Rackley, "Absorption Capture Systems," in *Carbon Capture and Storage*, Elsevier, 2010, pp. 103–131.

[114] C.-H. Yu, C.-H. Huang, and C.-S. Tan, "A Review of CO2 Capture by Absorption and Adsorption," *Aerosol Air Qual. Res.*, vol. 12, no. 5, pp. 745–769, 2012, doi: 10.4209/aaqr.2012.05.0132.

[115] G. D. Oreggioni, S. Brandani, M. Luberti, Y. Baykan, D. Friedrich, and H. Ahn, "CO2 capture from syngas by an adsorption process at a biomass gasification CHP plant: Its comparison with amine-based CO2 capture," *Int. J. Greenh. Gas Control*, vol. 35, pp. 71–81, Apr. 2015, doi: 10.1016/j.ijggc.2015.01.008.

[116] A. M. Ribeiro, J. C. Santos, and A. E. Rodrigues, "Pressure swing adsorption for CO2 capture in Fischer-Tropsch fuels production from biomass," *Adsorption*, vol. 17, no. 3, pp. 443–452, Jun. 2011, doi: 10.1007/s10450-010-9280-8.

[117] Z. Y. Yeo, T. L. Chew, P. W. Zhu, A. R. Mohamed, and S.-P. Chai, "Conventional processes and membrane technology for carbon dioxide removal from natural gas: A review," *J. Nat. Gas Chem.*, vol. 21, no. 3, pp. 282–298, May 2012, doi: 10.1016/S1003-9953(11)60366-6.

[118] M. Marchese, N. Heikkinen, E. Giglio, A. Lanzini, J. Lehtonen, and M. Reinikainen, "Kinetic Study Based on the Carbide Mechanism of a Co-Pt/γ-Al2O3 Fischer–Tropsch Catalyst Tested in a Laboratory-Scale Tubular Reactor," *Catalysts*, vol. 9, no. 9, p. 717, Aug. 2019, doi: 10.3390/catal9090717.

[119] L. J. F. Comidy, M. D. Staples, and S. R. H. Barrett, "Technical, economic, and environmental assessment of liquid fuel production on aircraft carriers," *Appl. Energy*, vol. 256, p. 113810, Dec. 2019, doi: 10.1016/j.apenergy.2019.113810.

[120] OPRA turbines, "OP16 Gas Turbine Genset." .

[121] J. P. Stempien, M. Ni, Q. Sun, and S. H. Chan, "Thermodynamic analysis of combined Solid Oxide Electrolyzer and Fischer–Tropsch processes," *Energy*, vol. 81, pp. 682–690, Mar. 2015, doi: 10.1016/j.energy.2015.01.013.

[122] F. J. Campanario and F. J. Gutiérrez Ortiz, "Techno-economic assessment of bio-oil aqueous phase-to-liquids via Fischer-Tropsch synthesis and based on supercritical water reforming," *Energy Convers. Manag.*, vol. 154, pp. 591–602, Dec. 2017, doi: 10.1016/j.enconman.2017.10.096.

[123] Gioele Marcoberardino, Dario Vitali, Francesco Spinelli, Marco Binotti, and Giampaolo Manzolini, "Green Hydrogen Production from Raw Biogas: A Techno-Economic Investigation of Conventional Processes Using Pressure Swing Adsorption Unit," *Processes*, vol. 6, no. 3, p. 19, Feb. 2018, doi: 10.3390/pr6030019.

[124] "Electricity price statistics," Eurostat, Nov. 2019.

[125] O. Eriksson, M. Bisaillon, M. Haraldsson, and J. Sundberg, "Enhancement of biogas production from food waste and sewage sludge – Environmental and economic life cycle performance," *J. Environ. Manage.*, vol. 175, pp. 33–39, Jun. 2016, doi: 10.1016/j.jenvman.2016.03.022.

[126] P. Marocco *et al.*, "A study of the techno-economic feasibility of H2-based energy storage systems in remote areas," *Energy Convers. Manag.*, vol. 211, p. 112768, May 2020, doi: 10.1016/j.enconman.2020.112768.

[127] "Brent Oil Contract," *Investing.com*. https://www.investing.com/commodities/brent-oil.

[128] G. Herz, E. Reichelt, and M. Jahn, "Techno-economic analysis of a co-electrolysis-based synthesis process for the production of hydrocarbons," *Appl. Energy*, vol. 215, pp. 309–320, Apr. 2018, doi: 10.1016/j.apenergy.2018.02.007.

[129] S. M. Jarvis and S. Samsatli, "Technologies and infrastructures underpinning future CO 2 value chains: A comprehensive review and comparative analysis," *Renew. Sustain. Energy Rev.*, vol. 85, pp. 46–68, Apr. 2018, doi: 10.1016/j.rser.2018.01.007.

Appendix A – Aspen model

Gasifier blocks

TABLE 63 - GASIFIER BLOCKS LIST

Block	Type	Description
DECOMP	R-Yield	It decompounds the biomass in its fundamental components as pyrolysis process. Outputs are gases (H_2, O_2, N_2, H_2O, etc.) and solids (solid carbon and ash).
CHARSEP	Sep2	It divides ash and a fraction of char from gasses.
COMB	R-Stoic	It makes C and all other potential fuel (see plant layouts chapter) react with oxygen. Nitrogen oxides, carbon monoxide, dust and all other reactions are neglected.
NSCL	R-Stoic	It produces pollutants: NH_3, H_2S and HCl
GASSEP	Sep2	It splits the pollutants just made from whole other gas. Unless they would be decomposed in the next part.
GASIF1	R-Equil	It has all the gasification reactions (see *Table 3* **– Gasification reactions [32]**)
GASIF2	R-Equil	It has the role to modify the CH_4, H_2, CO and CO_2 yield using different approach temperatures for only WGS and methanation reactions.
MIX	Mix	It mixes all the streams.
DRIER	Sep2	It removes whole the water from the syngas. It has no physical role, it just needs to make design specifications work easily.
RETURN	Mix	It mixes all the streams.
ASHSEP	Sep2	It removes ash from flue gas.

Syngas clean-up and conditioning blocks

TABLE 64 - SYNGAS CLEAN-UP AND CONDITIONING BLOCKS LIST

Block	Type	Description
TARCRACK	RStoic	The reactor converts the 20% of methane (SMR) and the 70% of the ammonia. It is adiabatic.
SCRUBBER	Heater	It represents half of the scrubber. It cools down the syngas. Inlet water flow is not simulated. Gas flows out already saturated in water.
SEP3	Sep2	It removes 100% of NH_3 and HCl.
LPCOMPR	Compr	Compressor with efficiency reported elsewhere. Discharge pressure: 6.75 bar.
MPCOOLER	Heater	Cooler up to 35°C. The condense is discharged. A 0.45bar of pressure drop is taken into account for the PSA system.
PSA	Sep3	It simulates the system for acid gas removal (AGR). It removes 95% of CO_2.
HPCOMPR	Compr	Compressor with efficiency reported elsewhere. Discharge pressure: 30 bar.

Syncrude production blocks

TABLE 65 - SYNCRUDE PRODUCTION BLOCKS LIST

Block	Type	Description
MIX5	Mix	It mixes up the syngas with the recirculated part.
CH4SEP	Sep2	It has no physical meaning. It is useful just to simplify the FT reactor treating. Only CO and H_2 are sent to the reactor.
FT-REACT	R-Yield	It produces paraffins and olefins according to the hypothesis.
MIXFIN	Mix	It re-mixes the FT products with other gases.

FLASH	Flash2	Liquids are separated from gases/vapor which are recirculated back.
RECIRC	Split	Only a fraction of the gases is recirculated.
FTCOOL	Heater	It cools down the stream before the distiller 1
DIST1	Flash3	It works with 25°C and 12bar. Water is separated, off-gas, methane and LPG fractions are separated from syncrude.
GAS-REM	Sep2	To completely remove methane, ethane and gasses.
MIX4	Mix	To mix the gasses separated in GAS-REM with the others in DIST1.
DIST2	Flash2	It works with 200°C and 1bar. It separates gasoline fraction (high-volatile liquids) from the syncrude.
DIST3	Flash2	It works with 320°C and 1bar. It separates diesel-kerosene (middle distillate) from waxes and heavy oils.
HX-END-1	Heater	It cools down the light products
HX-END-2	Heater	It cools down the middle products
HX-END-3	Heater	It cools down the heavy products

BOP blocks

TABLE 66 - BALANCE OF PLANT BLOCKS LIST

Block	Type	Description
AIRBLOW	Compr	It brings air to 1.2bar.
AIR-PRE	Heater	To pre-heat air up to the specified temperature.
FLUECOOL	Heater	To cool down the flue gases from combustor up to 200°C.
BIOHX	Heater	To pre-heat the inlet biomass. Generally, it is not used.
SPLIT	Split	It is used in a DS. It could be used if the steam generation would be done in a large magnitude (e.g. connected to FT reaction) and so it could be useful to have this split instead a general mass flow specification.
W-PUMP	Pump	It compresses water up to 12bar (boiling temperature about 190°C, 20°C less than the FT reactor).
ECO	Heater	It brings water up to 180°C.
FT	Heater	It produces steam at 190°C.
LAM	Valve	It laminates the steam at 1.11bar.
STEAMSUP	Heater	It brings the steam up to specified temperature.
TG-COMPR	Compr	It compresses air up to 6.7bar.
COMB	R-Stoic	It represents the combustor.
TG-TURB	Compr	It expands the gas up to 1bar.
GVR	Heater	It cools down the flue gas from TG up to 100°C.

Aspen design specifications

TABLE 67 - DESIGN SPECIFICATIONS LIST

Design specification	Description
DS-N2	Nitrogen is used as purge gas. On paper of Doherty et al. [23], they consider nitrogen as 1.4% of the dried syngas.
DS-HEAT	It adjusts the char fraction split in the CHARSEP in order to keep the thermo-neutrality of the gasifier. It contains all the heats needed or produced by the reactors.
DS-AIR	Mass flow of air is adjusted in order to have 2%±0.5 of oxygen of flue gases.
DS-HCR	In some cases, it is required to keep constant the H_2/CO ratio varying the S/B one. It is set to 2±0.05.

DS-TG	It finds the right amount of air flowing in the TG to have a maximum temperature of 1000±10°C at the combustor outlet.

Aspen calculators

TABLE 68 - CALCULATORS LIST

Calculators	Description
C-AIRTEM	To make easy the change of air pre-heat and steam temperatures.
C-CGE	It calculates CGE, syngas LHV, H_2/CO syngas ratio, η_{FT} and $\eta_{syncrude}$
C-CO2	It calculates the total CO_2 emitted from the plant and the water balance.
C-DECOMP	It is requested from DECOMP block. It calculates the quantity of each elements that have to be produced from inlet biomass.
C-FT	This calculator works with an Excel datasheet is used to calculate the right amount of hydrocarbons and off-gas according to the hypothesis.
C-PCRUDE	It calculates the thermal power of the produced syncrude
C-POWER	It calculates the electric balance in the plant.
C-QBALANCE	It calculates the thermal balance in the gasifier section.
C-SBR	It calculates the steam/biomass ratio. It considered the moisture in the biomass as steam and it is done on dry basis.
C-TEMP	To make easy the change of gasifier temperature. It contains the temperature of all the blocks.

Aspen parameters

TABLE 69 – ASPEN PARAMETERS LIST

Parameter	Description
1	Heat balance in gasifier section
5	CGE (standard configuration only)
6	Gasifier temperature
7	LHV syngas from gasifier
8	S/B ratio
9	Syngas thermal power
10	Temperature of pre-heated air (gasifier section)
12	Steam temperature
13	Biomass pre-heat temperature
16	Plant power balance
17	H_2/CO of syngas from gasifier
18	H_2/CO of syngas in FT
19	Total CO_2 emitted
20	Thermal power of syncrude
21	$\eta_{syncrude}$ (from biomass to syncrude)
22	Heat produced by FT reactions
23	Plant water balance
24	Electric power from TG
25	η_{FT} (from syngas to syncrude)
26	Thermal power requests from the plant
27	Thermal power available (T>=200°C)

General parameters

TABLE 70 - GENERAL PARAMETERS LIST

Parameter	Value	Comments	Reference
Pressure drop on gasifier (steam)	0.11 bar		[95]
Pressure drop on combustor (air)	0.2 bar		[95]
Compressor isentropic efficiency	0.92		[111]
Compressor mechanical efficiency	0.95	Supposed	
Turbine isentropic efficiency	0.822		[111]
Turbine mechanical efficiency	0.95	Supposed	
Pump isentropic efficiency	0.92		[111]
Pump mechanical efficiency	0.95	Supposed	
GT pressure ratio	6.7		[120]
GT combustor temperature	1000°C	Supposed to obtain ~600°C of discharge temperature	[120]

Aspen Plus schemes

Gasifier

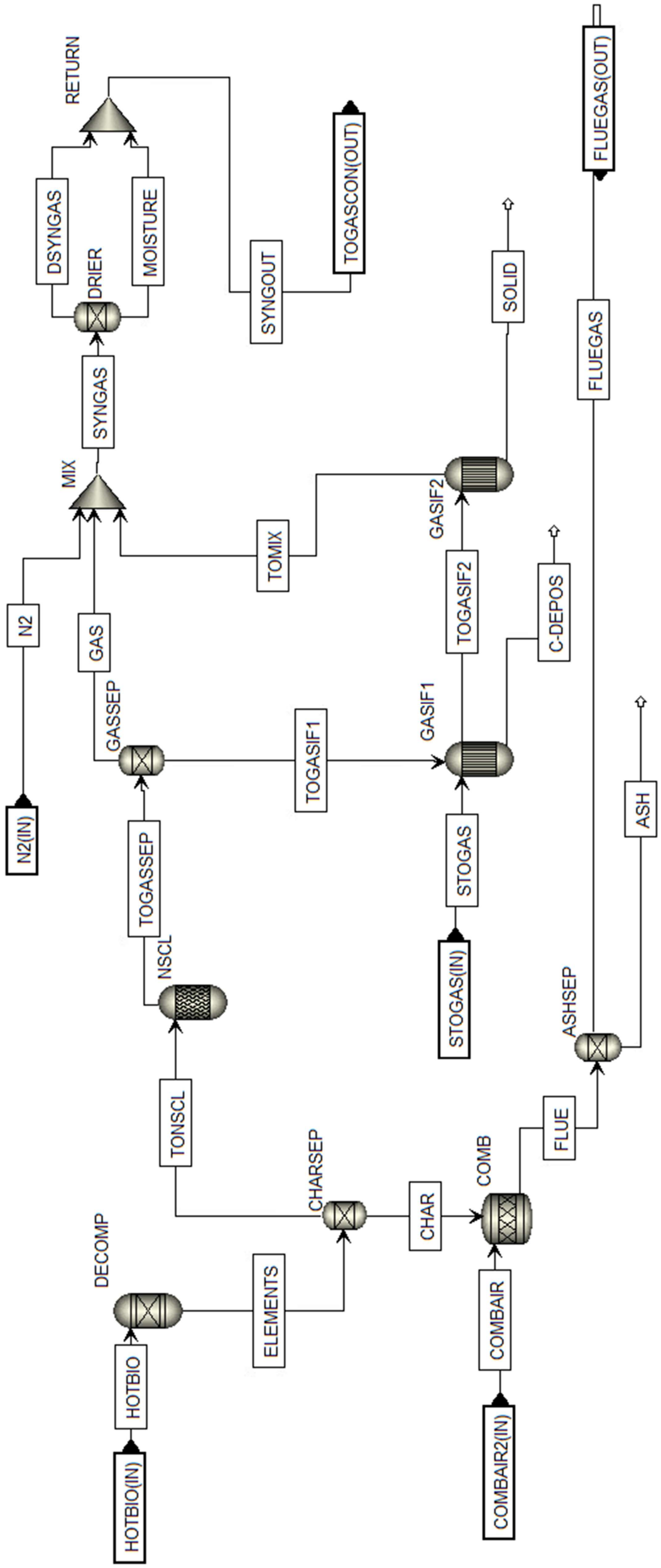

FIGURE 78 - GASIFIER ASPEN PLUS SCHEME

Syngas cleaning and conditioning

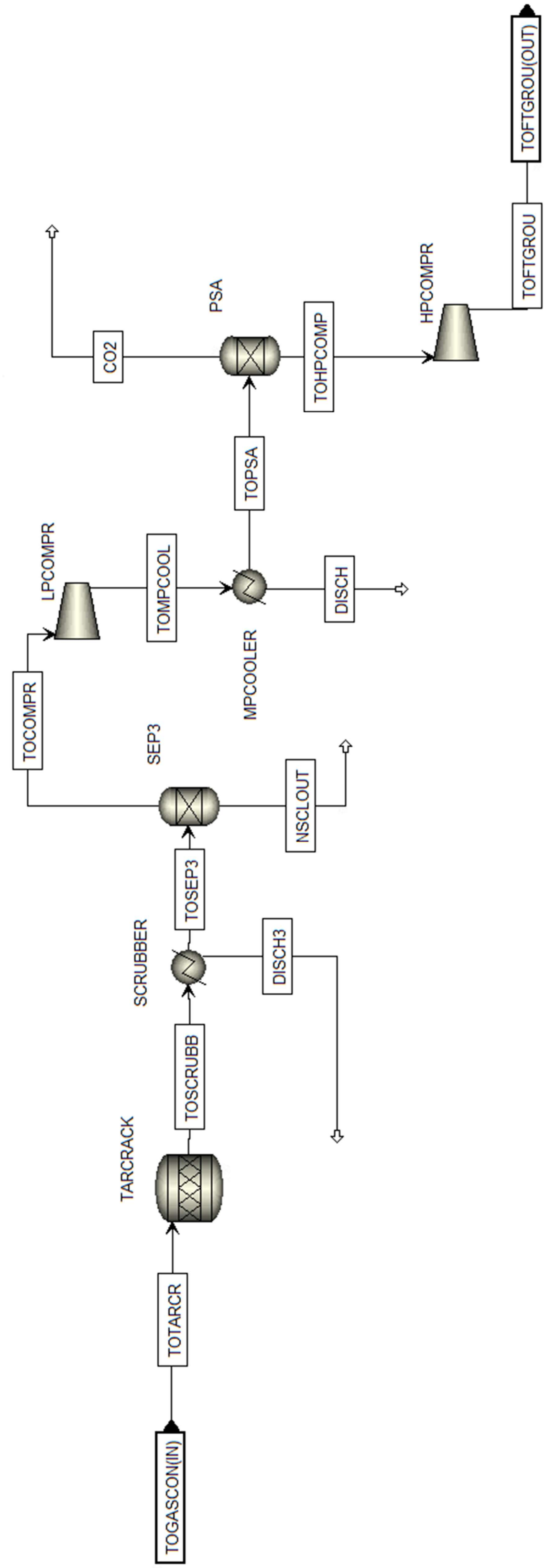

Figure 79 - Syngas cleaning and condition Aspen Plus scheme

Syncrude production

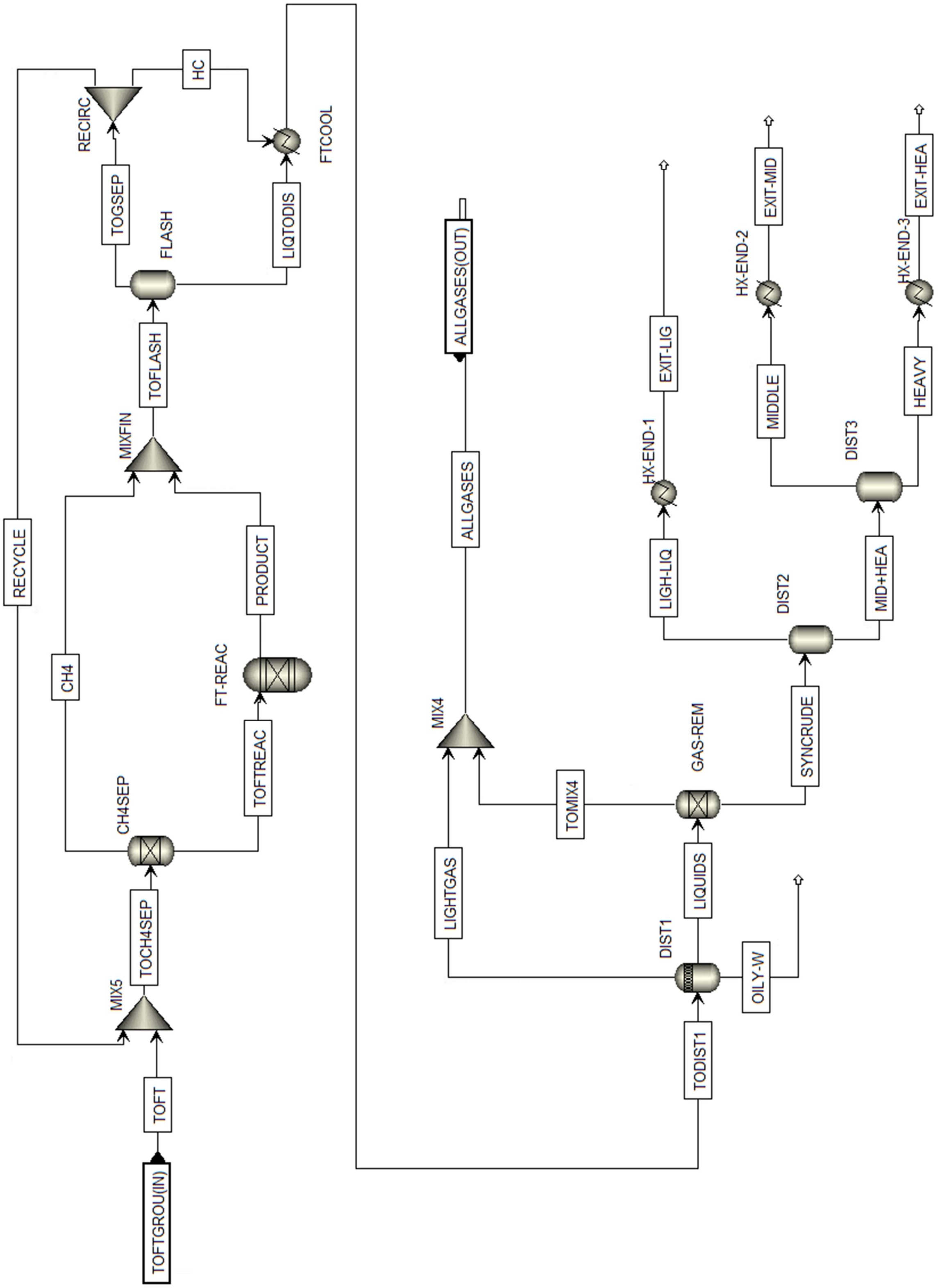

FIGURE 80 - SYNCRUDE PRODUCTION ASPEN PLUS SCHEME

BOP

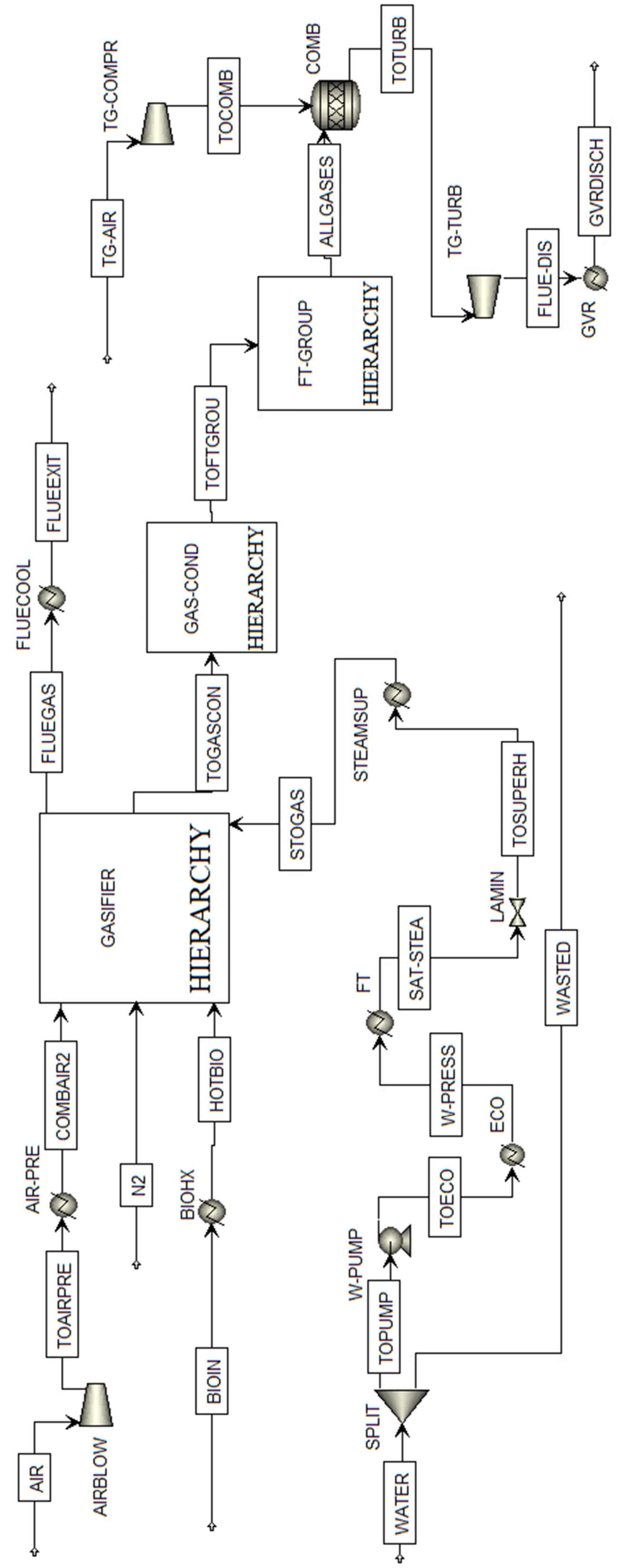

FIGURE 81 - BOP ASPEN PLUS SCHEME

Appendix B – Gasifier validation

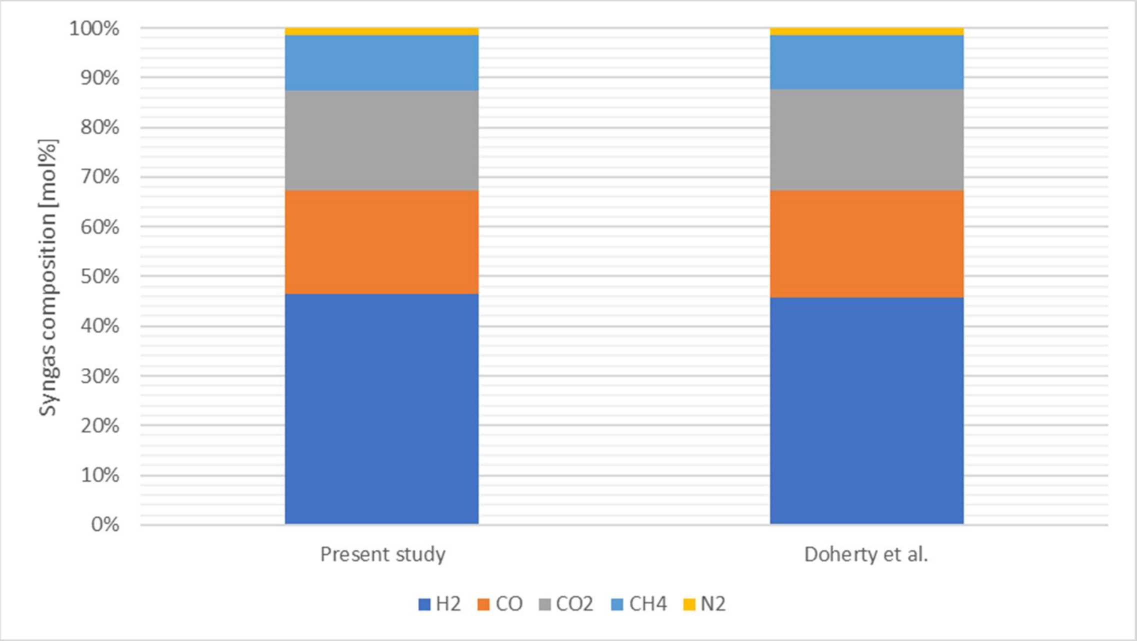

FIGURE 82 - SYNGAS COMPOSITION COMPARISON FOR VALIDATION

List of figures

List of tables

Acknowledgements

Questo lavoro è stato possibile grazie la collaborazione del mio relatore Andrea Lanzini e del mio correlatore Marco Marchese. Tengo fare un sentito ringraziamento a loro per il tempo speso per darmi consigli, informazioni utili e per revisionare l'elaborato. Ringrazio Marco non solo per l'aiuto tecnico, ma anche per la pazienza e disponibilità.

Voglio ringraziare tutte le persone che mi hanno dato una mano ad arrivare fin qui. In particolare voglio ringraziare i nonni tutti che mi hanno dato una mano dal punto di vista economico e che sono stati sempre orgogliosi di me. Ringrazio anche chi se n'è andato, molto prima o durante, ma che mi ha lasciato un segno, il quale, in modo diretto o indiretto, ha fatto sì che arrivassi qui.

Ringrazio gli amici e compagni di università, con i quali siamo riusciti a rendere meno duri i momenti difficili e sconfortanti. Sono stati importanti perché è anche grazie alla loro collaborazione che sono arrivato qui. Voglio quindi ringraziare Daniele, Fabrizio, Federica, Giacomo, Lorenzo, Luca, Silvia e Simone. Un ringraziamento speciale va invece ad Andrea, che con grande pazienza mi ha sopportato in questi anni, condividendo risorse ed energia e aiutandomi quando ne avevo bisogno.

Non posso dimenticare di ringraziare i miei amici fuori dall'università: sono cambiate tante cose in cinque anni, alcune amicizie sono andate e altre sono arrivate. Ci tengo a ringraziare quelli che ci sono stati sempre dal primo anno e che hanno reso questi anni indimenticabili. Ringrazio quindi Camilla, Giulia, Alberto, Emanuele, Matteo e Mattia, il quale ringrazio anche per le delucidazioni in materia economica che sono tornate utili nella tesi. Un sentito grazie va a Lorenzo, più di un amico, che ha saputo motivarmi e non lasciare che mollassi tutto, che quando avevo qualche problema era lì per ascoltarmi e sostenermi. Grazie anche a chi è arrivato durante il percorso come *la Bussola*, ma pure a chi se n'è andato contribuendo, anche se indirettamente, alla riuscita di tutto il percorso.

Infine, il ringraziamento più grande e speciale va a mio padre, che negli anni ha saputo incoraggiarmi e sostenermi sotto tutti i punti di vista, che ha sacrificato tempo ed energie perché fossi messo nelle migliori condizioni per affrontare l'università ed arrivare a concludere questo lavoro. Il suo contributo è stato fondamentale.

A tutti, grazie.