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Techno-economic evaluation of suitable conversion technologies for the production of biofuels from woody-biomass

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Preface

This thesis is an evaluation of conversion technologies for the production of biofuels from woody biomass which I have written this semester at the Norwegian University of Life Sciences (NMBU) Department of Mathematical Sciences and Technology. Bio-energy and especially biofuels has become one of my area of interest and it was very exciting writing about an industry which is under development here in Norway and in the rest of the world. I have gained knowledge during this semester which I will take with me after my stay at NMBU is over.

Ås, May 15th, 2015

Ola Sørby Omberg

Acknowledgements

I would like to thank my supervisor Dr. Jorge Mario Marchetti for the excellent job of supervising and motivating me this semester. My understanding and interest for biofuels grew as I was introduced by Dr. Marchetti to the field. I am very grateful for his support and encouragement.

My family has been behind me the whole time providing much needed comfort and support and I consider myself lucky to have such patience parents and siblings. Thanks to you all.

Abstract

In order to reduce emissions of greenhouse gases derived from the combustion of fossil fuels, renewable alternatives is currently being explored in order to replace conventional fossil feedstock for the generation of either heat and power or as transportation fuels and chemicals.

Woody biomass also referred to as lignocellulose biomass, constitutes a significant portion of the global biomass potential and provides a renewable feedstock for heat and power through direct combustion or it can be converted using suitable conversion-processes into chemical and fuels [1]. The scope of this thesis is to evaluate different conversion-technologies to identify the most suitable technology for producing biofuels from woody biomass.

In order to identify the most suitable conversion-technology using woody biomass as a feedstock for the production of biofuels an extensive literature review has been performed. In the literature review a selection of technologies has been presented and evaluated in order to find a suitable process able to produce liquid hydrocarbons from woody biomass. From the literature review two thermochemical conversion-pathways were considered best suited for utilizing woody biomass as feedstock. The processes to be further analyzed were pyrolysis and gasification. These technologies is evaluated and the process-path for producing liquid hydrocarbons is explained and compared against available literature and data.

Both technologies is found suited for producing gasoline and diesel from a woody biomass feedstock. When comparing the technologies, the pyrolysis-pathway provides a higher yield of hydrocarbons at lower investments cost and fuel selling price than the gasification-pathway. The challenge for the production of liquid hydrocarbons from woody biomass using pyrolysis is the low quality fuel produced which limits the marked. Liquid fuel produced from gasification and subsequent upgrading using Fischer Tropsch synthesis are of a higher quality and produces a significant fuel-fraction which can be utilized as fuel for aviation purposes. The opportunity of producing renewable jet-fuel from woody biomass has gained significant interest from the aviation industry. This helps accelerate the development and the technology is expected to be commercially viable within the decade [49]. At this point in time there seems to be no commercial production of transportation fuels from either pyrolysis or gasification due the technological and economic challenges described in this thesis.

Sammendrag

For redusere utslippene av drivhusgasser fra forbrenning av fossile brensler, har ført til at nye fornybare alternativer blir utforsket for å erstatte fossile råstoffer for produksjon av varme og energi eller produksjon av kjemikalier og drivstoff.

Biomasse fra energivirke/massevirke/skog (trevirke) utgjør en betydelig del av det globale biomasse potensialet og er en fornybar ressurs for fyring eller energiproduksjon gjennom forbrenning eller den kan omdannet til kjemikalier eller drivstoff gjennom egnede prosesser. Målet med denne oppgaven er å evaluere forskjellige teknologier for å finne den mest egnede prosessen for å omdanne denne type biomasse om til biodrivstoff.

For å identifisere den mest egnede teknologen som kan bruke denne type biomasse som råstoff for produksjon av biodrivstoff har det blitt gjennomført en omfattende litteraturstudie som en del av denne oppgaven. I denne studien har et utvalg av teknologier blitt presentert og evaluert for å finne egnede prosesser som kan produsere flytende hydrokarboner fra biomasse. Fra litteratur studien ble to termokjemisk prosesser ble vurdert som de mest egnede teknologiene for å bruke biomasse fra trevirke som råstoff. Prosessene som skal videre analyseres er pyrolyse og gassifisering. Disse teknologiene skal evalueres videre og prosess-veien mot flytende hydrokarboner er forklart og sammenlignet mot tilgjengelig litteratur og data.

Begge teknologiene foreslått er funnet egnet for produksjon av bensin og diesel fra trevirke. En sammenligning av de aktuelle teknologiene viste at pyrolyse produserte en større mengde hydrokarboner fra en gitt mengde trevirke med lavere investeringskostnader og lavere produksjonspris enn veivalget med gassifisering. Utfordringen med produksjon av flytende hydrokarboner fra trevirke ved bruk av pyrolyse er den lave kvaliteten på sluttproduktet som begrenser markedet. Flytende drivstoff produsert ved gassifisering og videre oppgradering gjennom Fischer Tropsch syntese er av en høyere kvalitet og produseres en betydelig andel bensin som kan brukes som drivstoff i flyindustrien. Muligheten til å produsere fornybar flybensin fra trevirke har vekket stor interesse blant forskjellige aktører. Dette har hjulpet med å akselerer utviklingen av denne teknologien og den er forventet å være kommersielt levedyktig innen et tiår [49]. På dette tidspunktet er det tilsynelatende ingen kommersiell produksjon av drivstoff fra enten

pyrolyse eller gassifisering som følge av teknologiske og økonomiske utfordringer som har blitt beskrevet i denne oppgaven.

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Abbreviations and Glossary:

AD   Anaerobic digestion

BCC   Biochemical conversion

BFB   Bubbling fluidized bed

BtL   Biomass to Liquid

CFB   Circulating fluidized bed

CPH   Catalytic pyrolysis and hydroprosessing

EF   Entrained flow

EJ   Etta joule

EU   European Union

FBR   Fixed bed reactor

FBTR   Fixed bed tubular

FP   Fast pyrolysis

FPH   Fast pyrolysis and hydroprocessing

FT   Fischer Tropsch

GE   Gasoline equivalent

GtL   Gas to liquid

GHG   Greenhouse gases

GTI   Gas Technology Institute

HDS   Hydrogen desulfurization

HPH   Hydropyrolysis and hydroprocessing

HTFT   High temperature Fischer-Tropsch

IPCC   Intergovernmental Panel on Climate Change

IRR   Internal rate of return

LHV   Lower heating value

LTFT	Low temperature Fischer-Tropsch
MFSP	Minimum fuel selling price
MJ	Mega joule
MT	Metric tons
MTPD	Metric tons per day
NMBU	Norwegian University of Life Sciences
NO_x	Nitrogen oxides
PNNL	Pacific Northwest National Laboratory
PSA	Pressure swing adsorption
R&D|	Research and development
SO	Sulphur oxide
SP	Slow pyrolysis
SP	Slurry phase
TEA	Techno-economic analysis
TPI	Total project investments
WS	Wet scrubber

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1. Introduction

The use of fossil fuels have laid the foundation for the rapid technological and economic development in our society and constitutes today according to IEA (International Energy Association) more than 80 % of the world's energy consumption [1]. Primary application of fossil fuels is for the generation of heat and electricity through combustion In addition to energy production fossil fuels is also refined into different chemicals for commercial use and fuels for the transportation sector [2]. Conventional use of fossil fuel results in emissions of greenhouse gases (GHG) into the atmosphere, which is the main reason behind the change in the global climate [2].

As a result of the global population increase, the energy-demand worldwide increases with it and as a consequence the emissions of GHG into the atmosphere increases. In addition to the atmospheric emissions, the use of fossil fuels have caused an increase of pollutants such as nitrogen oxides (NO_x) and Sulphur oxide(SO), which is believed to cause severe health complications in dense populated areas. Another concern is the limited supply of fossil fuel which is not distributed equal around the globe. This has a huge impact on the security of supply, which is also an important issue and is getting more relevant with the threat of global conflicts [1, 2].

To address the issues concerning the use of fossil fuels, there is a growing interest for exploring possible renewable alternatives to ensure a more sustainable development. One of the more promising available resources is wood as well as other types of biomass, which can be utilized as a direct replacement for fossil feedstocks [3]. Woody-biomass can be used for the same applications as fossil fuels, either for producing heat and power through combustion, or for the production of fuels and chemicals by utilizing certain conversion processes.

The main advantages with using woody-biomass as a feedstock is that the net emission of GHG from the combustion of wood is considered to be lower compared to the combustion of fossil fuels. Wood along with other types of biomass is considered to be a renewable resource, the global resources is much more equal distributed which makes the supply of security for biomass higher than for fossil fuels [1, 2].

Today there are well established "greener" alternatives (wood chips, bio pellets) to fossil fuel for the generation of heat and electricity, but for the transportation sector the alternatives are limited and come at a higher cost when compared to fossil fuel. These fuel alternatives derived from biomass are called biofuels, and is the collective term for fuels like biodiesel, bioethanol and

biogas. Biodiesel and bioethanol are liquid fuels mainly derived from different types of energy crops (fast growing plants with high energy content), and this has raised certain ethical questions regarding the use of crops for fuel and not for food. To find sustainable alternatives that do not compete with arable land, wood is being considered as a possible feedstock for the production of fuel and chemicals. Wood and other types of lignocellulosic biomass constitutes a significant fraction of the global biomass potential covering over 30 % of the planet's surface. Today wood and woody biomass is the most important renewable energy source for over 2 billion people and covering around 80% of the renewable energy production. This is what makes wood an important and promising alternative as a sustainable feedstock for biofuel and chemicals [4].

For the reasons above the scope of this work is to identify the conversion process which is most suitable for the production of biofuels from wood. This is done by a theoretical study where different technologies are systematically evaluated in order to find the most efficient method of converting woody biomass into biofuels. After presenting two potential candidates a further and more thorough evaluation based on the technologic and economic constraints needed for large-scale production will be performed to present the most suitable conversion technology. The secondary aim of this thesis is to provide a solid theoretical foundation for more master-thesis's on the field.

2. Background

2.1 Biomass, bioenergy and biofuel?

Biomass constitutes a wide array of organic subgroups, and is a field of study for many researches from various research areas. As a result, the definition of biomass may vary depending what kind of literature is used. This work investigates the potential of biomass as a feedstock for industrious purposes, and for that reason the definitions is collected from what is considered a reliable source in the field, the International Energy Agency (IEA) [1].

The term biomass is according to IEA defined as "*Any organic,* i.e. *decomposing, matter derived from plants or animals available on a renewable basis. Biomass includes wood and agricultural crops, herbaceous and woody energy crops, municipal organic wastes as well as manure.*" [1].

Bioenergy is energy obtained through the conversion of organic matter, either directly through combustion to generate heat or converted into a more manageable energy carrier such as liquid or gas. Biofuels are liquid or gaseous fuels derived from biomass or waste feedstock through a conversion process. In liquid biofuels the main types are bioethanol and biodiesel, these types of biofuel divided into three main groups known as "fuel-generation" based on the type of feedstock utilized [3].

Table 2.1 illustrates the classification of liquid biofuel, where each generation of biofuel is divided by the type of feedstock utilized and the product is determined by the process used (fermentation, transesterfication) in order produce the desired biofuel.

Table 2.1: *Classification of liquid biofuels based on the feedstock* [3].

1st generation	2nd generation	3rd generation
Feedstock: Seed, grains or sugars	**Feedstock:** Woody-biomass (Lignocellulosic biomass)	**Feedstock:** Algae, sea weeds
Products: Bioethanol or butanol produced through biochemical fermentation of starch or sugar	**Products** Bioethanol or butanol produced through enzymatic hydrolysis.	**Products:** Bioethanol derived from algae and sea weeds
Biodiesel produced from transesterification of oil either from plants and seeds or waste oil.	Diesel, gasoline, alcohol, other hydrocarbons produced through thermochemical processes	Biodiesel produced from algae

In this thesis the focus is the utilization of biomass for the production of 2nd generation biofuels, and in order to get an understanding of the potential of this type of biofuel the next chapter will present a short overview of the resources available for the production of biofuels from woody biomass.

2.2 The potential of biomass on a global scale

There are multiple studies performed in order to estimate the potential of the biomass feedstock, but the result from these studies varies and makes it difficult to compare results. The sources used for estimating the global potential for biomass as feedstock for biofuel production in this work, is based on a review study from IEA, "*Bioenergy – a sustainable and reliable energy source", 2009, and* compared to the review study by IPCC(Intergovernmental Panel on Climate Change), "*Special Report on Renewable Energy Sources and Climate Change Mitigation"*, 2011. This is not a complete review of the studies performed within this field, but a short summary from reliable sources in order to give an estimation of the global potential for biomass as a feedstock for biofuel production.

According to the study performed by the IEA, the use biomass primarily for the generation of heat electricity and to some extent liquid biofuels constitutes 10% or 50 EJ[1], of the annual global energy consumption [1].

Biomass used for bioenergy comes from three main sources:

- *Residue from agriculture, forest related industry and organic waste.*
- *Surplus of forestry.*
- *Crop farming.*

Biomass derived from high yielding agricultural crops has huge technical potential, but as mentioned earlier this raises several important questions regarding the sustainability in using farming land for fuel production instead of producing food, how this will affect the water supply and quality, how will the production of bioenergy affect the biodiversity and what will happened to the net emissions of GHG [1, 2].

In evaluating the main sources of biomass, these issues regarding the sustainability where imposed as constraints in order to estimate the global sustainable biomass potential in 2050.

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[1] 1 EJ = 10^{18} Joules (J) = 10^{15} kilojoules (kJ) = 24 million tons of oil equivalent (Mtoe).

Residue from agriculture, forest related industry and organic waste.

Biomass from residues does not compete with food crops or uses extra water, and as a result energy derived from this types of biomass has a very few or no constraints in terms of sustainability. The report from IEA, estimated a global sustainable potential in 2050, for this source of biomass to be between 50-150 EJ per year. A best estimate is to be around 100 EJ per year being considered as a best estimate [2].

Surplus of forestry.

In addition to the residue, the surplus from forestry could be utilized as a feedstock for bioenergy. In 2050 an estimation by the IEA of the global sustainable was expected to reach between 60-100 EJ per year [2].

Crop farming.

As mentioned above; Biomass derived from high yielding agricultural crops has huge technical potential. The study performed by the IEA estimated the global sustainable potential for crop farming to be 120 EJ per year; this estimate is based on the utilization of good quality farming areas, where water supply and land degradation have been taken into account. If areas of moderate quality were included in the estimate, the global sustainable potential increased to 190 EJ per year. Another factor to be included is the agricultural technology development, if rate of development increases at a faster speed than earlier, the global sustainable potential would increase to 330 EJ per year [2].

By adding all these potentials together the global sustainable is estimated to 510 EJ per year. To address the uncertainties around this estimate, the global sustainable potential could be adjusted to between 200-500 EJ per year. As there are other alternatives of renewable energy sources, using the biomass potential for the production of bioenergy might not be the optimal solution. In order to analyze this further, the future demand for biomass has been estimated to see if the use of woody biomass as a feedstock for biofuels can be feasible (*see figure 2-1*) [2].

Figure 2-1 compares the global biomass potential to the annual global energy demand (500 EJ (Orange) annually in 2008). Global energy demand is expected to increase to 600-1000 EJ per year in 2050. From this estimation the sustainable biomass potential has been estimated to be

somewhere between 200-500 EJ (Green) per year. This means that energy derived from biomass can provide a significant fraction of the annual global energy consumption.
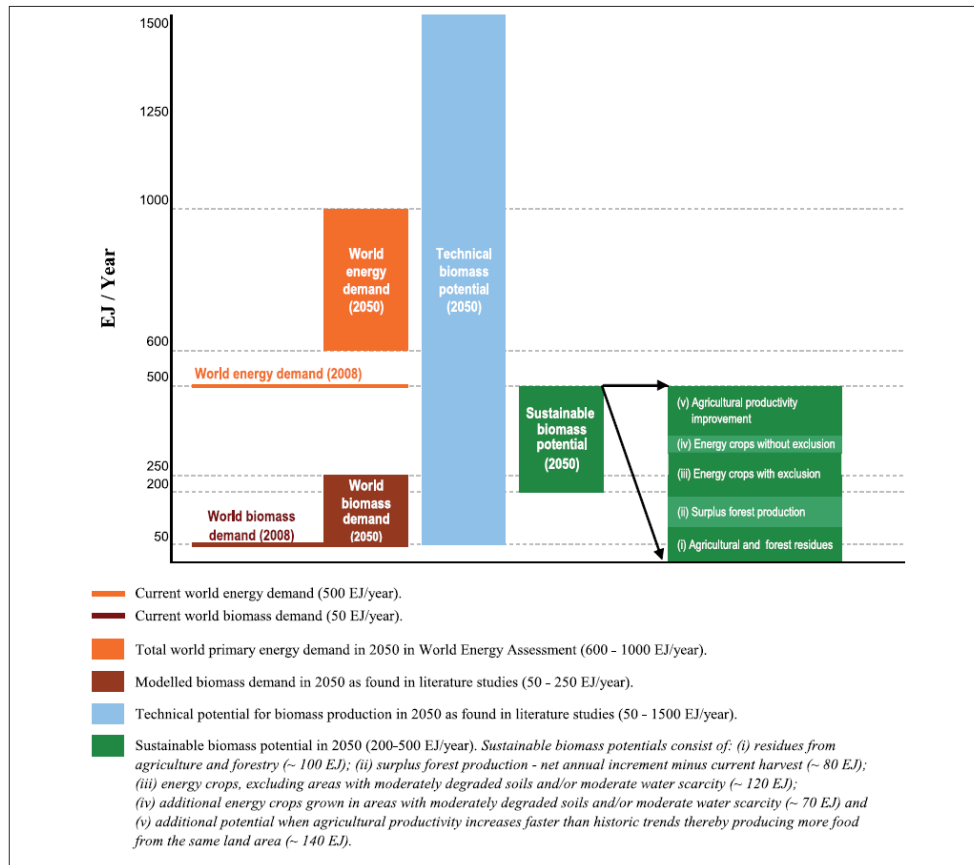
Figure 2-1: *Comparison of the global annual technical and sustainable potential for biomass in 2050, and in 2008 and predicted global demand for energy and biomass [1, 2].*

The demand for biomass was in 2008 50 EJ per year, while the estimated demand for biomass in 2050 were 50-250 EJ per year. Figure 2-1 compares theses estimates, and this comparison shows that the future demand for biomass can met by the estimated sustainable biomass potential. In comparison, the IPCC report "*Special Report on Renewable Energy Sources and Climate Change Mitigation",* 2011, estimates that the potential for biomass as feedstock for energy in 2050 was 100 to 300 EJ per year, while the demand for biomass was equal today's worldwide biomass extraction in agriculture and forestry (*200-250 EJ per year*) [1].

There are several constraints for the production of biofuel from biomass to insure a sustainable utilization of the resources available. One of the challenge faced when using woody biomass as a feedstock for biofuel and chemicals is to prevent an increase in the global

deforestation as this has the same impact on the climate as all the carbon dioxide released into the atmosphere form the burning of fossil fuel in the USA [4]. To prevent and possibly reduce the global deforestation using biomass from primary forest and agriculture should be avoided. In order to insure a sustainable production of biofuel from woody biomass the most interesting option is residue and waste from forest and agricultural related activities which allows biofuel production to coexist with traditional forest industry without increasing the price or affect supply of raw material. [4].

The challenges with producing biofuels from woody biomass lies in the available resources and with the need for developing technologies to establish a sustainable production on an industrious scale. With a well-established biofuel industry, liquid biofuel from woody biomass and other types of biomass has the potential to supply liquid biofuel corresponding to 10% of the fossil oil consumed annually [4].

2.3 Chemical composition and structure of wood

In order to understand how wood and other types of lignocellulosic biomass can be used as a feedstock for the production of liquid biofuel it's necessary to understand the chemical composition and structure of woody biomass to find the most suitable conversion process.

All types biomass contains the same substances in the form of cellulose, hemicellulose, lignin, and traces of other extractives. What separates the different plant species is the wt% of these substances which affects the physical properties of the material. Woody biomass comes from species which is characterized by a slow growth time and is composed of tightly bound fibres which results in a hard external surface. These fibres binds the cellulosic fibres together indicates a higher proportion of lignin, while plants and grass contains more loosely bound fibres as a result less lignin [5].

Table 2.2 shows the typical distribution of cellulose, hemicellulose, and lignin in certain biomass species. This table illustrates that woody biomass (softwood, hardwood) has a cellulose content representing 35-50 % of the dry weight of wood, while Hemicellulose makes up 20-30 % of the dry weight and lignin constitutes 20-30 % of the dry weight [5].

Table 2.2: *Cellulose/lignin ration of a selection of different biomass species (wt%)* [5].

Biomass	Lignin (%)	Cellulose (%)	Hemicellulose (%)
Hardwood	27-30	35-40	25-30
Softwood	20-25	45-50	20-25
Wheat straw	15-20	33-40	20-25
Switchgrass	5-20	30-50	10-40

The cellulose/lignin ratio is important in order to evaluate the feedstock suitability for certain conversion pathways and prompt the highest yield. This the case primarily for some biochemical conversion process which utilizes enzymes that cannot decompose lignin and to some extent hemicellulose because of it having a more complex molecular structure than cellulose. This can be resolved through extensive pre-treatments of the feedstock or by utilizing a different conversion method [5].

3. Literature review

3.1 Pathways for converting solid biomass

Achieving a transition from fossil to bio-fuels is challenging as there are major obstacles to overcome in order to reach this goal. Woody biomass as an primary energy carrier presents logistics challenges as a result of the physical properties of the feedstock, where bulkiness and inconvenient form of the raw material makes it hard to handle, store and transport. Compared to fossil fuel sources, the low energy density of woody biomass makes it challenging to develop technologies which are economical viable for large scale production.

The conversion of woody biomass into liquid and gaseous fuels creates an energy carrier with higher energy density than the raw biomass and reduces logistic challenges related to the storing and transportation. This is considered to be the main motivation for converting woody biomass into liquid or gaseous energy carrier. Converting woody biomass can be achieved by following one of two pathways: **1**) *biochemical,* and **2**) *thermochemical (see figure 3-1)* [6, 7].
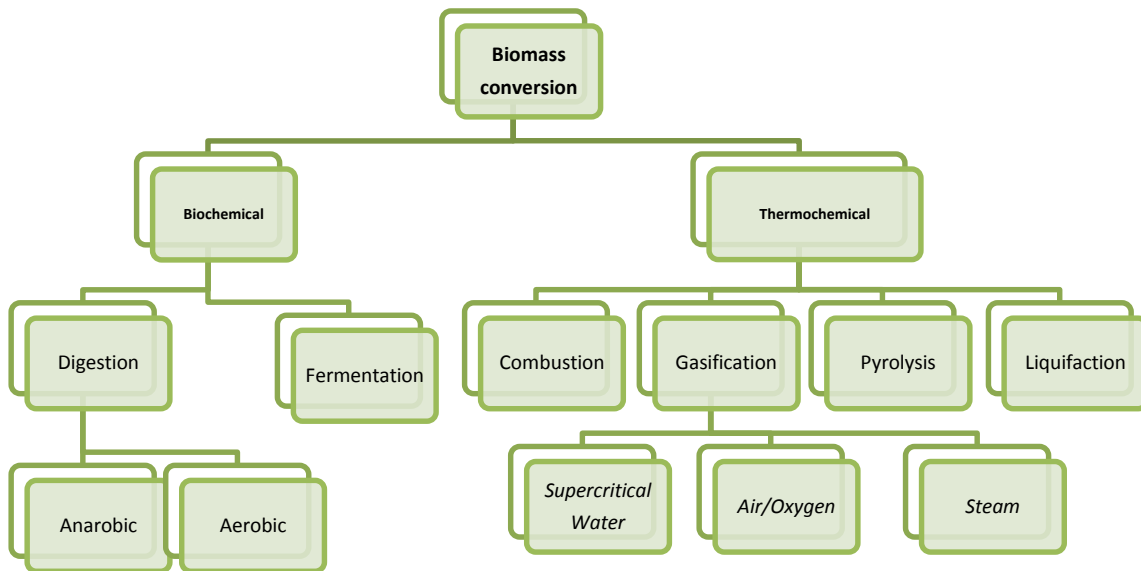
Figure 3.1: *The main conversion routes (Biochemical and Thermochemical) for transforming biomass into fuel, gases and chemicals* [6].

Figure 3.1 illustrates the two major pathways for converting woody biomass into liquid and gaseous fuels: (1) biochemical and (2) *thermochemical*, and these pathways are divided into different subcategories. Within the thermochemical pathway there are four methods for converting woody biochemical into different energy carriers: combustion, pyrolysis, gasification and liquefaction. The biochemical approach consists of two process options: digestion (msinly biogas production) and fermentation (for the production of bioethanol). This chapter will give a short description of these methods of conversion.

3.2 Biochemical conversion

Biochemical conversion (BCC) breaks down the molecular structure of a biomass molecule into smaller components by using enzymes or bacteria. The conditions of the chemical reactions related to BCC is milder compared to that of the reactions in thermochemical processes. This makes BCC processes a much slower method of conversion, but it requires small amounts of external energy in contrast to thermochemical conversion processes. The major commercial product of BCC is to this date bioethanol produced from the fermentation of sugarcanes, starch crops, sweet sorghum and sugar beet. Bioethanol produced through BCC is used as a substitute for gasoline used for automotive purposes [7].

In BCC there are two main routes of conversion is:

- *Digestion (anaerobic)*
- *Fermentation*

3.2.1 Anaerobic digestion

Anaerobic digestion (AD) is a conversion process, where an organic material is decomposed by microorganisms in an anaerobic environment where oxygen is absent. The product from this process is termed biogas, and is a gas mixture of primarily methane (50-70%) and carbon dioxide with traces of other compounds such as ammonia and hydrogen sulphide. AD is a commercially mature technology and biogas can either be used directly for cooking and heating, fuel for gas turbines etc. or upgrade to biomethane (85-90% methane) to be injected in the natural

gas grid. Feedstock sources used for AD are primarily agricultural waste with a high moisture content (80-90%) such as manure, plant materials, liquid wastes, food processing waste etc. In addition to the gaseous product, AD produces a solid residue called digestate, which can be used as fertilizer. Figure 3.2 illustrates the main process steps in the anaerobic digestion of biomass [7, 8].
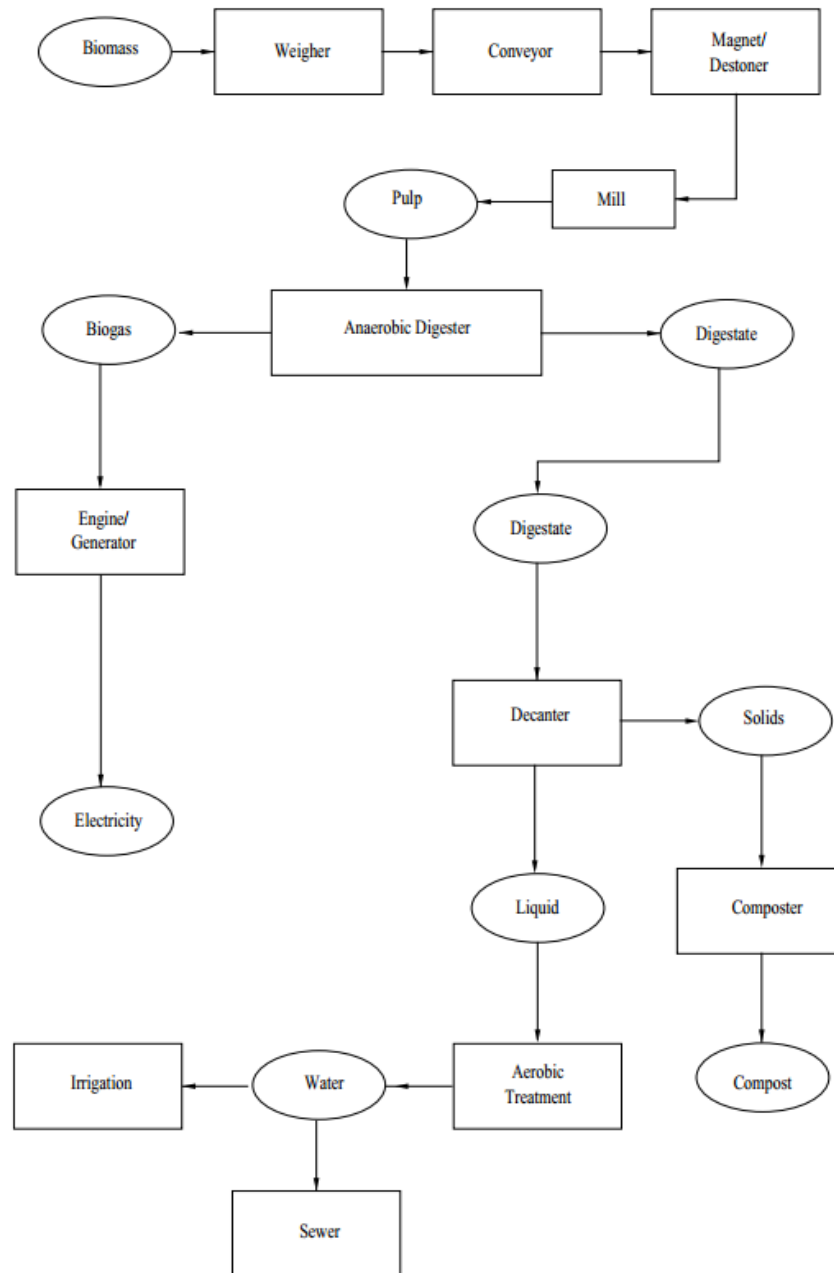
Figure 3.2: *Flow chart for anaerobic digestion of biomass [8].*

The problem with using woody biomass as a feedstock for AD is related to the low digestibility of these types of biomass. In order to utilize woody biomass for AD, the pretreatment of the material is important in order to break down the compact structure of the material in order to separate the lignin from the utilizable cellulose and hemicellulose. This can be achieved through physical, chemical or biological pretreatment processes.   The problem related with the pretreatment process is the high cost for all feedstock when compared to the price of the gas produced which limits the current possibilities of commercialization of this technology and explore further possibilities of producing liquid biofuels from biogas [9].

3.2.2 Fermentation

Fermentation is a conversion process which is commercially established on a global scale in order to produce ethanol on a large scale from a variety of sugar crops (sugar cane, sugar beet) and starch crops (corn, wheat). This is a process where the biomass is first grinded up and then the starch is transformed (using suitable enzymes) into sugars which is then transformed into ethanol by using yeast. Distillation is used in order to purify the ethanol. Fermentation yields about 450 l ethanol being produced per ton of dry corn [7]. Waste produced from the fermentation can be further utilized as food for livestock depending on the feedstock used [7, 8]. Figure 3.3 illustrates the process steps in the fermentation process for sugar and starch.
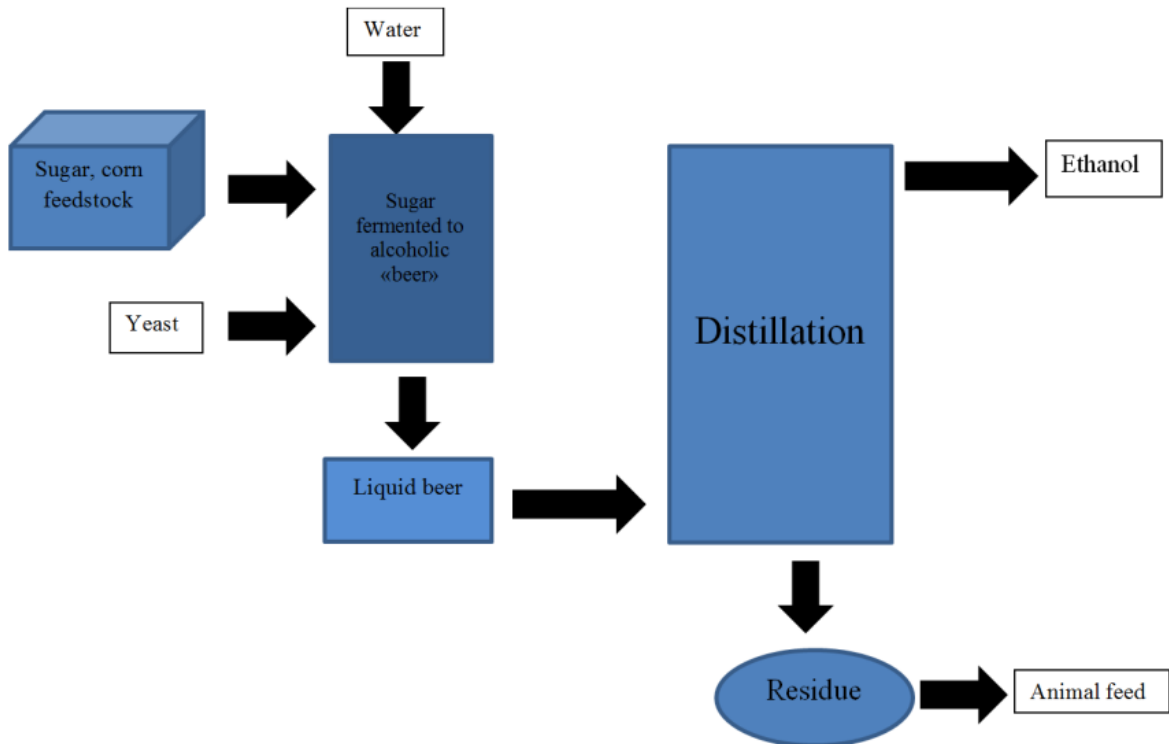
Figure 3.3: *The BCC for the fermentation of non-cellulosic sugar by using fermentation* [8].

In order to produce bioethanol from woody biomass special types of acid or enzymes are used in order to decompose the cellulose and hemicellulose in the material into simple sugars through hydrolysis. The sugar produced from fermenting the biomass is then converted into ethanol using yeast.

Figure 3.4 illustrates how the process path for bioethanol derived from a woody biomass feedstock, such as forest residue requires complex process steps in addition to energy consuming and relative expensive pretreatment with hydrolysis using acid, enzymes or a hydrothermal technique, in order to break down the components (*cellulose, hemicellulose and lignin)* of the feedstock into sugars that is needed for the fermentation process [7].
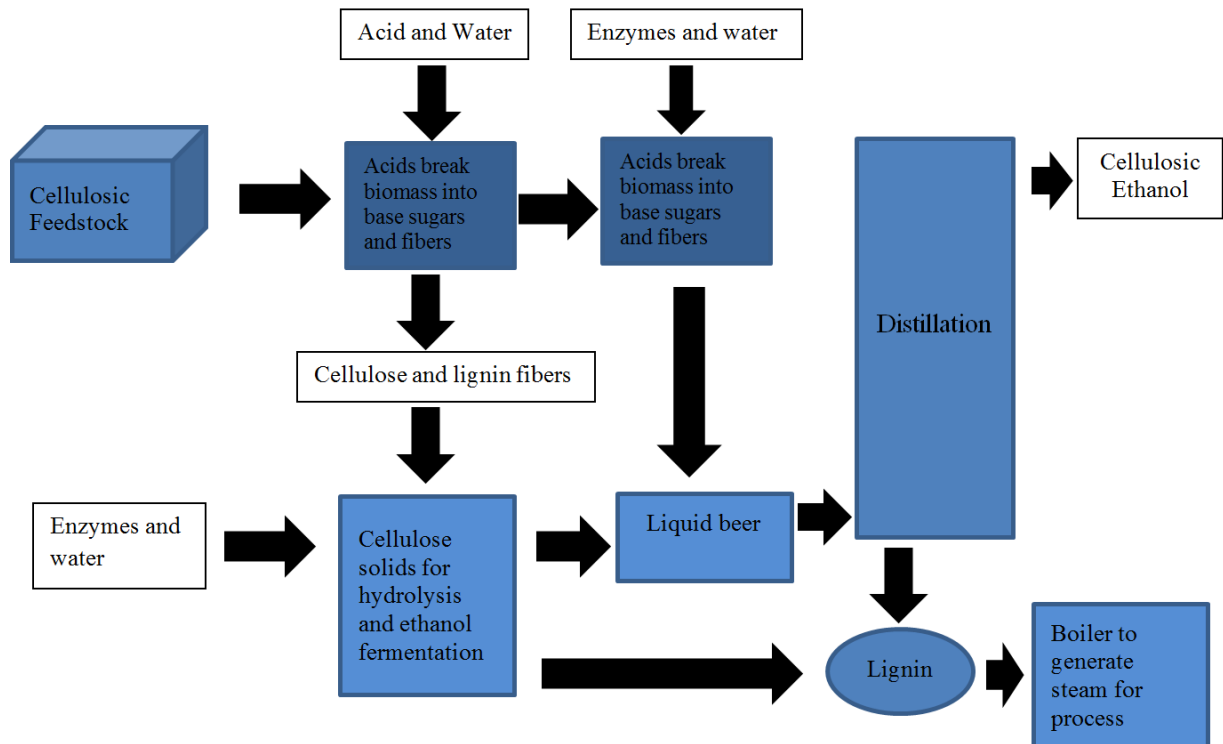
Figure 3.4: *Biochemical route for converting cellulosic biomass using acid hydrolysis* [7].

The recent development in the last decade in order to overcome the costs and technological difficulties in producing fermentable sugars from woody biomass has led to the first commercial production plant in countries such as USA and Brazil. With the rapid drop in oil–prices during the summer of 2014, this newborn industry is about to face its biggest challenge of which the outcome is uncertain.

3.2 Thermochemical conversion

In contrast to the biochemical pathway, thermochemical uses heat and a catalysts in order to convert biomass into thermal energy, gas or liquid which can used either directly for the generation of electric power and heat, or it can be further processed into fuel and chemicals [6, 7].
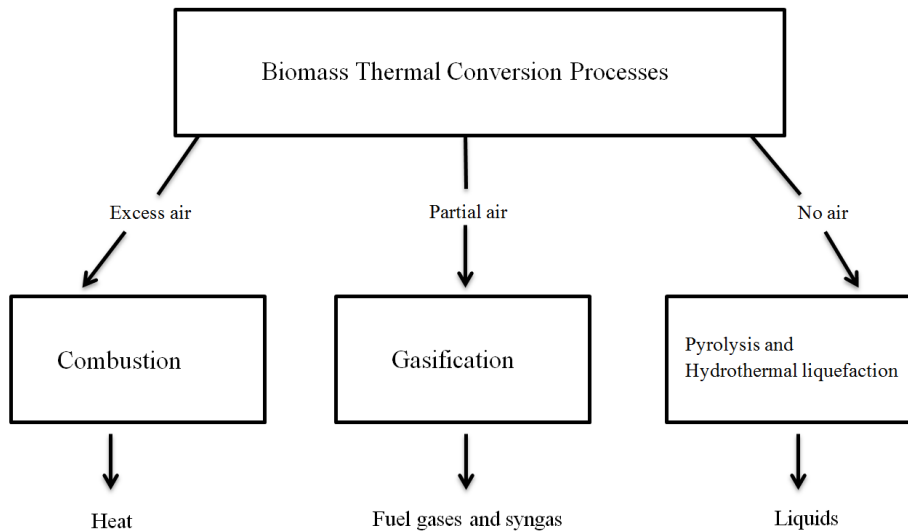
Figure 3.5: *Pathways for the conversion of biomass using thermal energy.*

Figure 3.5 depicts the main pathways for biomass using thermal conversion processes. By using these processes, the feedstock can be converted into either a solid fuel, liquid fuel or gasous fuel which can be further used for the generation of electricty, heat, chemicals and fuels [7].

The main processes for thermochemical conversion of biomass are:

- *Combustion*
- *Carbonization/Torrefaction*
- *Pyrolysis*
- *Gasification*
- *Liquefaction*

Combustion uses high temperature to convert biomass with an excess amount of oxygen (*oxidation*) into carbon dioxide and water in order to convert the energy stored in chemical bonds in the biomass into thermal energy.

Carbonization is a process which increases the carbon content in organic matter trough chemical decomposition in an oxygen-starved atmosphere. This is done by slowly heating the biomass until it has reached carbonization temperature (500-900°C). The by-product of this process is charcoal. Torrefaction is a similar process, where woody biomass heated to 200-300°C without the presence of oxygen in order to produce bio-coal.

In contrast to combustion, gasification of biomass takes place in a system with oxygen deficiency. The by-product from the gasification of biomass is a gas-mixture which can be further refined in order to produce ethanol, chemicals or liquid fuels.

Pyrolysis converts biomass using a low temperature in a system where oxygen is completely absent. The last method of thermochemical conversion is liquefaction, where the biomass feedstock molecules are decomposed into smaller components at low temperatures using a catalyst. Table 3.1 presents a comparison of the process conditions (*Temperature, pressure, etc.*) for the five main thermochemical methods for converting biomass.

Table 3.1: *Comparison of the process conditions for the different thermochemical conversion paths* [7].

Process	Temperature(°C)	Pressure(bar)	Catalyst	Pretreatment
Liquefaction	250 - 330	5-0200	Essential	Not required
Pyrolysis	380 - 530	1 - 5	Not required	Necessary
Combustion	700 - 1400	> 1	Not required	Not essential
Gasification	500 - 1300	> 1	Not essential	Necessary
Torre faction	200 - 300	1	Not required	Necessary

In this chapter a further overview on a selection of thermochemical processes used for the production of liquid hydrocarbons is presented.

3.2.1 Combustion

The combustion of biomass is probably the oldest technique for converting the chemical energy stored in biomass into thermal energy. Energy produced can be utilized in the generation of electricity, or used directly for stoves, boilers etc. This technique probably laid the foundation for our civilization to evolve as humans learned to utilize combustion to generate thermal energy for different purposes.

The products from the combustion of biomass are gases and vapours at temperatures around 800-1000 ℃. This is a result of the exothermic reaction between the carbon and oxygen in the fuel that releases a significant amount of heat, while forming water and carbon dioxide. The feedstock used for combustion can be any type of biomass, but in order to maintain an feasible energy output the moisture content must be <50 wt%. In order to utilize a feedstock with a higher moisture content, biochemical conversion processes is considered more suited [8].

Although combustion of biomass is the oldest method of producing thermal energy, it is still to this date one of the most important ways of generating heat and electricity. The heat generated through combustion is largest source of renewable energy in use today, where 90% of the energy is derived from biomass feedstock [6, 2].

Today the principles behind combustion processes are well known and it is utilized in many commercial technologies, mainly for producing heat and electricity. This makes it possible to optimize the process to the scale of operation and the characteristic of the biomass feedstock. In order to ensure an optimal production the size of combustion plants varies from domestic heating (small scale) up to large-scale thermal-plants capable of producing 100-3000 MW of thermal energy with a net bio-energy conversion efficiencies between 20-40% [8].

In addition to the traditional use of direct combustion of biomass, more modern concepts such as district heating are widely used in more cold climates for generating heat to a larger population. In a district heating plant steam is generated using boilers which are heated from the combustion of biomass, in order to heat a large group of households through a network of insulated pipes. This concept can also be used for generating electricity using steam turbines [6].

3.2.2 Torrefaction

Torrefaction is a thermochemical conversion process for organic matter derived from a woody feedstock. This process is used for improving the physical properties and chemical composition of biomass in order to produce a torrefaction-product with lower moisture content and higher energy density compared to the raw biomass [7]. This process changes the chemical structure of the biomass in order to remove oxygen from the biomass, by slowly heating the biomass to 230 to 300 °C in a system without oxygen [7].

The product from torrefaction of biomass consists of three fractions **1**) *Solid*: A uniform product of a brown/dark color with a high carbon content, **2**) *Liquid*: A mixture of moisture, acetic, acid and other oxygenates, **3**) *gas:* a gas mixture of CO_2, CO, and traces of CH_4. The mass and energy balance for torrefaction illustrates how 70% of the initial mass is preserved as a solid material. In this solid fraction, 90% of the initial energy content is contained, while the other 30% of the initial mass is converted into gas and liquid containing 10% of the initial energy content. By applying torrefaction to woody biomass the energy density of the feedstock increases with typical factor of 1.3 [7, 10].

By upgrading woody biomass using torrefaction, the biomass has improved fuel properties and more hydrophobic characteristics, making the feedstock more suitable for transportation and storage. In addition to these properties the torrefaction process provides a better product uniformity in terms of quality, as woody biomass from different sources (wood cuttings, waste wood) have more similar composition after undergoing torrefaction. This enhances the commercial potential for energy production and makes torrified biomass an alternative to conventional wood pellets, or as an pretreatment process for combustion or gasification [7, 10].

3.2.3 Pyrolysis

Pyrolysis is a thermochemical process which decomposes biomass with an operating temperature of 350-700 ^{o}C in a system deprived of oxygen in order to produce a mixture of gases, solids and liquids. For the production of biofuels from woody biomass there are four pathways via pyrolysis to consider: *slow pyrolysis and upgrading, fast pyrolysis and hydroprocessing (FPH), catalytic pyrolysis and hydroprocessing (CPH), and hydropyrolysis and hydroprocessing (HPH)* [11].

Slow pyrolysis (SP) is the collective term for thermal decomposition processes such as torrefaction and carbonization, where biomass is decomposed over a time interval ranging from minutes to days with a process temperature of around 400 ^{o}C. The products from SP is torrefied biomass or biochar depending on the residence time [7].

In fast pyrolysis, the biomass is heated in matter of seconds to a temperature of around 500 ^{o}C in order to produce mainly a liquid fraction known as bio-oil and a smaller fraction of gas and solid biochar. The gas and solids produced is low-valued products suitable for direct combustion in order to produce heat and power, while the bio-oil is composed of different compounds which can be further refined into hydrocarbons in the diesel and gasoline range. In order to refine the bio-oil, hydrotreating and hydrocracking is used. Hydrotreating utilizes a chemical reaction between organic compounds in the bio-oil and hydrogen at high pressure in order to remove oxygen and other unwanted compounds (nitrogen, sulphur and chlorine). The hydrotreating of bio-oil consumes large amount of hydrogen, but the oxygen is removed as water and is therefore considered a carbon efficient process (small carbon-loss). After hydrotreating the bio-oil still contains large molecule, which is too big for the use in transportation fuels. In order to break the larger hydrocarbons into smaller molecules, hydrocracking is applied. Hydrocracking is similar to hydrotreating, but at higher temperature and pressure [11].

Catalytic pyrolysis and hydroprocessing (hydrotreating and hydrocracking) removes oxygen in the product during the pyrolysis reaction and hydroprocessing as separate process steps. The removal of oxygen during the pyrolysis reaction is achieved by using a zeolite catalyst mixed in with biomass or using it downstream of the pyrolysis-reactor. By using a catalyst, CO and CO_2 are removed from pyrolysis vapours. The vapour is then condensed in order to be further hydro processed in the same way as bio-oil in the fast pyrolysis process. By using a catalyst, the bio-oil is of a composition which makes hydroprocessing easier, and as a consequence CHP uses less

hydrogen than FPH. CHP is less carbon efficient than FPH as result of the removal of CO, CO_2 and coke takes place during the pyrolysis-reaction [11].

The fourth pyrolysis reaction is HPH, where the pyrolysis reaction takes place in the presence of hydrogen and a hydroprocessing catalyst at high pressure. From this process a liquid fraction is produced which is converted into suitable molecules through hydroprocessing. In HPH oxygen is removed as water in the both steps of the process. As a result, HPH is more carbon efficient when compared to CPH. Another advantage with HPH is the use of hydroprocessing catalyst, eliminates the need for a separate hydrocracking step in order to produce suitable molecules for fuel. The disadvantage with the HPH is a higher hydrogen consumption when compared to CPH [11].

In commercial setting, pyrolysis for the production of liquid biofuels is still at a pilot scale/early commercialization stage as there are interest in optimizing the technology for the production of transportation fuels from a renewable feedstock such as residue from wood related industry [12].

3.2.4 Gasification

Gasification is a thermochemical conversion process which can convert any matter with high carbon content into a gaseous energy carrier. The gas produced is a mixture of mainly carbon monoxide (CO), hydrogen (H_2), methane (CH_4), carbon dioxide (CO_2), with traces of light hydrocarbons. This "product gas" can be used directly for combustion in order to produce thermal energy for power generation or upgraded into syngas, which can be refined into liquid hydrocarbon using Fischer Tropsch (FT) synthesis [12].

The process temperature for gasification ranges up from 800 ºC to 1500 ºC and even higher in some cases, depending on the feedstock and technology used. By have the ability to use a wide array of feedstock (fossil and non-fossil) for the production of fuels and chemicals, gasification is considered a flexible process. Although gasification can use biomass as a feedstock, fossil feedstock such as coal is the most common raw material to this date for the production of synthetic gases (syngas) [7, 12].
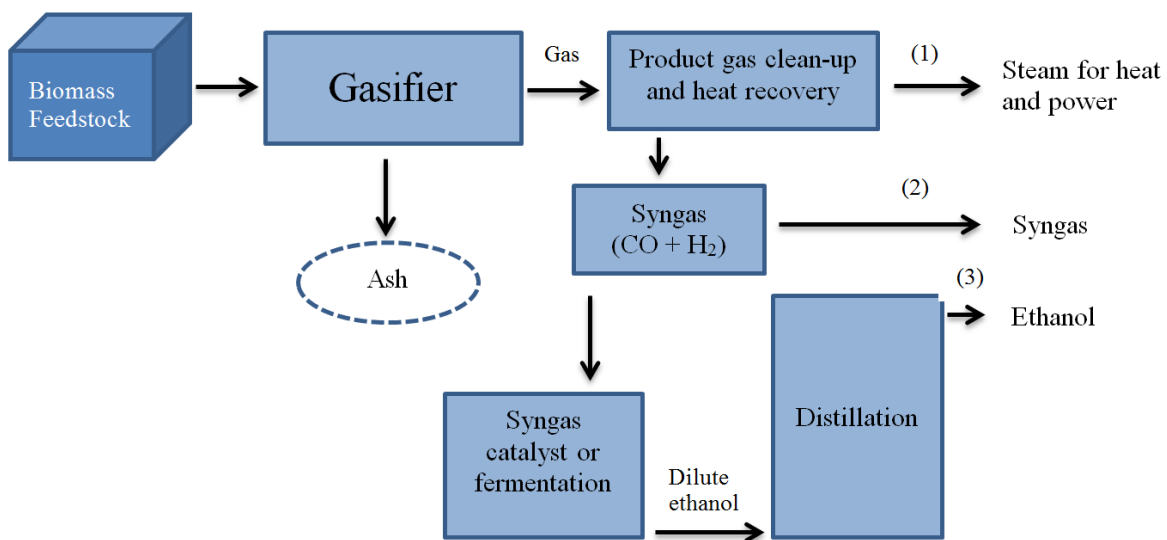
Figure 3.4: *Different pathways of utilizing the by-product from gasification* [7].

Figure 3.4 illustrates the different applications for the by-product from gasification **1)** Using the heat directly in order to produce steam for heat and power production, **2)** Refines the by-product to syngas, which can be "upgraded" by using technologies such as the Fischer-Tropsch synthesis where the syngas is converted into a high value product (*in terms of energy density*) such as synthetic diesel or other liquid hydrocarbons. **3)** Using the syngas for producing ethanol through fermentation [7].

Transforming a solid or liquid energy carrier into a gaseous energy carrier has several major motivations:

- *By removing noncombustible components like nitrogen and water, the by-product produced has a high heat value compared to the raw feedstock.*
- *During gasification sulfur is removed, so when the gasified fuel is burnt contaminants is not released to the atmosphere.*
- *Gasification reduces the carbon-to-hydrogen (C/H) mass ratio in the feedstock.*
- *Reducing the amount of oxygen in the feedstock.*

Table 3.2 shows the characterization of a selection of different fuels, where the C/H mass ratio, oxygen content and energy density is depicted. For gasification the transition from raw biomass to syngas reduces the oxygen content and lowers the C/H ratio of the feedstock.

Table 3.2: *Carbon/Hydrogen(C/H) ratio for a selection of fuels* [7].

Fuel	C/H Mass Ratio (%)	Oxygen (%)	Energy Density (MJ/kg)
Anthracite	~ 44	~ 2.3	~ 27.6
Bituminous coal	~ 15	~ 7.8	~ 29
Lignite	~ 10	~ 11	~ 9
Peat	~ 10	~ 35	~ 7
Crude oil	~ 9		~ 42 (mineral oil)
Woody Biomass (cedar tree)	~ 7.6	~ 40	~ 20
Gasoline	~ 6	~ 0	~ 46.8
Natural gas (mainly CH4)	~ 3	Negligible	~ 56 (LNG)
Syngas($CO:H_2 = 1:3$)	**~ 2**	**Negligible**	**~ 24**

Both pyrolysis and gasification increases hydrogen content (*H/C ratio*) in the feedstock, this is essential as a higher hydrogen content lowers the temperature of vaporization and increases the probability of a fuel being in a gaseous state [7]. This can achieved through: (**1**) *Direct exposure:* Exposing the fuel to hydrogen at high pressure in order to increase the hydrogen content of the feedstock (**2**) *Indirect exposure:* By subjecting the feedstock to steam at high pressure and temperature where the hydrogen is added as an intermediate to the fuel. (**3**) *Pyrolysis* or *devolatilization*: reduces the carbon content by rejecting it through as a solid residue with a high carbon content (*char*) or gas (CO_2) [7].

Gasification has since the 1940s been used for the production of liquid transportation fuels through FT-synthesis on commercial scale using mainly coal as a feedstock. In the recent years the focus has been on using this technology with a biomass feedstock in order to produce liquid fuels. The maturity of this technology is considered to be one of its main advantages and is on the threshold for being fully commercialized for the production of aviation fuel from biomass. Challenges with the use of gasification and FT synthesis is related to the high capital cost due to the complexity of process design and the investment cost in order to build large scale plants to make the production profitable. The development focus on this technology has been on reducing the capital cost by optimizing different aspects of the production such as gasification reactor design.

3.2.5 Liquefaction

Liquefaction is a thermochemical conversion where biomass is converted directly into a liquid product in the presence of a pressurized solvent between 1-240 bar and a temperature range of 150-450 ℃. At milder process conditions, the liquefaction product is a liquid consisting of different sugars and partially deconstructed lignin. Under higher conditions the liquid product has a chemical composition similar to the liquid product produced from fast pyrolysis. The solvent used for liquefaction varies depending on different parameters, but water is a frequently used as due to low cost and the possibility of converting feedstock with a moisture content of over 90 wt%. As with the product from pyrolysis, the liquefaction product also requires further processing [7, 12 13]. This process for converting woody biomass directly into a liquid is far away from a technical and economic feasibility, and is still only present at a lab-scale production capacity [13].

3.3 Comparing biochemical and thermochemical conversion process.

Woody biomass has a potential as a feedstock for biofuels when compared to other alternative biofuel feedstock due to the cost and availability. Previous chapters presented a brief overview of some of conversion processes used for biofuel production from woody biomass and the difference between the main conversion pathways (biochemical and thermochemical). Biochemical approach to produce alcohol based fuels from a woody biomass feedstock needs complex pretreatment technology in order to break down the structure of the wood fibers in order to make sugars available for fermentation. The challenge for this process from a technological point of view is how to utilize the lignin, which makes up about 30% of the weight of the feedstock, depending on the feedstock used. Lignin can be used for the production of biofuels through the use of a thermochemical process such as pyrolysis or gasification, but in order to produce a high quality fuel, the product from these processes (bio-oil or syngas) have to be upgraded through a suitable process.

The challenges for both pathways is to develop technology which is more cost-effective and to reduce the carbon footprint of the process, in order to make the production of biofuel more sustainable and economically viable. At the same time the more critical factor when analyzing the different pathways, is to consider the feedstock availability and composition in order to ensure the best production margins. So in that sense there should be room for both pathways in todays and future marked and development, or even a hybrid technology.

Table 3.3 shows the main difference in converting biomass using the thermochemical and biochemical route. In terms of commercial use, the biochemical route of converting a feedstock into ethanol is more developed than the thermochemical route. When analyzing the source of feedstock used for conversion, the table shows that biochemical conversion needs sugar or starch in order to produce ethanol. The source for sugar and starch that can be utilized is for example in corn, only found in the kernel. This implies that the rest of plant, which are mainly ligno-cellulosic can't be utilized for the production of ethanol and is considered to be waste. So in using the biochemical route of conversion, much of the feedstock is not converted into ethanol.

Table 3.3: *Comparison of the thermochemical and biochemical conversion of biomass* [7].

	Biochemical	Thermochemical
Raw-material	Sugar-crop feedstock: Sugarcane, starch, corn	Woody feedstock such wood, agricultural residue, forest residue,, and some types of municipal waste
Reactor mode	Batch-process	Continuous-process
Reaction time	2 days	Less than10 min
By-products	Organic residue	Syngas/electricity
Yield	450 liter/ton	265 – 492 liter/ton
Technology maturity	> 100 in U.S plants	Pilot and demonstration plants

In order to utilize wood as a feedstock for the production of biofuels, a thermochemical process could be considered a more suitable option for the production of hydrocarbon fuel. For this purpose, pyrolysis and gasification is further analyzed in order to find the most suitable option for the production of transportation fuels.

4. Pyrolysis for biofuel-production

4.1 Pyrolysis principles

Pyrolysis is as stated in the previous chapter, a rapid high temperature thermochemical process where the woody-biomass is directly decomposed into a solid (char), liquid and gas fraction in the absence of oxygen. The different long chain compounds in the wood, containing carbon, hydrogen and oxygen are transformed into primary products consisting of a condensable gas, non-condensable gases (CO, CO_2, H_2 and CH_4) and a solid residue (Char). From the condensable gas, secondary reactions prompts the production of non-condensable gases , liquid and char. Figure 4.1 illustrates the reaction process for the pyrolysis of a biomass particle. The product distribution in pyrolysis is controlled by several factors such pyrolysis temperature, heating rate, pressure, reactor configuration, feedstock composition, etc. [7].
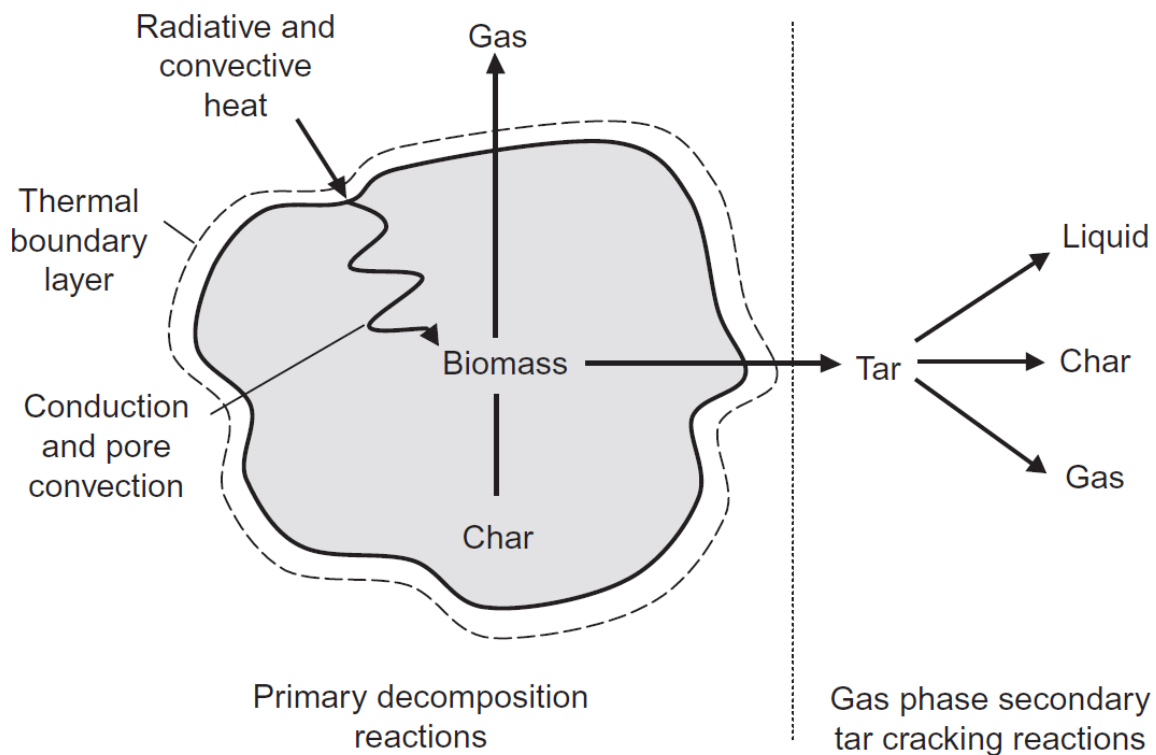
Figure 4.1: *Principles of pyrolysis process on biomass particle [7].*

4.2 Types of pyrolysis reactions

Pyrolysis can be divided into three main types of reactions which is classified by operating temperature, heating rate and residence time. The main difference between the reactions is the product distribution, where a high liquid is desirable for further refining into transportation fuel [14].

4.2.1 Slow pyrolysis

Slow pyrolysis is used when the desired product is char. This is done by heating the biomass at a slow heating rate (5–7 C^o/min) at relative low temperatures (650 C^o). In addition to the solid residue, some amount of gas and bio-oil is also produce through slow pyrolysis. In order to maximize the liquid yield, other pyrolysis processes should be considered [7, 14].

4.2.2 Fast pyrolysis

Fast pyrolysis is used to produce a larger fraction of liquid called bio-oil. During this process, the biomass is rapidly heated until it achieves the peak temperature (pyrolysis temperature) before the material starts to decompose. The heating rate for fast pyrolysis can be in the range of 1000-10000 C^o/s, but in order to ensure a high liquid yield, the peak temperature should be below 650 C^o and the vapour residence time should be short in order to minimize secondary reactions [7, 15]. A typical product distribution from fast pyrolysis on a weight basis contains 60-75% bio-oil, 15-25% solid fraction and 10-20% primary gases depending on the feedstock used. The most important factors for increasing the liquid yield is: *1) High heating rate, 2) reaction temperature (between 400-600 ^oC, 3) short gas residence time (>2 sec), 4) rapid cooling of the product vapours* [7]. In order to optimize the process a suitable reactor configuration must be employed.

4.2.3 Flash pyrolysis

Flash pyrolysis is reaction where the process conditions are similar to that of fast pyrolysis, but with a shorter residence time (30-1500 ms). The product distribution is also similar to the flash pyrolysis reaction, and as a consequence the distinction between flash and fast pyrolysis has been replaced with a broader definition for fast pyrolysis. [15, 16].

4.2 Pyrolysis products

4.2.1 Solid – char

From the pyrolysis process a solid yield is produced, and this solid fraction is often referred to as char or "Biochar". The composition of this solid residue is mainly carbon (85%), but it also contains large fractions of hydrogen and oxygen. Char produced from pyrolysis has a lower heating value (LHV) in the area of 32 MJ/kg, which is far greater when compared to the raw feedstock. The relative high LHV makes char produced from pyrolysis suitable as fuel for combustion [7].

4.2.2 Gas

Pyrolysis yields a gas fraction from the primary decomposition, which consists mainly of H_2, CO_2, CO, CH_4 and traces of other light primary gases. The primary decomposition also produces a vapor fraction consisting of heavier molecules, which condenses when cooled adding to the liquid yield. From secondary decomposition of the vapor at high temperature, more non-condensable gases is produced. The final gas fraction from pyrolysis is the non-condensable gases produced from both the primary and secondary decomposition. When analyzing the LHV of the gas produced from pyrolysis, the heating value ranges from 11-20 MJ/Nm^3 depending on how severe the secondary reactions are [7].

4.2.3 Oil

The liquid fraction produced from pyrolysis is a black, high viscosity fluid called tar or "bio-oil". This liquid has a high moisture content (typical 20 wt %) and consist of several complex hydrocarbons with a high oxygen content Compared to the raw feedstock (19-21 MJ/kg), the LHV of the bio-oil is in the range 13-18 MJ/kg, but the density is significant higher [7].

The main application for bio-oil is as a chemical feedstock and for the use as fuel for co-firing plants (district heating) [17]. In order to utilize bio-fuel as a feedstock for transportation fuel, the bio-oil needs to be upgraded by reducing the oxygen content and increasing the hydrogen content.

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4.2.4 Properties of bio-oil from pyrolysis

Raw bio-oil presents a challenge for the production of transportation fuel as a result of its complex chemical composition compared to the chemical composition of petroleum oil. The chemical composition of bio-oil consists of several hundred organic compounds such as acids, alcohols, aldehydes, esters, ketones, phenols and lignin-derived oligomers [18]. This complex mixtures gives bio-oil certain undesired properties such as high viscosity, high ash content, relative low heating value due to high oxygen content, and high acidity in addition to a large amount of moisture (15-30 et%). The unwanted properties of bio-oil limits its direct application as a transportation fuel and further upgrading is necessary in order to improve the properties of bio-oil

Table 4.1 compare selected properties to pyrolysis oil from wood and heavy petroleum and shows how the higher oxygen content in the bio-oil results in a heating value less than half of that fuel oil. The acidic nature of bio-oil presents a challenge for storage, transport and further refining and will require suitable alloys/plastic in order to limit the extent of the problems related to corrosion. Another undesired characteristics of bio-oil is a result of slower secondary reactions which causes an increase in viscosity and moisture content over a longer period of time [18].

Table 4.1: *Comparison between the physical properties for bio-oil derived from wood and petroleum fuel oil* [19, 20].

Properties	Bio-oil from wood	Heavy petroleum fuel oil
Moisture content (wt%)	15-30	0.1
pH	2-5	-
Specific gravity	1.2	0.94
Elemental composition (wt%)		
C	54-58	85
H	5.5-7.0	11
O	35-40	1.0
N	0-0.2	0.3
Ash	0-0.2	0.1
HHV (MJ/kg)	16-19	40
Viscosity (at 50%) (cP)	40-100	180
Solids (wt%)	0.2-1	1

4.3 Pyrolysis reactor configuration

In order to maximize the yield of bio-oil from pyrolysis, a suitable reactor configuration has to be chosen in order to provide a continuous production and stable process-conditions according to the parameters listed in table 4.2. The classification of pyrolysis reactors is determined by the contact between gas and solids. Reactors can be divided into three main groups: fixed bed, fluidized bed and entrained bed [7]. This chapter will present an overview of the main types of reactor configuration for production of bio-oil.

Table 4.2: *Effect of process conditions on the desired pyrolysis yield* [7].

Maximize Yield of	Maximum Temperature	Heating Rate	Gas residence time
Char	Low	Slow	Long
Liquid	Low (In the range of 500ºC)	High	Short
Gas	High	Low	Long

4.3.1 Bubbling fluidized bed reactor

In a bubbling fluidized bed (BFB) reactor small particles of biomass (2-6mm) are fed into a bed of bubbling sand or another suitable material. In order to fluidize the reactor bed, an inert gas (such as recycled exhaust gas) at high velocity. The advantages of a BFB system is that the intense mixing of the bed material provides a good and uniform temperature control, which is essential for a steady production. A BFB reactor also provides a high heat transfer to the biomass particles and the vapors released have a short residence time in the reactor, making it suitable for fast pyrolysis [7]. Figure 4.2 depicts a schematic overview of a BFB reactor and the working principles for this reactor.
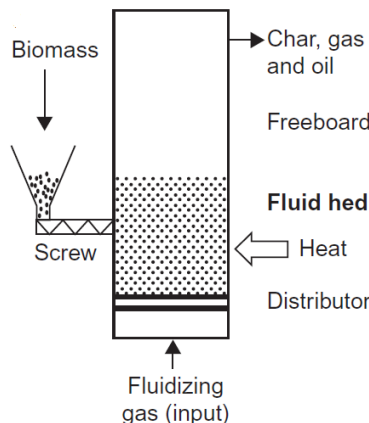
Figure 4.2*: Schematic overview of a BFB reactor* [7].

In order to provide enough heat for the pyrolysis process, a part of the gas produced could be combusted in the reactor bed using an integrated gas burner or by burning the residue (mainly char) in a separate combustion-chamber and transfer the heat generated back to the reactor bed [7]. Figure 4.3 depicts a simplified layout for a pyrolysis plant, where entrained solids from the primary decomposition are removed from the product-stream using cyclones in order to prevent secondary reactions in the vapors catalyzed by the char which will reduce the liquid yield [7].
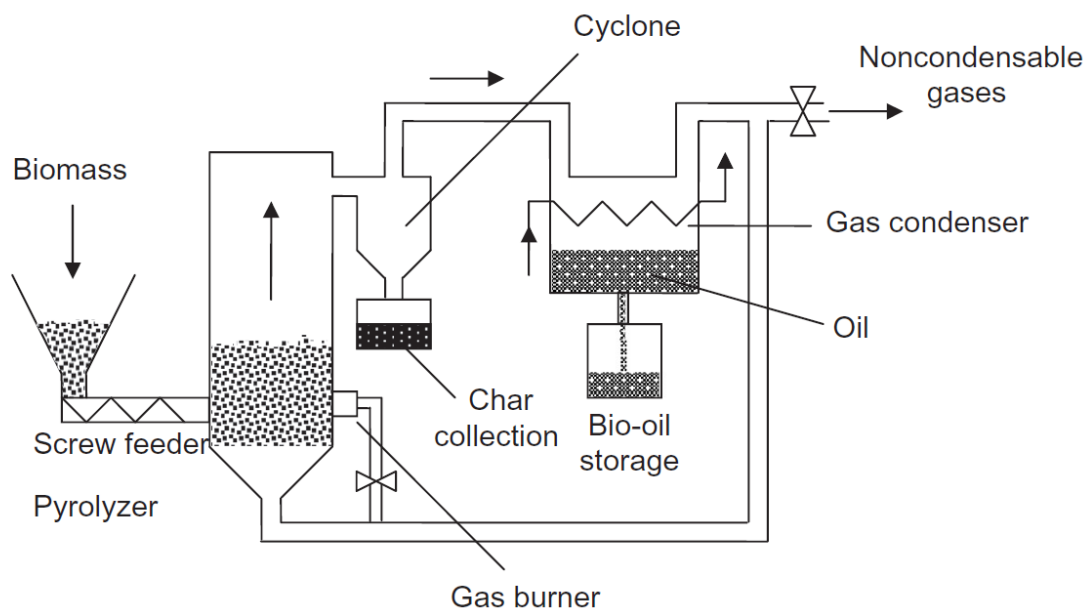
Figure 4.3: *Simplified layout of a pyrolysis plant* [7].

After the unwanted solids are removed from the product stream, the remaining gas and vapors must be cooled down rapidly in order to prevent further cracking of organic molecules. This can be achived by using bio-oil or suitable hydrocarbon liquid [16]. The liquid yield from using a BFB reactor configuration is typically in the range of 70 wt% of the untreated woody biomass feedstock [16].

4.3.2 Circulating fluidizing bed reactor

A circulating fluidizing bed (CFB) reactor is based on the same principles as BFB reactor, but the CFB has an external loop where solids are recycled into the reactor using a cyclone and loop seal (see fig 4.4). This integrated loop allows the entrained char from the product stream to be easily recycled and burnt in an external fluidized bed. Heat generated from the combustion of the residue char is transported back by using a loop seal. The residence time for char and vapours are shorter when compared to a BFB reactor, this allows a CFB to handle a larger "flow" of biomass. [7, 17].
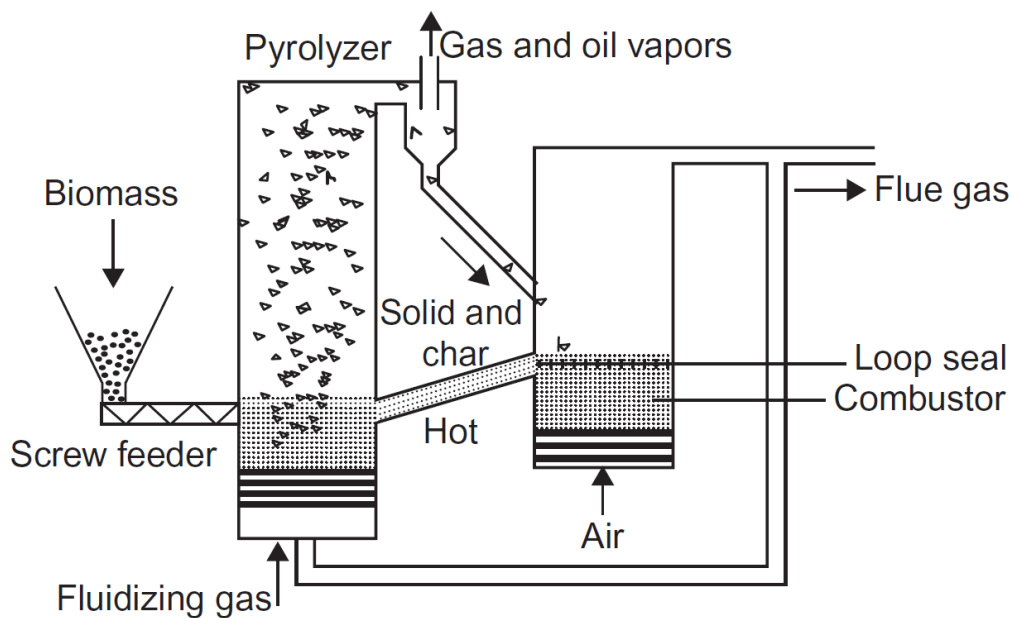
Figure 4.4*: Schematic overview of a BFB reactor* [7].

The limitations of this reactor configuration is mainly related to a higher investment cost as a result of a more complex system when compared to a BFB reactor.

4.3.3 Ablative reactor

A reactor configuration which is based on a different concept than typical bed-reactor is the ablative reactor which is built on the premise that the heat transfer from a heated surface will soften a biomass particle in contact with the surface under pressure. The pressure can be generated mechanically or by centrifugal force [7, 17]. This leads to a reactor configuration which can use larger wood particles without the need for a carrier gas, but the reaction rate is limited by the heat supply to the reactor [17]. Figure 4.5 illustrates the principles of ablative reactor, where a biomass particle is pressed against a heated surface which is rotating. As the area of contacted reaches pyrolysis temperature the reaction produces an oil film as the biomass particle is pushed away, this oil film rapidly evaporates to produce vapors which can be collected by rapid cooling [17].
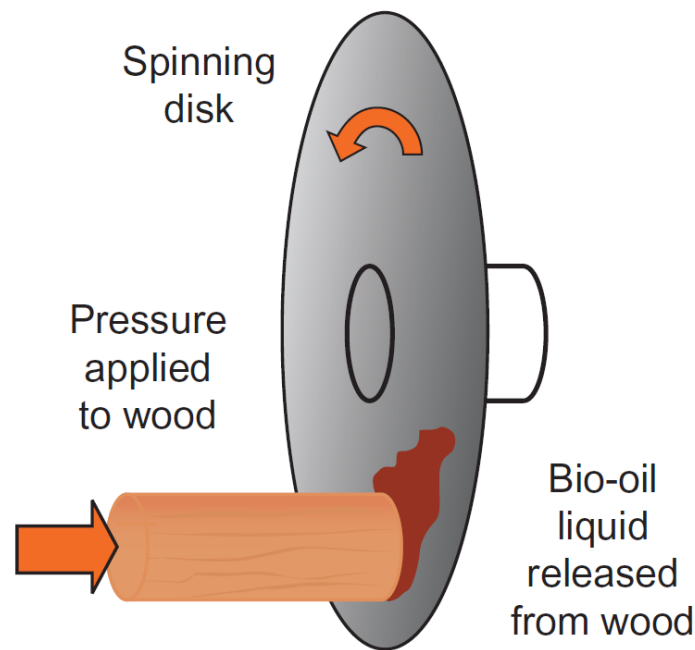
Figure 4.5 *Principle of an Ablative reactor* [7].

The main advantages with this type of reactor configuration is that the design is more compact compared to conventional bed-reactors and as a result of short residence time and high heat transfer typical liquid yields is in the range of 80 wt% [7]. Disadvantages with this reactor is that the design are more complex as result of mechanical parts moving at high temperature and it is costly to scale as the process is surface-area controlled [17].

4.3.4 Rotating-cone reactor

This reactor-configuration operates by utilizing the centrifugal forces generated from rotating at 360-960 rev/min in order transport biomass particles together with some of the heat-carrier solids (sand) [7]. Figure 4.6 illustrates how biomass particles is fed into the bottom of a rotating cone together with a hot solid particles. In the rotating cone the biomass is pushed against a heated wall where it reaches pyrolysis temperature fast due to the rapid heating rate (5000 K/s) and evaporates. The vapors produced leaves the reactor, while the solid residue is separated and falls over the edge of the cone to be combusted in a fluidized bed. Heat generated from the combustion is used in order to heat the cone and the heating the recycled heat-carrier material [7, 17].
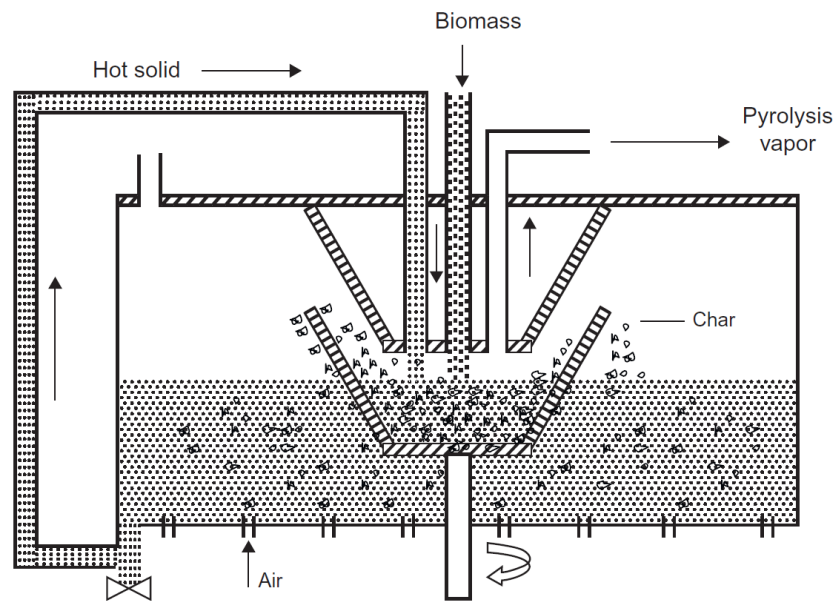
Figure 4.6: *Principle of rotating-cone reactor* [7].

The advantages of this reactor-configuration is the short residence time for the vapors (0.3s) and solids (0.5s) which prompts a liquid yield in the range of 60-70 wt% of the biomass. Using the centrifugal forces in order to separate the solids from the vapors reduces the need for a carrier gas (only to transport the heat-carrier material). Challenges related to this design is the complex geometry of the reactor-configuration which limits the scaling possibilities [7].

4.3.5 Ultrarapid reactor

Critical requirements in order to yield a high liquid fraction from pyrolysis are high heating rate and short residence time (see table 4-2). An ultrarapid reactor-pyrolysis is designed to operate in range of 650 °C have total residence time of 100-240 ms, from mixing the biomass and heat-carrier material, to the cooling of the vapors. Under these conditions an ultrarapid reactor yields a liquid fraction up to 90% [7]. Figure 4.7 depicts the principles behind an ultrarapid reactor, where biomass particles are transported into the reactor and "bombarded" with a stream of heat-carrier material and an inert gas heated to 100 °C above the reactor temperature at a high velocity. From the high-impact between the biomass, solids and gas, an extremely high heating rate is archived and the biomass reaches pyrolysis temperature in less than a second [7]. The product-stream leaves the reactor and undergoes rapid cooling in order reduce secondary cracking of the vapor.
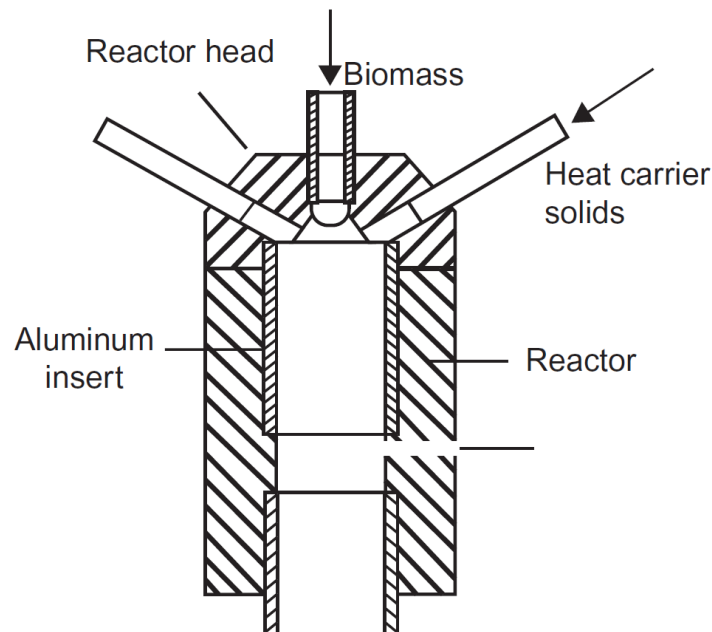
Figure 4.7: *Principle of an ultrarapid reactor* [7].

4.4 Upgrading bio-oil to bio-fuel

The motivation for upgrading bio-oil is to reduce the unwanted properties in order to produce a product which can be used for transportation fuel. For the production of transportation fuel, the oxygen content of bio-oil has to be reduced in order to make it compatible with conventional fuel, reduce the viscosity, remove solids and make the final product more chemical stable. Bio-oil can be upgraded using either a physical, chemical or catalytic process to increase the fuel quality in order to make it more suitable for different applications which requires a higher quality feedstock [21]. Figure 4.2 illustrates the different pathways for upgrading biomass to bio-fuel, where the focus in thesis will be on the production of hydrocarbons in the gasoline and diesel range by hydro –treating of bio-oil.
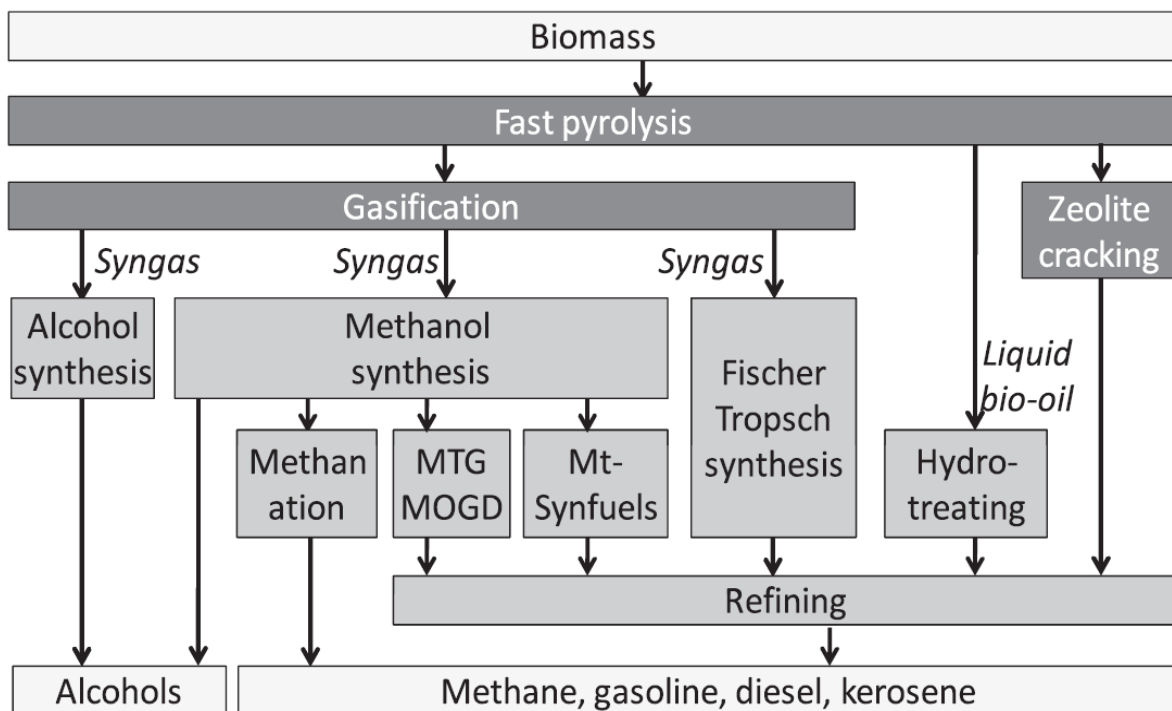
Figure 4.2: *The main pathways for upgrading bio-oil to bio-fuel* [21].

Upgrading bio-oil to conventional gasoline and diesel requires a complete deoxygenation and conventional refining methods. This can be done through separate operations or through an integrated catalytic pyrolysis process [21].

4.4.1 Hydrotreating

Hydro-processing utilizes a catalytic reaction with hydrogen to remove oxygen from bio-oil in the form of water. This process is performed at high pressure (up to 200 bar) and at temperatures in range of 400°C and requires a separate hydrogen source (on-site or external) [22].

Upgrading bio-oil using hydro-processing is considered as a separate process to fast pyrolysis which can be carried out at another nearby location. Complete hydrotreating of bio-oil yields a mixture of hydrocarbons similar to that of naphtha, which requires further refining in order to produce conventional transport fuel. The upgrading of bio-oil using hydro-processing can be performed on-site in an existing petroleum refinery in order to take advantage of existing equipment and knowledge [21].

Upgrading bio-oil through hydrotreating yields a typical naphtha fraction of about 25wt% of the biomass feedstock or 55% in energy terms if the hydrogen is supplied from a separate process or purchased directly from a supplier. If hydrogen was produced using the same biomass feedstock the yield would be reduced to 15 wt% and 33% in energy terms [21]. Figure 4.3 depicts several hydrogen production pathways using residue from the pyrolysis process, the raw biomass feedstock, by direct production/purchase or by using hydrogen-surplus from a refinery.
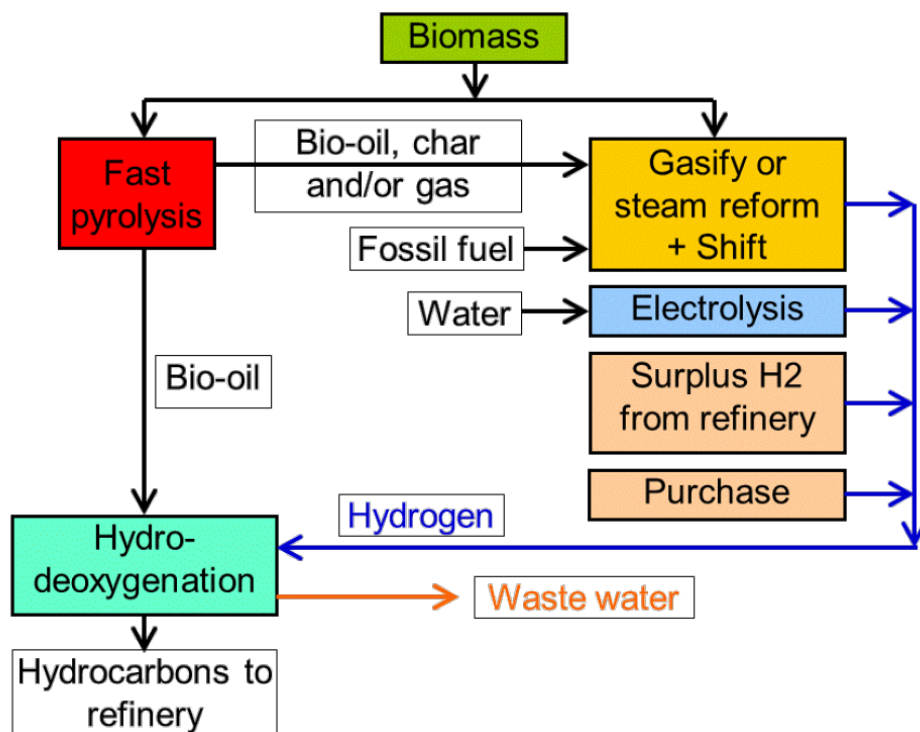
Figure 4.3: *An overview over potential hydrogen sources for hydroprocessing* [23].

The fuel quality and yield of the naphtha fraction is determined by the catalyst used, reactor configuration and operating conditions. For the hydroprocessing of petroleum a fixed bed reactor configuration is used and this is common for upgrading bio-oil [23].

Bio-oil contains several heavier organic compounds in the form of a tar-like product, and this product has proven challenging to hydroprocess in a single stage process. In order to perform a complete deoxidization of bio-oil, a multi-stage process is required. Multi-stage hydroprocessing consist of a mild hydrotreating followed by a hydrotreating at higher temperature and a lower residence time. The mild hydrotreating is used as a pre-treatment for the bio-oil in order to reduce the oxygen content in the most reactive compounds, while a complete deoxygenation is performed in the more severe hydrotreating [23, 24].

Upgrading bio-oil through hydroprocessing involves a series of complex chemical reactions as illustrated in figure 4.4, where the combination of hydrodeoxygenation and decarboxylation results in almost a complete deoxygenation of the bio-oil in the form of water and CO_2 [24, 25].
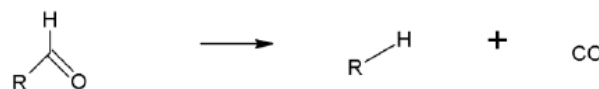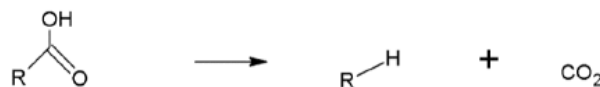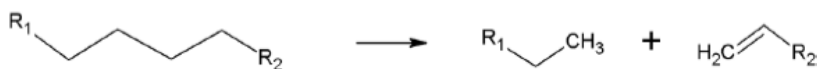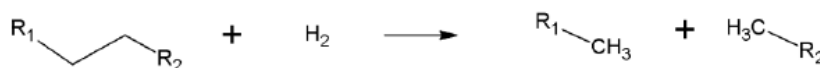
Figure 4.4: *A selection of hydroprocessing reactions* [25].

4.4.2 Overview upgrading methods

While the commercialization of bio-fuel from bio-oil has not taken place yet, there have been extensive research and studies in order to optimize and discover new techniques for upgrading bio-oil in order to make bio-fuel production economically feasible [26]. Table 4.3 present an overview and characterization of some techniques for upgrading bio-oil for the production of bio-fuel.

Table 4.3: *Overview and characterization for some bio-oil upgrading processes* [26, 27].

Upgrading technique	Process conditions	Process Description	Technique Feasibility Pros.	Cons.
Hydrotreating	- Temp ~500 ºC - Low pressure - Catalyst required - Chemicals needed	Hydrogenation (no cracking reactions) removes N, O and S as NH_3, H_2O and H_2S	- Cheaper method, - Extensive use in petroleum industry.	- High coking (8-25%) - Low quality fuel produced
Hydrocracking	- Temp > 350 ºC - High pressure - Catalyst required - Chemicals needed	Hydrogenation with simultaneous cracking-reaction	- High yields of lighter hydrocarbon products	- Complicated process - High Costs - Catalyst deactivation - Reactor clogging
Zeolite cracking	- Temp: 300-600ºC - Almost 1 atm pressure	- Upgrading pyrolysis vapors directly through cracking reactions using zeolitt catalyst	- No H_2 co-feeding required	- Lower yield of liquid hydrocarbons - deactivation of catalyst - Infant technology
Solvent addition (Added directly or esterification of the bio-oil using alcohol and acid catalyst)	- Mild conditions - Uses polar solvents(water, methanol, ethanol)	- Reduces viscosity - Increase stability - Increase heating value	- Simple approach - Low cost	The reaction mechanisms involved in the adding of solvents are not fully understood.
Emulsification	- Mild conditions - Use surfactant	Upgrades bio-oil un order to mix directly with diesel.	- Simple process - Reduce pH of the bio-oil	- High energy requirements

4.5 Woody biomass to liquid hydrocarbons: Pyrolysis biorefinery

This chapter presents a brief overview over the main process and unit operations in a biorefinery producing transportation fuels from woody biomass.

4.5.1 Pretreatment of biomass

In the pretreatment process, the biomass feedstock usually in the form of wood chips are dried and grinded in order to prepare the feed for the pyrolysis process. Pretreatment is essential in order to reduce the moisture content and the particle-size to ensure an optimized bio-oil production [7].

Before pretreatment, the feedstock biomass usually has a relatively high moisture content (30-50 wt%) which has to be reduced to about 10-15wt% in order to maximize the heating value of the bio-oil produced from pyrolysis. Drying the biomass takes place using suitable equipment in order to dry the feedstock using hot flue gas from another process. The size-reducing process is dependent on the specification of the reactor used in order to provide optimal heat transfer and operations in the reactor. Figure 4.6 depicts a process flow overview for the pretreatment process for woody biomass in the form of wood chips with a moisture content of 30wt%. The pretreatment process is designed to meet the specifications of a Circulating fluidized bed, using hot flue gas to reduce the moisture content and grinding to reduce the size of the feedstock in order to meet the reactor specifications [7, 23].
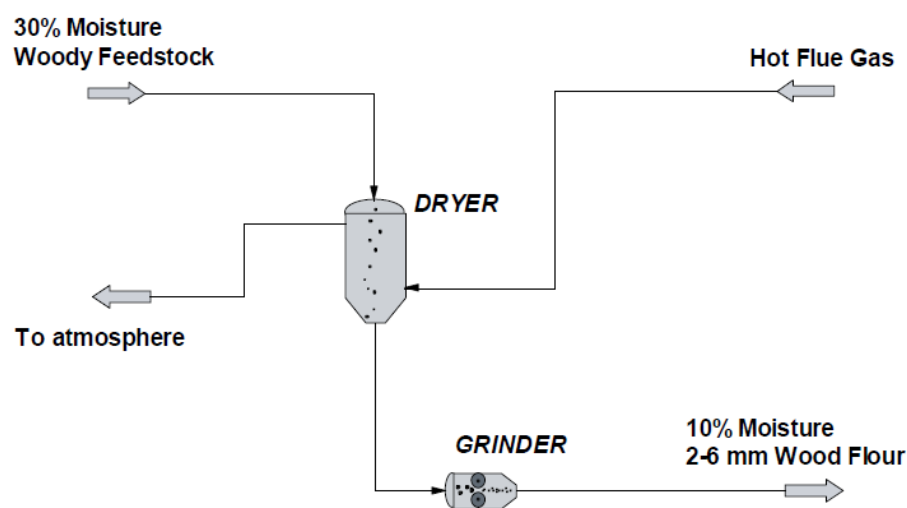
Figure 4.5: *Simplified flow sheet for the pretreatment of woody biomass* [23].

4.5.2 Fast pyrolysis

Figure 4.6 illustrates a flow diagram for the pyrolysis process using a CFB-reactor and vapor cooling, where the finely grinded and dried biomass is heated to reactor operating temperature before feeding the biomass into the pyrolysis-reactor. The grinded biomass particles archives pyrolysis temperature using sand as a heat carrier in order to achieve a high heating rate. Using high velocity gas in order to fluidize the stream in the reactor provides a residence time under 2 seconds [23]. When leaving the reactor, the product from the pyrolysis reaction is a mix of vapors and char. A series cyclones are used in order to separate char and sand, in order to prevent further cracking of the vapor. After the cyclone stage, the vapors are rapidly cooled and condensed using bio-oil or a suitable hydrocarbon liquid. The figure below illustrates two step condenser unit, where the vapors are cooled down using recycled and indirect air-cooled bio-oil in order to separate the primary gases. In the second condenser, the recirculating bio oil is indirectly cooled by water. The gas surplus from the process is recycled in order to assist fluidization, while the char and some of the gases is burned in order to heat the sand. After the pyrolysis process the bio-oil is transported to hydrotreaters, while the remaining gas is transported to an onsite hydrogen plant [23].
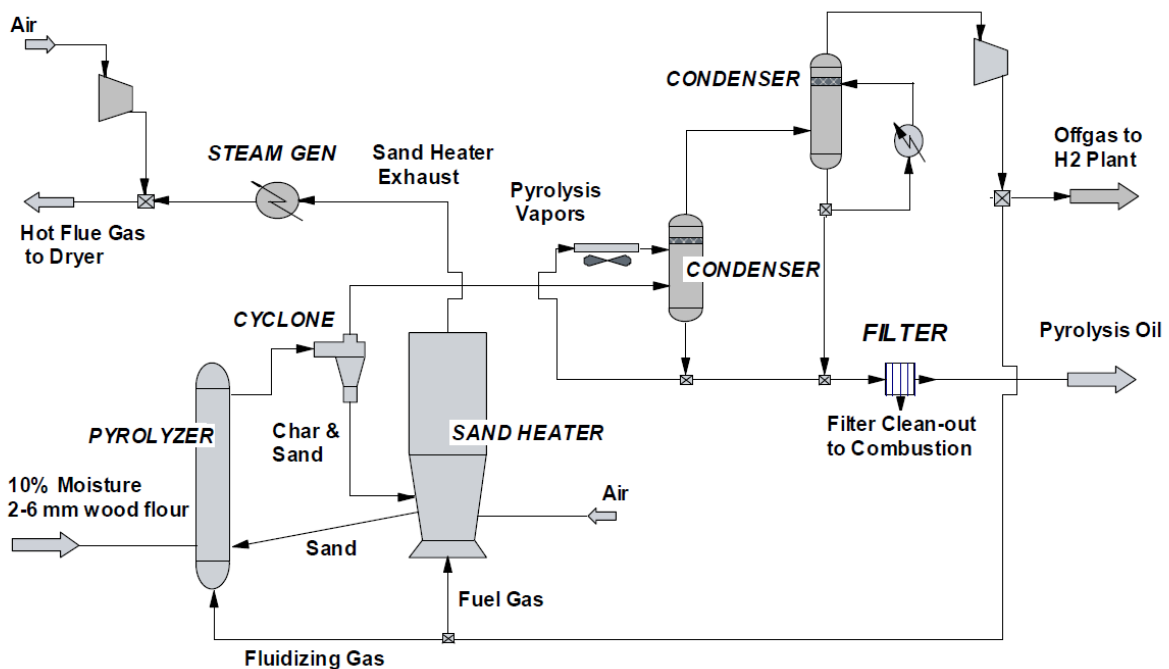
Figure 4.6: *Overview of the unit-operations in the bio-oil production* [23].

4.5.3 Hydroprocessing

After the pyrolysis stage, the bio-oil is pressurized and preheated together with compressed hydrogen at high pressure. The following process steps is multi-step hydroprocessing where the process conditions increases in subsequent step, in order to produce a mixture of liquid hydrocarbons. The product leaving the last hydrotreater consists of two liquid phases (Aqueous and oil phase) and a gas fraction consisting of non-condensable hydrocarbons (methane, ethane, propane, and butane), carbon dioxide and hydrogen [23]. Hydrogen is recycled using pressure swing adsorption (PSA). The liquid phases can be easily separated using a suitable separation technique which produces significant amounts of wastewater that requires treatment. After hydroprocessing the hydrocarbon-phase contains less than 2 wt% oxygen and is fractionated into a gasoline and diesel- blendstock together with a mixture of heavier liquid hydrocarbons which has to undergo hydrocracking to produce lighter hydrocarbons [23, 28]. Figure 4.7 illustrates a simplification of the hydroprocessing of the bio-oil in order to produce a mixture of hydrocarbons.
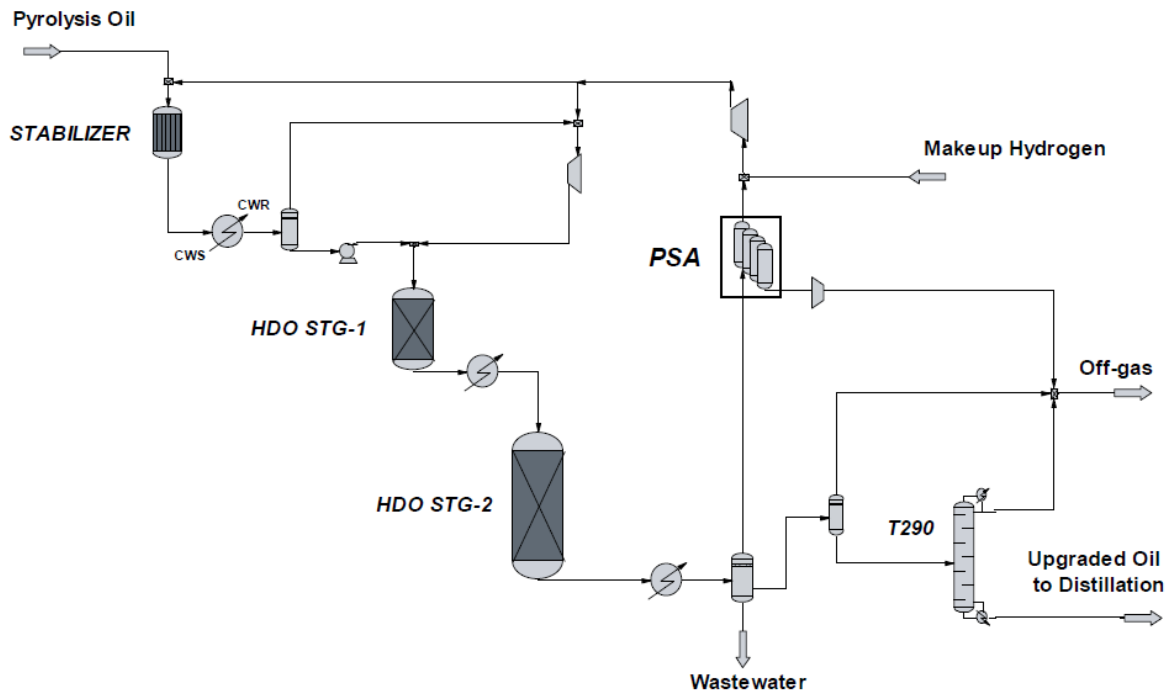
Figure 4.7: *Process flow-sheet for hydroprocessing bio-oil* [23].

4.5.4 Hydrocracking

The heavier fraction which remains after the distillation is sent to a reactor, where a catalytic cracking reaction takes place in order to produce hydrocarbons in the gasoline and diesel range. Figure 4.8 illustrates a simplified schematics for the hydrocracking and product separation stage with a recycle-loop for "uncracked" product.
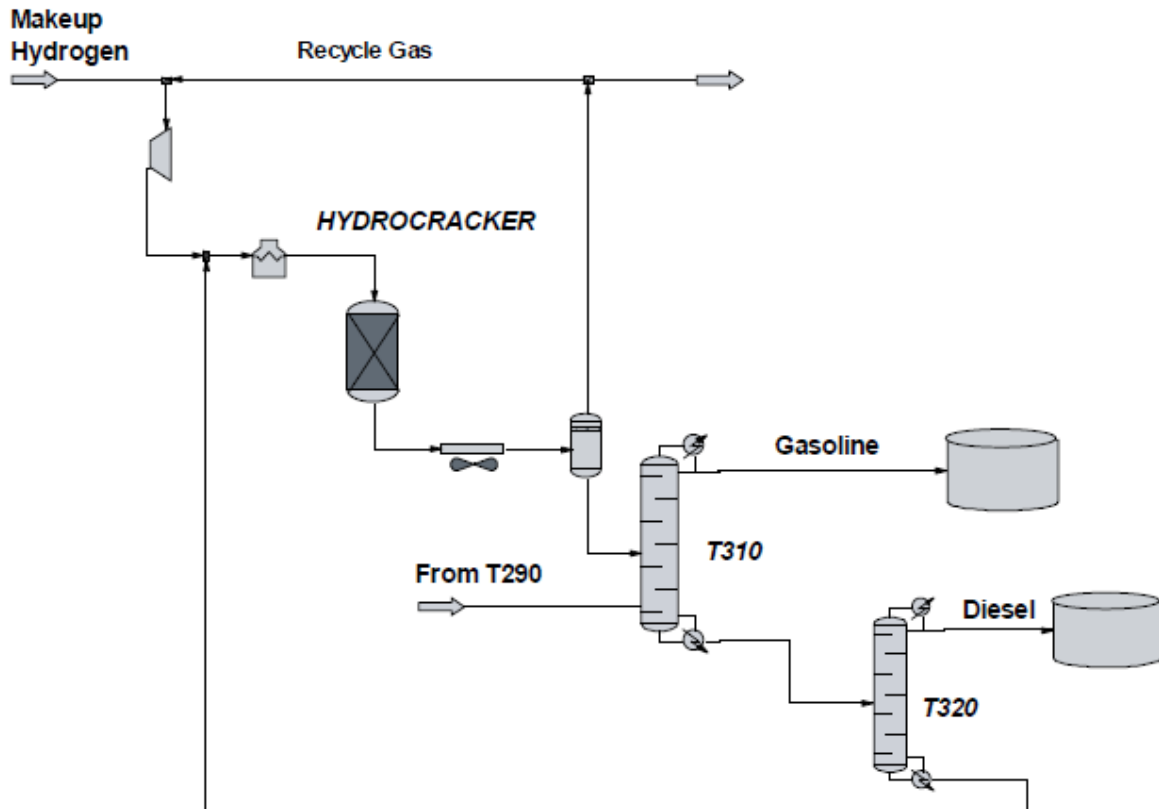
Figure 4.7: *Process flow-sheet for hydrocracking the heavy fraction from bio-oil* [23].

4.5.5 Hydrogen production

In order to provide enough hydrogen for the hydroprocessing and hydrocracking there are several production pathways to evaluate, where the most suitable solutions is either direct purchased or by on-site production through steam reforming gases produced during pyrolysis supplemented with natural gas [23, 29]. Figure 4.8 illustrates the pathway for an on-site production of hydrogen using off-gas from the pyrolysis reactor and supplemented with natural gas as the gas produced is not sufficient to provide enough hydrogen for the hydrocracker and hydroprocessing processes. The need for natural gas is a result of the combustion of-gas produced from different processes which is needed for providing thermal energy for the reformer. Of-gas which are not combusted is compressed and mixed with natural-gas which are conditioned using hydrogen desulfurization (HDS) [23].
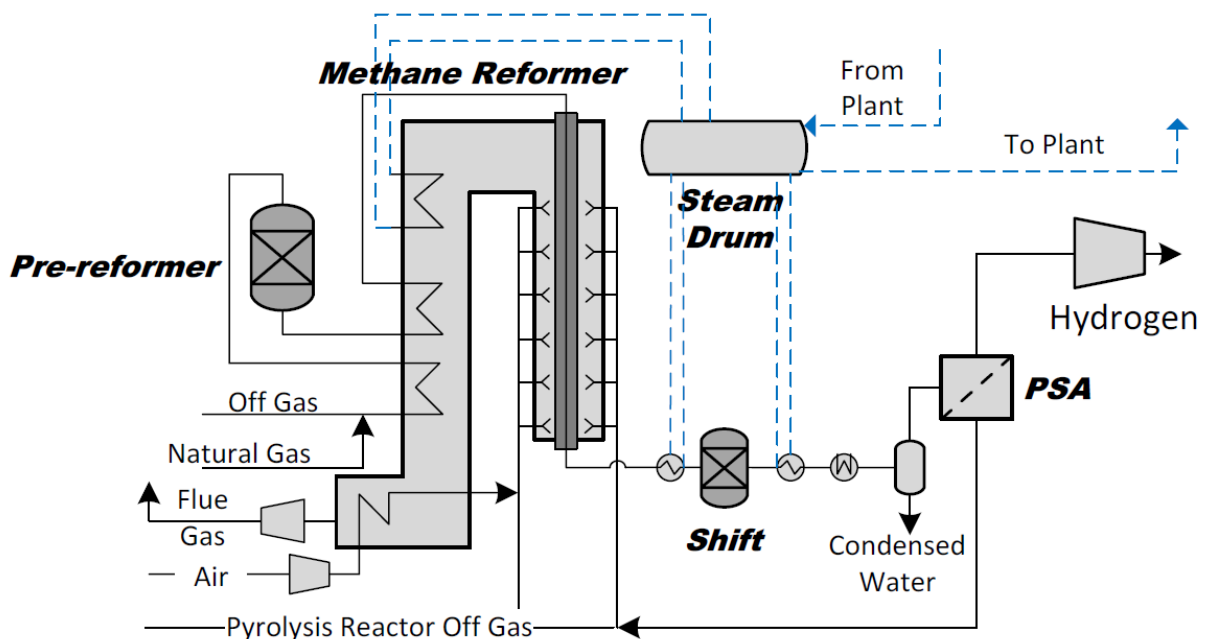
Figure 4.8: *Process flow-sheet for on-site hydrogen-production* [23].

After undergoing HDS, the gas is mixed with superheated steam and processed in a pre-reformer to convert C_2+ compounds into methane before reforming the gas into syngas (H_2+CO) in the main reformer. This is necessary in order to reduce the coking of the main-reformer, which is critical for the stable production of hydrogen [23]. The H_2/CO ratio is then increased using a high temperature shift reactor followed by a condensation step, which removes condensed water.

After the condensation a purification is performed on the gas by using pressure swing adsorption (PSA) to separate the hydrogen from the remaining of-gases. The exhaust-gas is then recycled back to provide thermal energy for the reformer. Steam can be generated from recycling the heat from the reformers and from cooling down the shift-reactor, which can be utilized in the reformer reaction or for process heating.

The hydrogen could be derived from a renewable feedstock by either gasifying the biomass for the production of syngas (CO and H_2) or by steam-reforming a fraction of the bio-oil. In order to produce hydrogen from these feedstock, approximately one third of the biomass feedstock would be require in order to provide enough hydrogen for upgrading of the bio-oil and reducing the fuel yield from the process [29].

4.5 Pyrolysis Economics.

Several studies has been performed the last decade on the economic viability of a commercial bio refinery using the fast pyrolysis-pathway and hydroprocessing(FPH) in order to produce transportation fuel from woody biomass. All these studies were based on a commercial bio refinery with a plant capacity of 2000 metric tons of per day (MTPD) using a feedstock derived from wood chips or corn-stover [23,29,30]. Table 4.4 shows the results from these studies combined with the result from studies using catalytic fast pyrolysis (CPH) and hydropyrolysis (HPH) in order to produce bio-oil with a lower oxygen-content, which is upgraded using hydroprocessing in both cases [31,32]. The results from the studies are compared on the basis of total project investments (TPI), and minimum fuel selling price (MFSP –*USD $ per litre gasoline equivalent*).

Table 4.4: *Summary of the techno-economic models for Pyrolysis.*

Pathway	Feedstock cost (USD $/MT)	TPI (USD $MM)	MFSP (USD $l/ge)	Source
FPH	60.50	329	0.58	[23]
FPH	90	217	0.60	[29]
FPH	83	429	0.68	[30]
CPH	90	457	0.97	[31]
HPH	96	286	0.48	[32]

A TEA (techno economic analysis) on a 2000 MPTD biorefinery using FPH were performed by the Pacific Northwest National Laboratory (PNNL) in 2009 [23]. Based on an assumption of a 20-year lifespan, 10% IRR and USD $60.50/MT feedstock cost (wood chips), the analysis estimates a TPI of USD $329 million with a MFSP of USD $0.58 l/ge. In this design-case the hydrogen needed for hydroprocessing was done on-site in the biorefinery. Another study was performed by Iowa State University in order to make comparison of a FP biorefinery with internal and external hydrogen production [29]. From this analysis, the internal hydrogen-supply scenario had a TPI of USD $311 million while the external hydrogen supply scenario had a TPI of $217 million. The assumptions for this analysis was a 20-year lifespan, 10% IRR and USD $90/MT feedstock cost (corn-stover) resulting in MFSP of USD $0.88 l/ge and USD $0.60l/ge for the

internal and external hydrogen supply scenario respectively. An updated study using the same assumptions was performed in 2013 to reflect the changes in the marked conditions and commercialization-status for the FP-pathway [30]. In the updated analysis, the TPI was estimated to $429 million for a 2000 MPTD biorefinery with an external hydrogen supply resulting in a MFSP of $0.68 l/ge. The main contribution to higher TPI compared to the 2010 analysis, is the need for more expensive hydro processing units more suitable to process bio-oil. In addition to the expensive hydroprocessing unit, a boiler and turbo generator was included to provide the necessary electricity for the biorefinery [30].

TEA of variations of the FP-pathway using Catalytic pyrolysis (using zeolite catalyst) and catalytic pyrolysis in the presence of pressurized hydrogen (catalytic hydro-pyrolysis). The motivation for these technologies is to produce hydrocarbons directly using HPH or a partial upgraded product (lower oxygen content) through CPH [31, 32]. A study was performed by Thilakaratne et al. (2014) on a 2000 MTPD biorefinery utilizing CPH in order to produce a diesel and gasoline blendstock from woody biomass. The hydrogen needed for hydroprocessing in this scenario is produced on-site from the reforming of natural-gas. In this analysis the TPI were estimated to $457 million under the assumptions a 10% IRR, 30-year lifespan and a feedstock cost of $96.57/MT. The MFSP is estimated to $0.97l/ge, where the feedstock cost contributes to 45% of the MFSP [31].

A TEA based on HPH-technology patented by Gas Technology Institute was performed by Tan et al. 2014 in order to provide the techno-economic analysis necessary for a commercial-scale biorefinery based on data collected from a pilot-scale HPH-plant [32]. From this analysis the TPI was estimated to $286 million under the assumption of a 10% IRR, 30-year lifespan, and $85.59/MT feedstock cost. The MFSP was estimated to $0.48 l/ge [32].

5. Gasification for biofuel-production

The previous chapter presented a biofuel production pathway using pyrolysis and hydroprocessing in order to produce liquid biofuel from wood biomass. This chapter will describe the process pathway from woody biomass to liquid hydrocarbons using gasification. Figure 5.1 illustrates the pathway for producing bio-fuels from woody biomass using gasification, where the first step is the pretreatment of feedstock in similar manner compared to pyrolysis in order to reduce moisture content and reduce the size of the feedstock particles. After the pretreatment, the biomass particles are converted to a gas consisting of several compounds by the gasification process. For the production of liquid hydrocarbons, the product gas produced through gasification has to be cleaned in order to achieve syngas-standard. This is done by several gas-conditioning processes in order to remove unwanted compounds in the gas-stream. The cleaned gas consists of mainly carbon monoxide and hydrogen [7]. In order to produce liquid fuel from syngas, a suitable process, such as the Fischer Tropsch synthesis is used to create a mixture of hydrocarbons which needs more processing using conventional refining processes.

| Pretreatment | Gasification | Gas-conditioning | Synthesis | Refining |
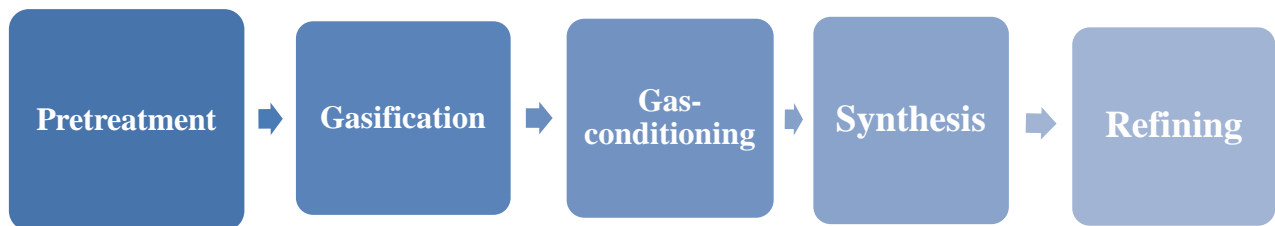
Figure 5.1: *Pathway for producing bio-fuel from woody biomass using gasification.*

5.1 Gasification principles

Gasification is a thermochemical process where a fossil or non-fossil feedstock is converted into a gaseous energy carrier called syngas. Syngas can either be utilized directly through combustion or it can be refined into high quality products. The difference between pyrolysis and gasification is that the gasification reaction needs an oxidation medium. Suitable mediums for gasification is supercritical steam, air, oxygen, carbon dioxide or a combination of these mediums [7].

The main difference between combustion and gasification, is that gasification converts the chemical energy in the biomass into a gaseous energy carrier by partial oxidation. By doing so much of the energy is stored in the product-gas, while the complete oxidation in a combustion reaction converts more chemical energy into heat [8]. The partial oxidation reaction is achieved by regulating the amount of oxygen medium present in the reactor.

Gasification can be divided into four main reactions: 1) drying, 2) pyrolysis, 3) gasification and 4) reduction. The drying process occurs above 100 ℃ and removes loosely bound moisture in the biomass particles. As temperatures increases, the thermal decomposition (pyrolysis) of the biomass will remove volatiles, and when these substances comes in contact with the oxidation medium, the gasification reaction starts. The reaction which occurs in the gasifying step can be summarized by the following equations [8]:

Partial Oxidation: $C + \frac{1}{2}O_2 \longleftrightarrow CO$ **(-268 MJ kg/mole) (5-1)**

Complete Oxidation: $C + O_2 \longleftrightarrow CO_2$ (-406 MJ kg/mole) **(5-2)**

Water gas reaction: $C + H_2O \longleftrightarrow CO + H_2$ (+118 MJ kg/mole) **(5-3)**
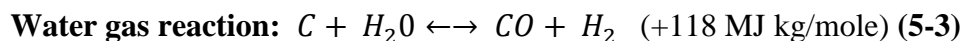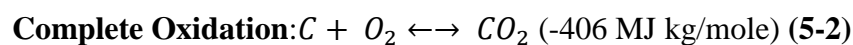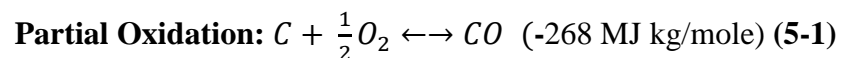
These reactions illustrates that the largest amount of energy released comes from the complete oxidation of carbon to carbon dioxide while the partial oxidation releases about 65% of the same energy amount [8]. In contrast to the product produced from combustion, hydrogen and carbon monoxide can undergo further reactions:

Water gas shift reaction: $CO + H_2O \longleftrightarrow CO_2 + H_2$ (-42 MJ kg/mol) **(5-4)**

Methane formation: $CO + 3H_2 \longleftrightarrow CH_4 + H_2O$ (-88 MJ kg/mol) **(5-5)**
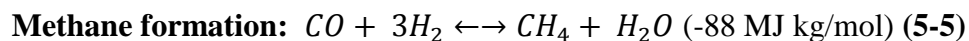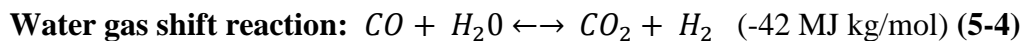
The arrows depicted in these reaction equation depicts these reactions in an equilibrium and depending on conditions (pressure, temperature, concentration) the reaction can proceed in either direction [8]. The product from these reactions is gas containing CO, CO_2, CH_4 and H_2.

5.2 Oxidation medium

Oxidation medium or gasifying medium reacts with the carbon and hydrocarbons in order to produce simpler "building blocks" in the form of low-molecular gases (mainly CO, H_2, CH_4, and CO2), The oxidation medium used in the gasification process affects the composition of the gas produced. This has an impact on the process economics, as some oxidation medium such as oxygen has a higher cost than using air, but produces a gas with a higher heating value [33]. Table 5.1 illustrates how different types of oxidation medium affects the quality of the product gas obtained from gasification.

Table 5.1: *Overview of quality of product gas related to the oxidation medium used* [33].

	Heating Value (MJ/Nm^3)	Oxidation medium
Low heating value	4-6	Air – Air/Steam
Medium heating value	12-18	Oxygen or Steam
High heating value	40	Hydrogen

Product gas with a low heating value is often used for direct applications such as combustion, while product gas with a medium/high heating value can be used as a feedstock for chemicals or liquid fuels by upgrading through a suitable chemical synthesis reaction [7]. The use of oxygen as an oxidation medium is considered to be too expensive for the production of thermal energy, so using air is more common as an oxidation medium for low heating value product gas for direct applications. The low heating value is a result of a dilution effect from the high nitrogen content in air [7, 33]. In order to produce a product gas to be used as a feedstock for chemicals and fuel steam is preferred as a oxidation medium, as this medium prompts the formation of a product-gas from the gasification process contains more hydrogen per unit of carbon (higher H/C ratio) [7].

5.3 Gasification reactor configurations

There are three main types of gasification reactors/gasifiers. Figure 5.2 depict an overview of the main groups1) fluidized bed, 2) entrained bed and 3) fixed/moving bed, with a selection of subgroup technologies. In this chapter a brief description of some of these technologies will be presented and how gas-solid mode in the reactor affects the sequence in the gasification reactions.
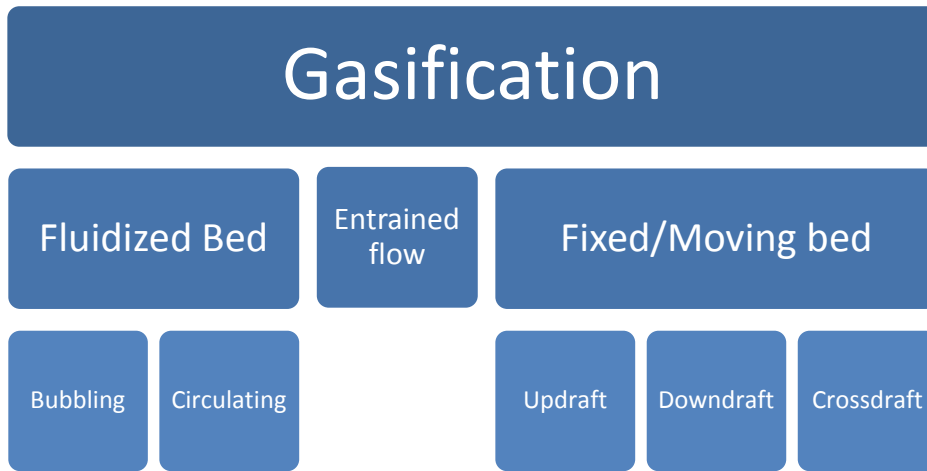
Figure 5.2: *Overview of a section reactor configuration used for gasification of biomass.*

Figure 5.3 shows the range of application for the different reactor configurations.
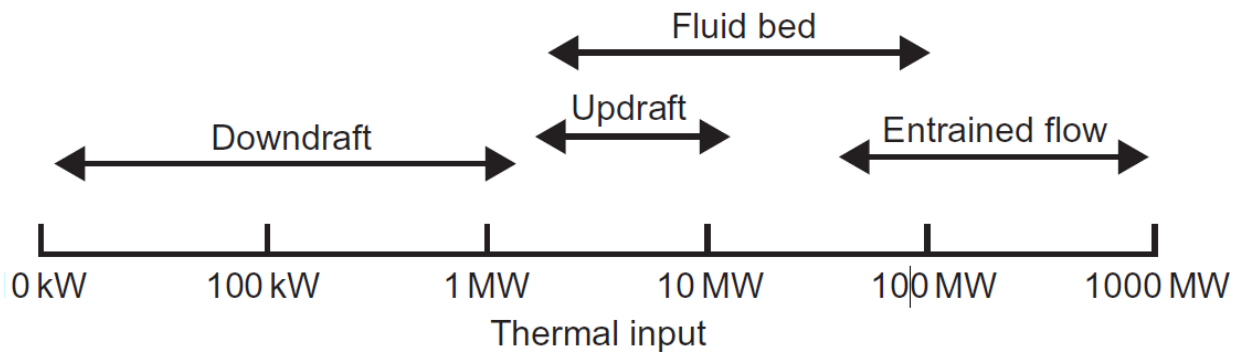
Figure 5.3: *Area of application for a selection gasification reactors* [7].

5.3.1 Fixed bed gasifiers

In a fixed bed reactor (FBR), the biomass is added through the top of the reactor while the oxidation medium travel upwards in order to achieve a countercurrent flow between solids and gas. The gasification reactions occurs in series as the fuel moves down the reactor and is always added through the top of the reactor, but the inlet for the oxidation medium and the outlet for the product-gas depends on what type of FBR is utilized. Figure 5.4 illustrates three different FB reactor configuration, and how the design affects reactions which occurs during gasification [7].
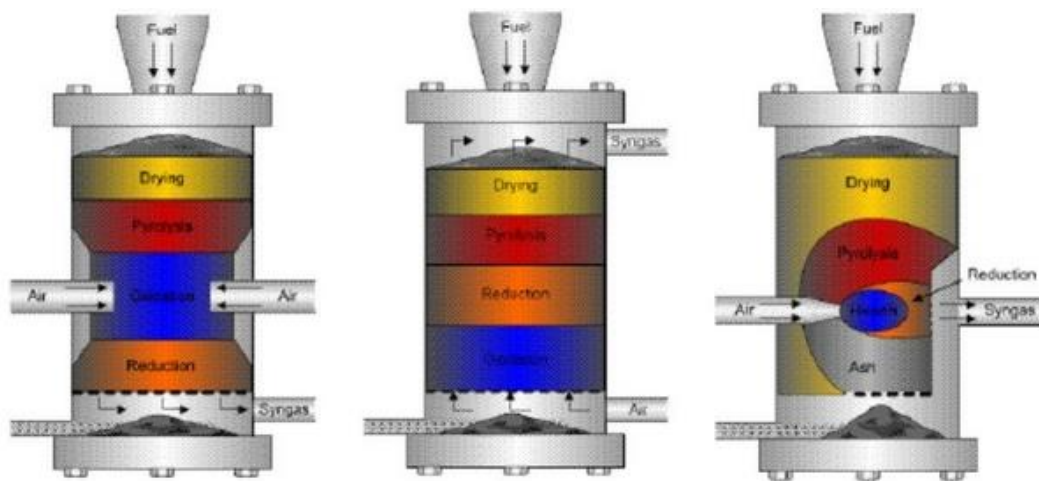
Figure 5.4*: Different FB-reactors and gasification profile.. Left: Downdraft, Middel: Updraft, Right: Cross-flow* [34].

The advantages of this design, is that the construction is simple and easy to dimension for small scale application. A simple construction makes the mixing of fuel and oxidation medium challenging, in addition the heat transfer in fuel is limited and the product-gas from FB-reactors has a lower quality and a higher amount of impurities [7].

5.3.2 Entrained flow reactor

For large scale gasification the favored reactor design is the entrained flow (EF) gasifier . In an EF reactor the oxidation medium (oxygen or steam) and pulverized fuel particles are entrained together by feeding them co-current at high velocity. This causes fuel particles to be surrounded by the oxidation medium and transported through the reactor. In a EF reactor the combustion reaction occurs at the entry point of the oxidation medium followed by the gasification reaction further downstream in the reaction (see Fig 5.5). Reactors of this type operates at higher temperatures in the range of 1400 $^{\circ}$C and pressure in the range of 20-70 bar [7].

Fuel particle   Fuel particle path   Gas particle

Pulverized
fuel + O$_2$

Combustion
zone

Gasification
zone

- - - - Fuel particle path   ——— Gas path
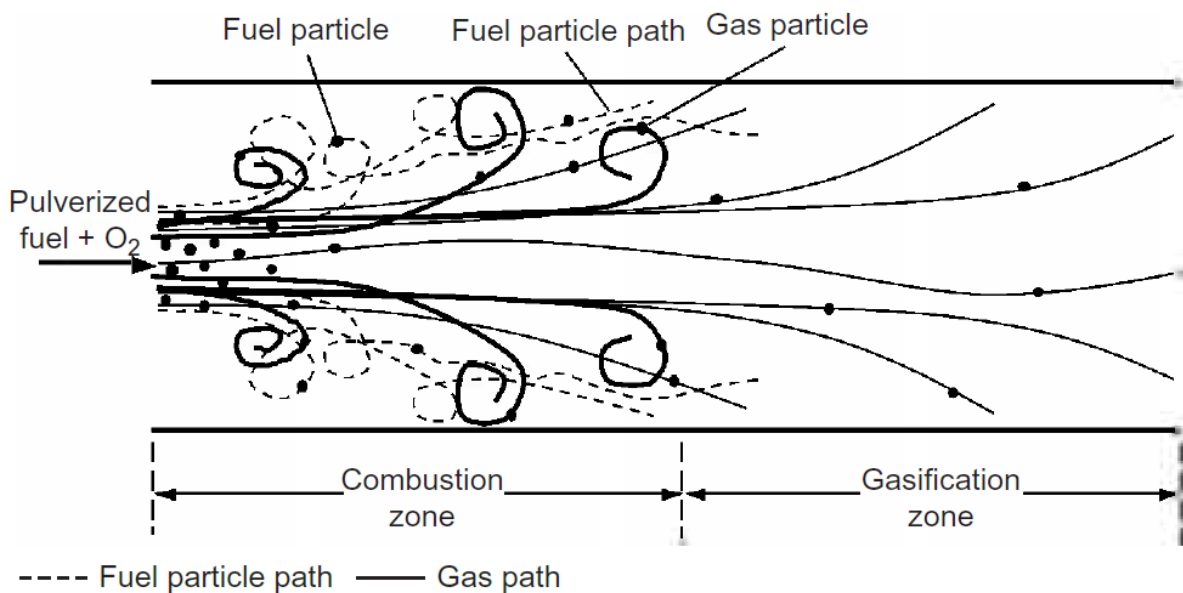
Figure 5.5: *Simplified sketch of an entrained flow in an EF reactor* [7].

The use of EF gasifiers in order to produce syngas from woody biomass has certain challenges to overcome in order to establish a commercial technology. In order to achieve entrained conditions and short residence time, the fuel has to be grinded into a fine powder in order to make it suitable for the reactor. Grinding biomass into a powder is challenging as a result of the fibrous structure of the feedstock. A solution for this could be additional pretreatment using torrefaction in order to change the structure of the biomass making it more similar to the structure coal and easier to grind [7,35]. The chemical nature of woody biomass also provides a challenge as ash from biomass is considered highly corrosive and melts at high temperatures producing a liquid slag. This issue presents a maintenance and operation challenge for the reactor. As a result,

EF reactors are not favored for the gasification biomass, but the high temperatures which leads to a higher quality product gas with a lower tar and methane content reducing the need for gas-conditioning. [7, 36]

Figure 5.6 illustrates a top-fed ET reactor, where high velocity jets produces a turbulent flow near the entry point where the oxidation medium and fuel are fed into the reactor. The fuel particles are heated fast by heat transfer from the reactor walls. The product gas leaves the reactor through a outlet, while the slag is collected at the bottom of the reactor [7].
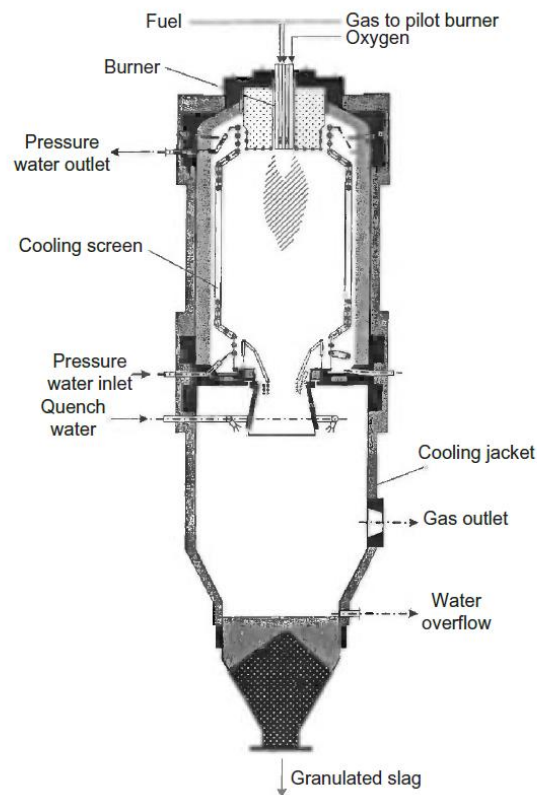
Figure 5.6: *Overview of a top-fed entrained flow reactor* [7].

5.5.3 Fluidized bed reactor

Fluidized reactors (BFB and CFB) has been briefly explained in the previous chapter and the reactor design for gasifier is based on the same principles as the equivalent pyrolysis reactor configuration. The main difference is the medium used for fluidizing the bed material also acts as the oxidation medium. In fluidized bed reactor, the fuel is fed into reactor near the top of the reactor bed. Here the fuel mixes with the hot bed material providing a high heat and mass transfer [36]. Process temperature are in the same range as the FB reactor. Figure 5.7 shows the reactor design principles for the main types of fluidized bed a) *Bubbling fluidized-bed gasifier*, b) *Circulating fluidized bed reactor.* Thermal energy is provided to the gasifier by combustion reactions in the reactor bed. From these reactions a mixture of gas and solids is produced. In a BFB-gasifier the solids are separated from the product gas using a cyclone, while a CFB recycles the solids back into the bed [7, 36].

(a) Bubbling fluidized-bed gasifier   (b) Circulating fluidized-bed gasifier
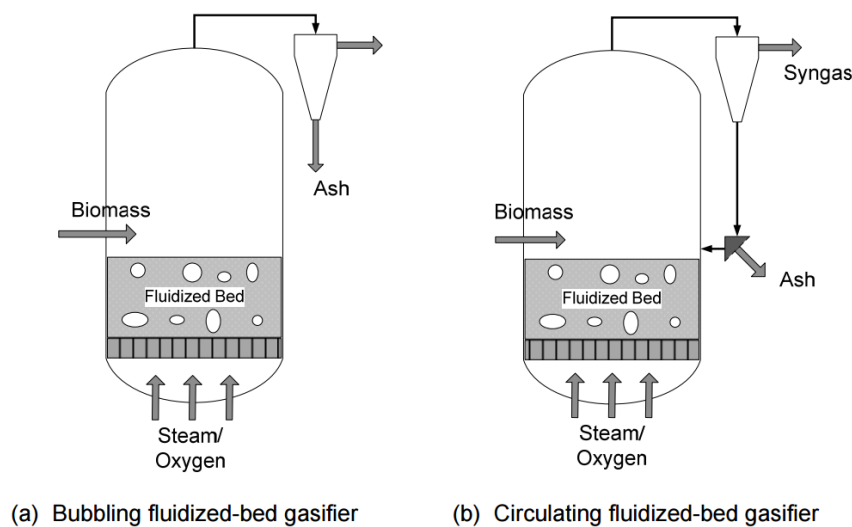
Figure 5.7: *Fluidized bed reactor design: a) BFB and b) CFB* [36].

The advantages with the fluidized bed which makes it suitable for biomass gasification is the flexibility in terms of feedstock type and quality, good mixing capabilities provide a uniform temperature profile in the bed , high volumetric capacity and high carbon conversion efficiency. In addition the relatively simple design and construction makes it easy to scale up a fluidized bed reactor [7, 36]

5.5.4 Overview of gasifiers

In this section the three main types of reactor configuration for gasification has been reviewed. Table 5.2 shows a summary of a literature review on these technologies, where a comparison of operating conditions and parameters on order to identify a suitable reactor configuration to utilize a biomass feedstock [37].

Table 5.2: Comparison *of operation parameters for the main type of gasifiers* [37].

Parameter	Fixed Bed	Fluidized Bed	Entrained Bed
Feed size	< 51 mm	< 6 mm	< 0.15 mm
Tolerance for fines	Limited	Good	Excellent
Tolerance for coarse	Very Good	Good	Poor
Feedstock tolerance	Low quality coal	Low quality coal and excellent for biomass	Most types of coal, refinery residue. Unsuitable for biomass
Gas exit-temperature	450-650 °C	450-650 °C	>1260 °C
Reaction-temperature	1090 °C	800-1000 °C	1990 °C
Oxidation-agent requirement	Low	Moderate	Low
Steam requirements	High	Moderate	Low
Nature of ash produced	Dry	Dry	Molten-«Slag»
Cold-gas efficiency	80%	89%	80%
Area of application	Small capacities	Medium-size units	Large capacities
General Problem areas	- High tar content - Utilization of fines	- Carbon conversion	- Cooling of product gas

5.4 Product-gas cleaning

In order to use the product gas from gasification as a feedstock from bio-fuel, unwanted compounds and particles has to be removed by suitable methods. This can either be by the physical removal of particulates such as soot, char, and ash by special filters, cyclones or other separation methods. The removal of unwanted chemical compounds is done by more complex methods of removal such as absorption, adsorption, and scrubbing. Table 5.3 shows the product-gas composition from the gasification of biomass using a CFB reactor and EF reactor with different operating pressure and oxidation medium [38].

Table 5.3: *Common product-gas composition from the gasification of woody biomass using a CFB reactor and EF reactor* [38].

Gasifier	CFB	CFB	CFB	EF	EF
Pressure[bar]	1	1	20	1	20
Oxidation medium	Air	Oxygen/Steam	Oxygen/Steam	Oxygen	Oxygen
Hydrogen (vol%)	14	32	19	33	27
Carbon monoxide (vol%)	21	27	20	53	53
Carbon dioxide (vol%)	14	29	40	13	19
Methane (vol%)	5	8	15	0	0
C_2 + hydrocarbons (vol%)	2	3	5	0	0
Benzene (vol%)	0.4	1	1	0	0
Nitrogen (vol%)	44	0	0	0	0
Tar (g/m^3)	8	8	11	0	0
Water (vol%)	11	28	30	19	22
Lower heating value (MJ/m^3)	7.7	12.4	14.9	10.3	9.6

In literature the gas produced from gasification is often referred to as syngas, while in this thesis the cleaned product-gas containing a mixture of mainly carbon monoxide and hydrogen is called syngas.

5.4.1 Conditioning and purification technologies

The motivation for gas conditioning is to provide a product with a higher quality and less impurities than the raw product gas in order to insure stable conditions for further synthesis reaction which uses catalysts to produce hydrocarbons from the syngas. In order to "upgrade" the product gas to a syngas-standard gas impurities such as methane, carbon dioxide and water/steam has to be removed or reformed to hydrogen/carbon monoxide. In addition several compounds has to be removed through gas conditioning. Table 5.4 illustrates the level of impurities needed to use syngas as a feedstock for bio-fuels using Fischer Tropsch (FT) synthesis [39].

Table 5.4: *Syngas specifications for FT synthesis* [39].

Impurities	Allowable levels
Sulphur compounds (H_2S + COS + CS_2)	<1 ppm
Nitrogen compounds (NH_3 + HCN)	< 1 ppm
Halogen-compounds (HCL + HBr + HF)	< 10 ppb
Alkali-compounds (Na + K)	< 10 ppb
Particles (soot, ash	Almost complete removal

Figure 5.8 depicts an overview the main cleaning and upgrading process in order to upgrade the product-gas into syngas [39]. A selection of methods will be discussed further in this section.
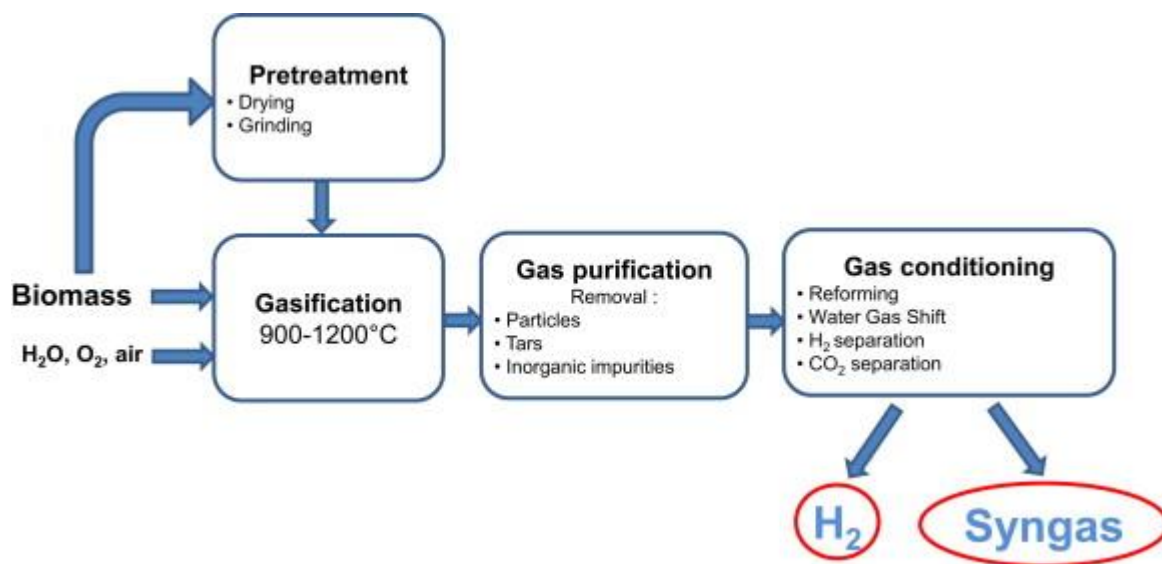
Figure 5.8: *Overview of a selection of gas condition technologies* [40].

5.4.2 Absorption

The product-gas generated from the gasification of woody biomass impurities such as char, soot, tar, and bed material. Motivation for removing these impurities from the product stream early is to ensure stable operation by preventing accumulation in the system causing disturbance in the system and excessive wear on system-components. Adsorption removes impurities by sending the product gas through an absorption- medium which purifies the product-gas by chemical or physical means using water, filters or a catalyst as a absorption-medium. For gasification, techniques such as scrubbing, physical and chemical adsorption is considered suitable [12, 36].

5.4.3 Cyclone

Cyclones are simple conic units used for removing particles larger than 50 micrometer from the product-gas [39]. Figure 5.9 illustrates how cyclones operates by removing particulates downstream of the reactor. This is meant as a" rough "purification and more suitable methods are needed to clean the smaller particulates.
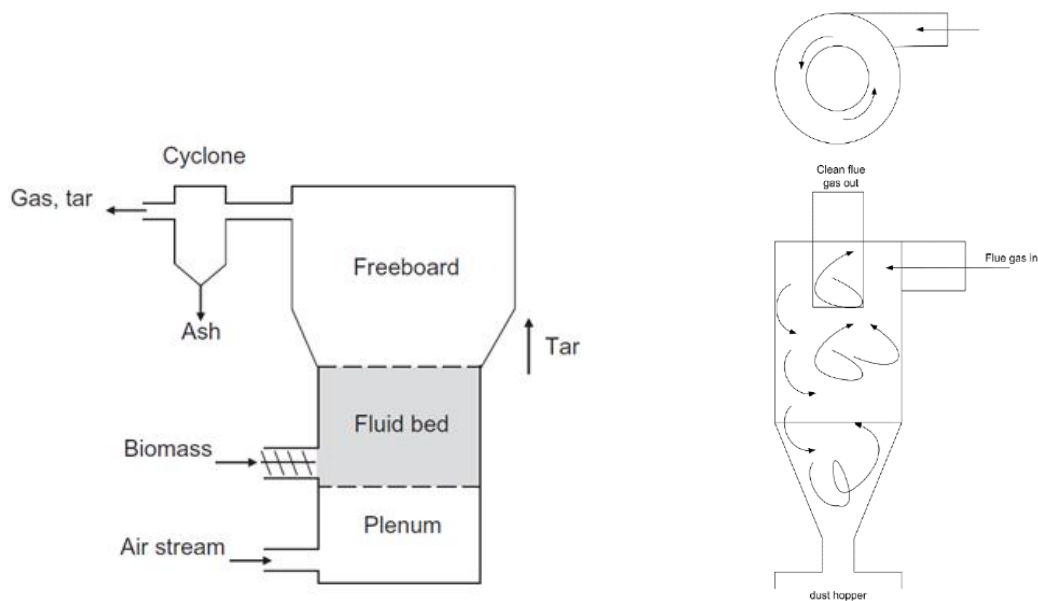
Figure 5.9: *Left) A fluidized bed reactor with a cyclone installed downstream, Right) Working principles of a cyclone* [7, 40].

In order to prevent the tar in product gas from condensing on the inside of the cyclones the cyclone and other mechanical purification processes needs to be placed inside the reactor. Tar condenses at temperatures below 300 ºC [39].

5.4.4 Filters

In order to remove dust and particles smaller than 50 micrometers from the products-gas, two types of filters are common: 1) cloth-filter, 2) Electrostatic filter.

Cloth filter:

Cloth filters are used in high temperature systems in order to remove particle smaller than 5 micrometer [39]. This is necessary in some systems where the concentration of smaller particles can be 8000-100000 mg/Nm^3, depending on the gasifier used [39]. Figure 5.10 illustrates the principles behind a "Baghouse fabric filter ". In this filter the gas from the gasifier is sent through a fabric-tube and the impurities is absorbed by the fabric, while the purified gas is sent downstream. In order to prevent the tube from collapsing, the tube-frame is made of metal.
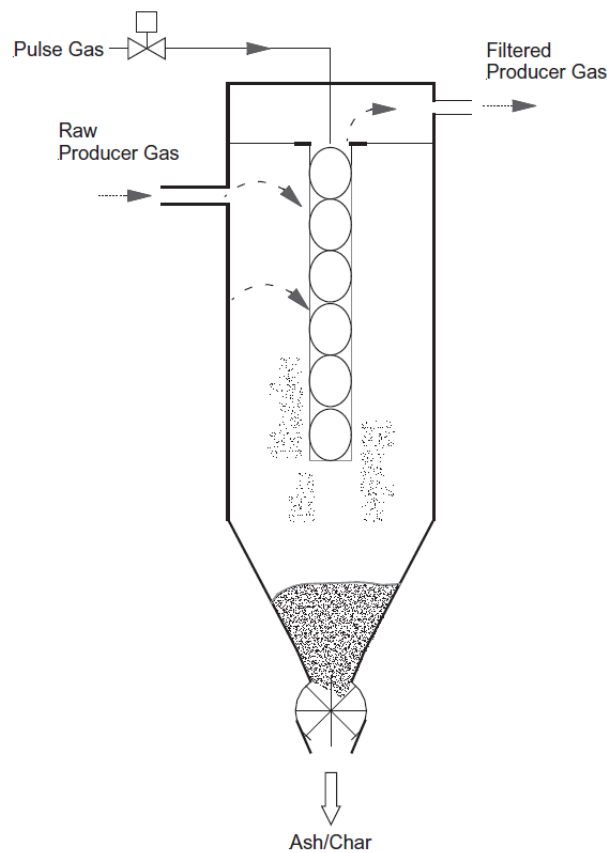
Figure 5.10: *Working principles of a baghouse cloth filter* [39].

When the filter starts to get saturated, an inert gas is sent through the tube in order to clean the filter. A challenge for this types of filter is the condensation of tar on the fabric, which reduces the efficiency of the filter [39]

Electrostatic Filter

A widely used filtration method for gasification is the *«wet electrostatic precipitator»* (WESP). In a WESP (see figure 5.11) the product-gas from the gasifier is sent through a chamber where electrodes generate an electric field. The particles and droplets are charged by anode with electric potential between 30-75 kV. As the positive charged particles moves downstream from the anode they are "caught" by the cathode collection plates. The advantage of this system is that the cleaning efficiency is not affected by accumulation on the collection-plates, but it requires maintenance in order to prevent short-circuiting the collection plates and disturbance in the gas-flow [7].
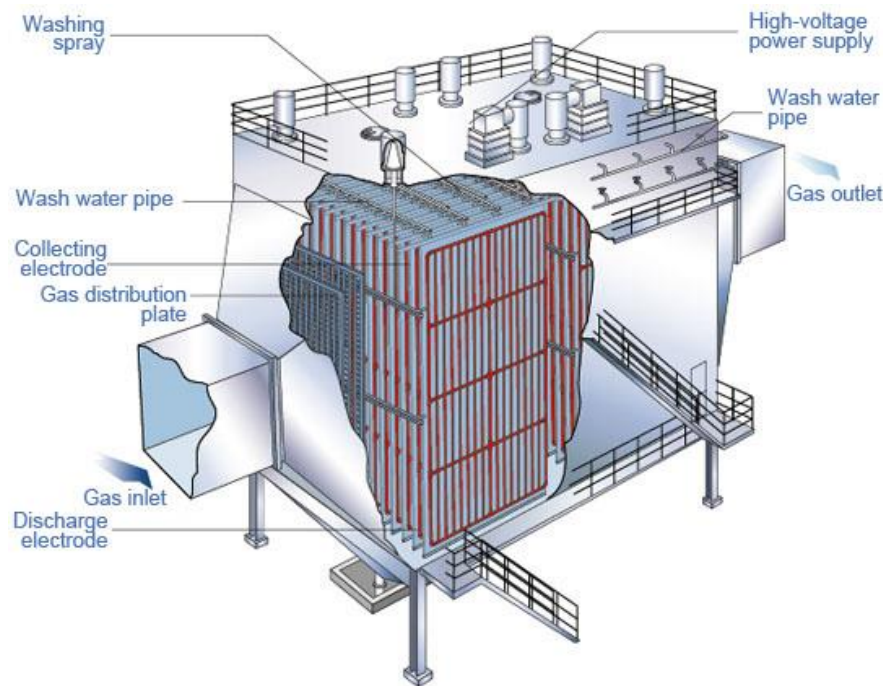
Figure 5.11: *Working principles of a WESP filter* [42].

The particles removed using WESP can be removed mechanically, but removing tar on the collection-plates it is necessary to wash the plates with a thin water-film. WESP has a high removal efficiency and with newer technologies 99% of the particles down to 0.5 micrometer can be removed. The use of WESP leads to challenges as a result of higher safety demands and larger investments cost [7].

5.4.5 Wet Scrubbing

A wet-scrubber (WS) has a removal efficiency between 60-90% of the particles in the gas from the reactor. Figure 5.12 illustrates the working principles of a WS, where the product-gas is quenched using water, as the water droplets attaches to ash/char particles falls down into a wastewater reservoir in the bottom of the WS. Together with particles, tar will also be collected in the reservoir forming a sludge which is transported from the WS, while water is filtered and recycled back into the tower. A demister column is used for removing moisture droplets from the product gas before the gas leaves the WS [39].
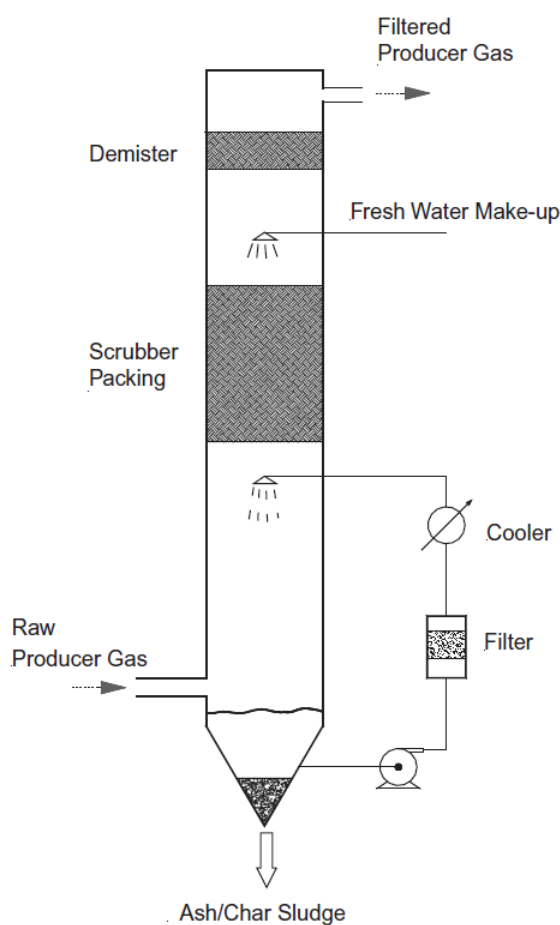
Figure 5.12: *Working principles of a "Wet scrubber"* [39].

A challenge for the use of WS is the accumulation of tar on critical components, reducing the efficiency of the scrubber [39].

5.4.6 Adsorption

In addition to the removal of solids particles, impurities in the form of different gas-compounds. Special methods is needed for removing specific compounds from the product gas. Adsorption is considered a well suited method for removing unwanted gas-compounds [42]. «Pressure Swing Adsorption» (PSA) is adsorption technology for separating different compounds from a pressurized gas mixture. PSA functions as a molecular sieve, separating molecules based on the size of the pore-diameter used. This property allows a PSA unit to remove a significant of the impurities in the product-gas, achieving a removal efficiency 99-99.99% [42]. Figure 5.14 illustrates the working principles of a PSA unit, where CO_2 is removed from a process stream. After the CO_2 is absorbed, a change in temperature or pressure causes desorption and subsequent removal of the CO_2 [42].
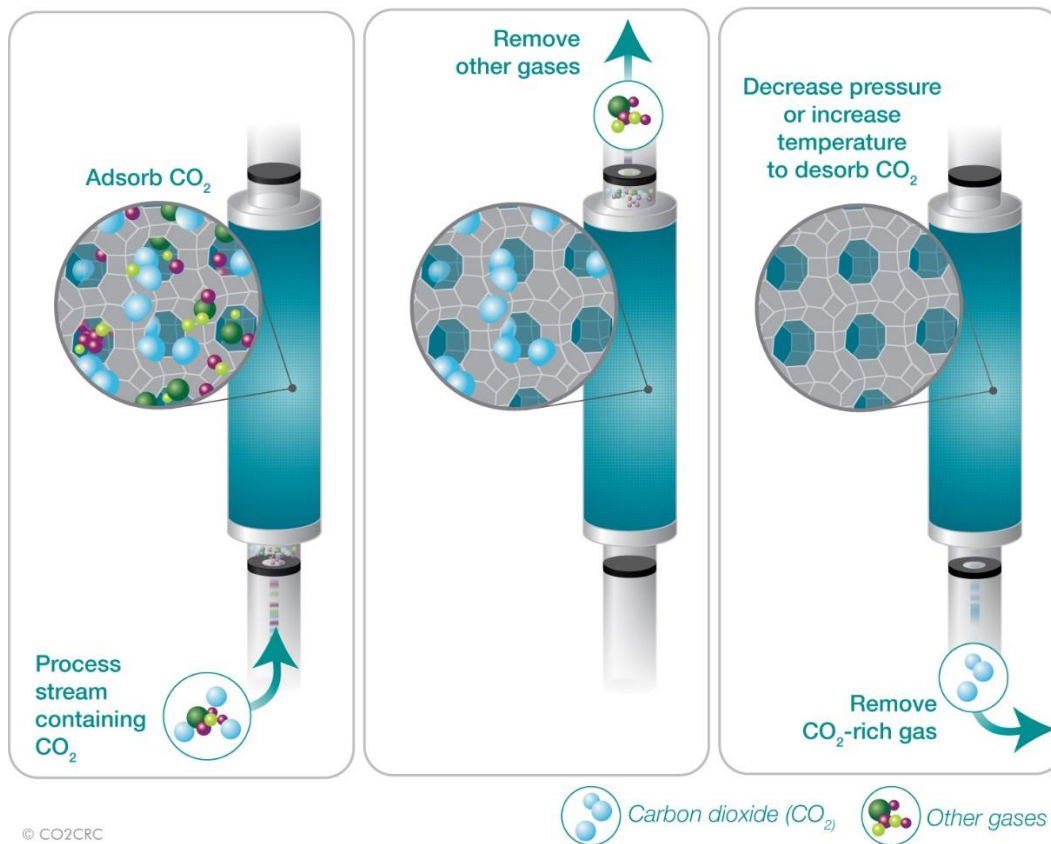
Figure 5.13: *Working principles of a PSA* [43].

5.4.7 Tar removal

From the gasification process several condensable organic compounds called tar are produced. Tar presents a significant challenge as it condense at high temperatures causing fouling and clogging in the system and deactivation of catalysts used in synthesis reactions. Tars can be removed by physical removing by cooling down the tar until it condensates and can be removed using a WESP or scrubber or it can be removed through thermal or catalytic cracking [44].

Thermal cracking decomposes the heavier tar compounds into lighter non-condensable gases using high temperatures (1100-1300 ^oC) [44]. This can applied by using gasifiers operating at sufficient high temperature such as the EF gasifier, where the production of tars are negligible. The disadvantage of thermal cracking is related to higher costs of complex gasification equipment and higher energy consumption [36, 44]. Catalytic cracking converts tars into non-condensable gases using a suitable catalyst at lower reaction temperatures (800^oC). The challenges related to the catalytic cracking is the operational problems related to the deactivation of the catalyst [44].

Conversion methods such as cracking (thermal or catalytic) alters the gas composition (increase in CO_2), which could affect the quality of the final product from synthesis reactions, and as a result the physical removal is preferred in some cases [44].

5.4.8 Upgrading through shift reactions

The hydrogen and carbon monoxide ratio is an important parameter for synthesizing the syngas into liquid hydrocarbons [7]. In order to adjust this ratio the water-gas shift (WGS) reaction is used, where excessive carbon monoxide is converted into hydrogen as seen in eq 5.5 [7].

$$CO + H_2O \xrightarrow{Catalyst} CO_2 + H_2 \quad \text{(-42 kJ/mol) -}\textbf{(5-5)}$$
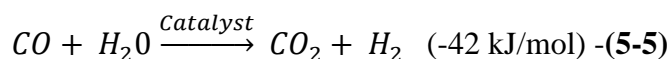
WGS reaction often performed in a separate reactor downstream of the gasifier, in order to provide optimal condition at lower temperatures (400-500^oC) than the gasification process using a catalyst based on oxides of iron and chromium [7].

5.5 Producing hydrocarbons from syngas.

Syngas provides the basic building blocks for the production of hydrocarbon based transportation fuel. In order to assemble these blocks together, a chemical reaction called Fischer Tropsch (FT) synthesis is used. This is a well-established technology used for the production liquid hydrocarbons from the gasification of coal. The motivation for using FT-synthesis is to produce a high quality product (in terms of energy density) from a low quality feedstock (coal, biomass) [7]. Using woody biomass as feedstock for FT-synthesis is called "Biomass to liquid", and have gain much attention in the recent years for the possibility of producing sustainable fuel for aviation purposes [12,44].

5.5.1 Fischer Tropsch

FT-synthesis can be either used for the production of transportation fuels or chemical. In addition to the desired products such as olefins, parafins and alcohols, undesired products such as methane, acids and carbon is also produced during FT—synthesis. Eq 5-6 shows the generic form for FT-synthesis:

$$nCO + 2nH_2 \xrightarrow{Catalyst} (CH_2)_n + nH_2O + heat \text{ (5-6)}$$
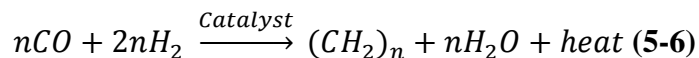
In this expression a generic hydrocarbon product is represented by $(CH_2)_n$. In addition to hydrocarbons significant amounts of water is produced from this reaction. "n" denotes how many moles of each compound is produced or consumed, and it also shows the length of the hydrocarbon molecules. The desired lengths for transportation fuels is C_3-C_{11} (gasoline range) and C_{12}-C_{19} (diesel range).

5.5.2 FT-synthesis pathways

Depending on what the desired product is (gasoline or diesel), there are two main process pathways to choose from 1) High Temperature Fischer Tropsch Synthesis (HTFTS), 2) Low Temperature (LTFTS) [7, 36].

In order to encourage the formation of hydrocarbons in the gasoline-range HFTS is the preferred pathway. HFTS utilizes an iron based catalyst at temperatures between $300\text{-}350^{\circ}C$ and pressure between 10-40 bar [7, 36]. Hydrocarbons in the diesel-range and wax products are favored by the LTFTS using a cobalt catalyst at lower temperatures ($200\text{–}240°C$) at similar pressure as HFTS.

5.5.3 Product distribution

From FT-synthesis a wide array of hydrocarbons with different chain-lengths are produced and the selectivity of products are strongly dependent on the process-conditions, type of catalyst and the composition of the syngas [7]. The product distribution can be calculated by the «Anderson-Schulz-Flory chain-growth probability model», where the selectivity of the hydrocarbons can be expressed by:

$$W_n = n(1 - \alpha)^2 \alpha^{n-1} \textbf{ (5-7)}$$

W_n is the weight-fraction to a product containing *n* carbon atoms and α is the «chain growth probability». Figure 5.14 illustrates a product distribution for conditions favouring hydrocarbons in the diesel range. From this product distribution prediction the value of alpha should be in the range of 0.8-0.9. This distribution can be adjusted according to type of reactor configuration used for the FT-synthesis and syngas composition, as the "chain-growth factor" is depend on the partial pressure of H_2 and CO [36,46].

Weight Fraction of Alkanes across Chain Growth Factor Range
C1 = methane, C2 = ethane, C3 = propane, etc.
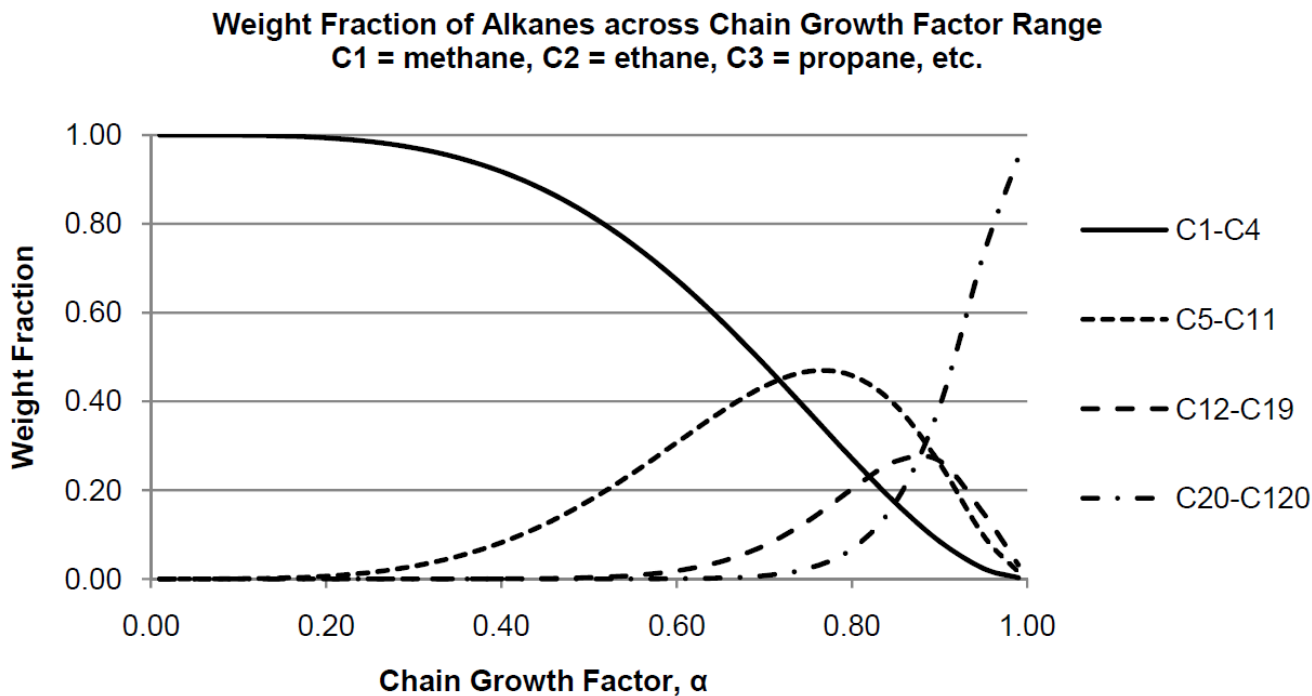
Figure 5.14: *Product distribution from FT-synthesis as a function of chain growth factor* [36].

At process conditions favouring the diesel-rang (200 °C and 25 bar) an α-value of around 0.85-0.9 is suitable, but this also result in a fraction of nearly 30 wt% wax, which needs further refining by hydrocracking in order to be added to the final product mixture [36]. The conditions of the hydrocracking determines the product distribution, but the main product from hydrocracking is diesel kerosene and naphtha [46].

The main advantages with the FT products is that the diesel produced has a higher cetane number than fossil diesel and it is free of contaminants such as sulphur , nitrogen, nickel, aromatics, etc. which all can be found in fossil oil. As a result the combustion of FT diesel has a lower emission than the fossil equivalent [46].

5.5.4 FT-reactor configuration

FT-synthesis is an exothermal reaction and in order to maintain this reaction the thermal energy produced needs to be removed. The consequence for not removing sufficient heat is the deactivation of catalyst causing reduction in production and economical loss [36]. In order to provide an efficient thermal control of the FT-process there are two main reactor configuration suitable for LTFT [36]: 1) Fixed bed tubular (FBT) reactor, 2) Slurry phase (SP) reactor. Figure

5.15 illustrates the working principles of these reactor-designs, where the main purpose is to achieve a good thermal control of the process in order to ensure optimal conditions.
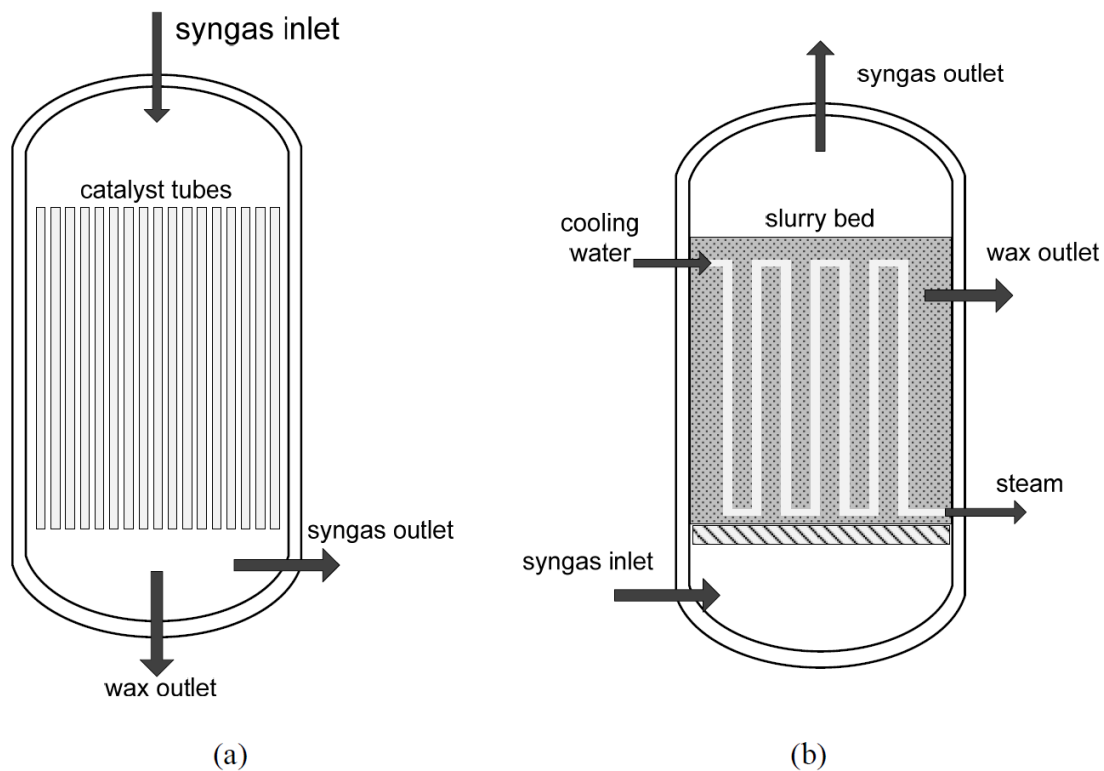
Figure 5.15 *Working principles: a) fixed bed tubular reactor, b) Slurry phase reactor* [36].

A FBT-reactor is built on a simple principle, where the catalyst is contained in several tubes and the heat-removal done by the production of steam outside of the tubes. The syngas is transported in to the reactor and through the catalyst-tubes. The main advantage with a FBT-reactor configuration is the ease of operation and suitable for diesel production as the amount of wax produced from FT-reaction is easy to transport the liquid/wax fraction out of the reactor for further processing. Disadvantages related to this design is the high cost of the catalyst tubes which also causes a significant pressure drop over the reactor [36, 46].

A SP-reactor operates by suspending the catalyst in the molten wax product, and syngas bubbles through this "slurry" from the bottom of the reactor. This reactor-configuration is about 25% less expensive than a FBT-reactor and have a better thermal control by integrating a heat exchanger in the design, which improves the life of the catalyst [7]. The challenges with this design is separating the product from the catalyst. Table 5.5 provides an overview of the differences between these reactors.

Table 5.5: *Comparison of FT-reactors for LTFT* [7, 46].

	Fixed bed	Slurry
Economic		
O&M	High cost due to periodically changing catalyst tubes.	Low cost due to longer catalyst life. Easy to change catalyst
Scaling	Easy, by multiplying tubes.	Difficult due to complex design
Conversion efficiency		
One pass conversion	Up to 80% possible	Up to 80% possible
Technical aspects		
Wax/catalyst separation	Easy and low cost	Difficult
Pressure Drop	3-7 bar	<1 bar
Process Control	Hard due to lack of thermal control	Easy
Status		
	Mature technology. R%D will improve will provide a higher one-pass conversion	Overall considered a mature technology. Complicated Wax/catalyst separation-process

5.5.5 FT-Economics

The production of liquid hydrocarbons from the gasification of woody biomass using Fischer Tropsch synthesis has gained a lot of attention due to the success of the "Gas to liquid" (GtL) concept in countries such as South Africa. In South Africa, 44% of the fuel consumed is derived from the gasification of coal and FT-synthesis [36]. Several studies has been performed on the concept of using woody biomass as a feedstock for the production of fuels using gasification and FT-synthesis, this concept is referred to as "biomass to liquid" (BtL) [46]. Table 5.6 presents a summary of some of the more extensive techno-economical evaluation (TEA) of the BtL concept. The results from the studies are compared on the basis of total project investments (TPI),) and minimum fuel selling price (MFSP –*USD $ per litre gasoline equivalent*)

Table 5.6. *Summary of the techno-economic models for Fischer Tropsch synthesis (FTS)*.

Pathway	Capacity (MTPD)	Feedstock cost (USD $/MT)	TPI (USD $MM)	MFSP ($l/ge)	Source
FTS:					**[36]**
HTFTS	2000	85	540	1.22	
LTFTS	2000	85	657	1.38	
FTS	1371	30	408	0.71	**[46]**
FTS					**[47]**
	2472	112	359	1.88	
	2472	112	371	1.83	

An extensive evaluation was performed by the University of Utrecht in 2002 where "Aspen Plus" where used in order to compare 11 pathways using five different gasification reactors [46]. In this evaluation a large scale bio-refinery processing 1371 tons per day was expected to need an investment cost ranging from USD $408 million to USD $587 million. In this scenario 75% of the total equipment cost was related to the pretreatment of feedstock, gasification reactor using oxygen, and the gas cleaning. The minimum fuel selling price were estimated to be USD $0.71 l/ge using woody biomass as feedstock.

A TEA was performed in 2010 by Iowa State University on a scenario comparing bio-refinery using high temperature Fischer Tropsch synthesis (HTFTS) and a low temperature Fischer Tropsch (LTFTS) [36]. The refinery capacity was 2000 tons per day and using a feedstock based on woody biomass derived from corn stover. The HTFTS operates at gasification temperatures of 1300 ^{o}C, while the LTFTS operated at 870 ^{o}C.

The result from this analysis shows that HITFS has the highest investment cost at $657 million while the LTFTS had an investment cost of USD $540 million. This difference was a result of a higher capacity and higher cold gas efficiency (energy ratio product-gas/fuel) for the HTFTS which results in a higher yield of 230 lge/MT compared to 178 lge/MT from LTFTS scenario. In this analysis the feedstock cost were assumed to be USD $89.83/MT and the IRR is 10%. The MFSP was found to be more affected by the higher yield than the investment cost, and as a result the MFSP were estimated to 1.22 l/ge for the HTFTS and 1.38 l/ge. When it comes to the sensitivity of the MFSP, the analysis concludes that the feedstock price and TPI has the greatest impact [36].

In 2013 an analysis on the FT-upgrading process was performed by the Karlsruhe Institute of technology and the University of Saskatchewan [47]. In this analysis two scenarios were presented using syngas at 40 bar and 80 bar. In contrast to the other TEA, the supply of syngas were assumed to be available at $0.43/m^3 rather than evaluating the pretreatment, gasification and gas conditioning. This price is according to the authors comparable to a feedstock price of USD $112/MT. From this analysis, the TPI for the FT-reactor is estimated to USD $359 million and USD $371 million for the 40 bar and 80 bar scenarios consuming syngas at a rate 2472 MTPD. The assumptions for this report is a bio-refinery lifespan of 20 years and a 10% IRR in order to produce FT-products at a MFSP of USD $1.88 in the 40 bar-sceneario and at USD $1.83 for the 80 bar-scenario. The sensitivity analysis is this report also concluded with the MFSP being most affected by feedstock cost and TPI.

6. Comparison: Pyrolysis and Gasification

6.1 Processes

6.1.1 Pretreatment

Pretreatment of the woody biomass feedstock is essential for reducing the particle size and moisture content. This process step applies to both the pyrolysis and gasification pathway in order to reduce the logistics challenges related to transportation and handling of the feedstock. Some of the pretreatment can be done on a remote facility in order to provide a more suitable feedstock form (wood-chips instead of logs), but in order to ensure a continuous operation in both cases both drying and further size reduction is needed depending on the technology utilized [12].

6.1.2 Conversion

The pretreated biomass is fed into a reactor. In a gasification-reactor the biomass is converted to a gaseous energy carrier through several chemical reactions at high temperature and pressure in the presence of an oxidation-medium. The process conditions varies depending on what type technology and oxidation-medium utilized in the gasification process but for the production of liquid hydrocarbons, temperatures in the range of 800-1300 $^{\circ}$C and pressure in the range of 1-36 bar. From the gasification-process, a gas containing mainly CO, H_2, CO_2 and unwanted impurities is produced.

In contrast to gasification, the pyrolysis reactions occurs in an oxygen-free atmosphere. During this process, the biomass particle is decomposed into gas, oils and solids, with the product distribution being depend on temperature and heating rate. Fast-pyrolysis (FP) is as mentioned in previous chapter, a pyrolysis-process which favor a high liquid yield (80 wt% of the dry feedstock) by utilizing high temperatures of around 400-650 $^{\circ}$C and a heating rate less than 2 seconds [7]. The vapors produced from pyrolysis undergoes a fast cooling in order to condense the vapors into a liquid product called bio-oil. This product is not suitable for transportation fuel, as a result of corrosives, high viscosity, high moisture content, and low heating value.

6.1.3 Product cleaning and conditioning

Both processes produces a product which requires further processing in order to become a suitable feedstock for liquid fuels. The most critical for cleaning-process for the pyrolysis-product is the removal of solids (ash, char, charcoal) which can be performed by a cyclone.

In order to produce transportation fuels from the gasification of biomass, the product-gas undergoes extensive cleaning and conditioning in order to remove CO_2, tars and impurities (H_2S, COS, HCN, NH_3 and HCl). This cleaning and conditioning consists of several complex steps and accounts for as much as 23% of the installation cost in a BtL (biomass to liquid)-plant [36]. After cleaning and conditioning the product gas consist of a mixture of H_2 and CO which is called syngas.

6.1.4 Product upgrading

Bio-oil or syngas needs to undergo a upgrading-process in order convert the product from pyrolysis or gasification into liquid hydrocarbons. Syngas from the gasification of woody biomass is converted into a mixture of hydrocarbons ranging from light gases to wax by using Fischer Tropsch (FT) – synthesis, where the syngas undergoes a chemical reaction over a metallic catalyst (Iron or cobalt). This process operating temperatures between 150 ºC and 300 ºC and at pressure ranging from 10 to 40 bar. The liquid mixture of different hydrocarbons can be upgraded to liquid fuels utilizing techniques used in conventional petroleum refineries such as hydrocracking and distillation.

A similar process is usually considered when upgrading bio-oil into liquid hydrocarbons. This can be achieved by utilizing a two-step hydroprocessing method in order to reduce the oxygen content. The first step involved a mild hydrotreating at low temperatures (250 ºC) and at high pressure (200 bar) in the presence of a catalyst [30]. The second step is a more severe hydrotreating at the same pressure but at higher temperature (around 500 ºC). From this upgrading-process the bio-oil is converted into a diesel and gasoline blendstock together with a heavier hydrocarbon fraction which needs to undergo further processing by hydrocracking [30].

6.2 Fuel output

From the TEAs on a biorefinery with a 2000 MTPD capacity the fuel output using different technologies can be compared. An overview of the fuel output from these scenarios is presented in table 6.1.

Table 6.1: *Fuel output from a 2000 MTPD biorefinery utilizing different technologies.*

Pathway	Capacity (MTPD)	Total Yield (l/MT dry feedstock)	Operation (d/year)	Fuel produced (MM l/year)	Diesel (MM l/year)	Gasoline (MM l/year)	Source
FPH	2000	349	329	229	119.6	109.4	[23]
FPH	2000	334	329	220	-	-	[29]
FPH	2000	330	329	217	-	-	[30]
CPH	2000	-	-	-	-	-	[31]
HPH	2000	298	350	230	78	152	[32]
FTS: HTFTS LTFTS	2000	231 179	310 310	145 112	98 76	47 36	[36]

6.3 Carbon-to-fuel efficiency

Another important measure on how effective a process is to produce liquid fuel is the carbon-to-efficiency [23]. Table 6.2: depicts the carbon-to-fuel for some of process reviewed in this thesis.

Table 6.2: *Carbon-to-fuel efficiency for a 2000 MTPD biorefinery utilizing different technologies.*

Pathway	Biomass Carbon-to-fuel efficiency (C in fuel/ C in biomass)	Source
FPH	47 %	[23]
FPH	-	[29]
FPH	~ 45 %	[30]
CPH	-	[31]
HPH	-	[32]
FTS: HTFTS LTFTS	34 % 26 %	[36]

6.4 Economic

Table 6.3 illustrates an economic comparison of the different process-pathways for a bio-refinery with 2000 MTPD capacity. The results from the studies are compared on the basis of total project investments (TPI), and minimum fuel selling price (MFSP –*USD $ per liter gasoline equivalent*).

Table 6.3: *Economic comparison of biorefinery with a capacity of 2000 MTPD.*

Pathway	Feedstock cost (USD $/MT)	TPI (USD $MM)	MFSP (USD $l/ge)	Source
FPH	60.50	329	0.58	[23]
FPH	90	217	0.60	[29]
FPH	83	429	0.68	[30]
CPH	90	457	0.97	[31]
HPH	96	286	0.48	[32]
FTS:				[36]
HTFTS	85	540	1.22	
LTFTS	85	657	1.38	

6.5 Technology maturity and commercial status

Producing liquid fuels by gasification and FT synthesis from a fossil feedstock (coal, natural gas) is mature technology and the process has been developed on an industrious scale for several decades. Using woody biomass as feedstock for transportation fuels has not yet been optimized for large scale production. This is due to limitations of the existing gasification technologies and further development is needed in order to utilize woody biomass. The technology used for FT-synthesis needs little adjustment as the product-gas undergoes extensive conditioning in order to produce syngas [12].

The commercialization of BtL has in the recent years gained attention for the potential of a renewable source for aviation fuel [45, 48, 49]. Several BtL demonstration plants has been constructed such as the NSE Biofuels Oy in Finland which is a joint venture between Neste Oil and Stora Enso where the goal is to optimize the BtL-process [50].

The Finnish company UPM was recently awarded a grant of EUR 170 million for the construction a BtL plant in Strasbourg, France to produce biofuels from woody biomass. The final decision on this project was expected in 2014 [52]. Another joint-venture to commercialize the BtL process using woody biomass as a feedstock is the BioTfueL project, where 5 company collaborates (Axens, IFP Energies Nouvelles, Avril, ThyssenKrupp Industrial Solutions and Total). The test-phase of this project is expected to be completed within 2017 with a goal of commercial production by 2020 [52].

There have been little research on the production of biofuels from pyrolysis as result of a small marked for pyrolysis technology itself, but in the recent years this technology has faced increasing interest and research [53]. Today there are several demonstration plants capable of producing biofuel from woody biomass worldwide such as KiOR (catalytic fast pyrolysis/fluid catalytic cracking) and Dynamotive/Renewable Oils Corporation (fast pyrolysis/hydroprocessing) [54].

In March 2014 a joint-venture between Fortum, UPM and Valmet in a 5 year project called LignoCat (lignocellulosic fuels by catalytic pyrolysis) involving the production of biofuels from woody biomass using catalytic pyrolysis. This project is based on experienced gained through the planning and construction of CHP (Combined heat and power)-plant in Joensuu, Finland with an integrated bio-oil production from pyrolysis [55].

The production of transportation fuels from woody biomass was in an early commercialization stage, where a large scale production facility in Columbus, US built by KiOR produces fuel from woody biomass using fast pyrolysis. This bio-refinery was built in 2012 and production started in early 2013 with annual production of about 45 million liters of gasoline, diesel and fuel oil blendstock. Due to complication of a technologic and economic nature KiOR filed for bankruptcy in late 2014 [56, 57].

7. Discussion

The production of liquid fuels from woody biomass using either gasification or pyrolysis faces both technical and non-technical barriers in order to reach full commercialization. In this chapter some of these barriers will be identified and discussed in order to identify the most suitable technology for producing biofuel from woody biomass.

7.1 Technical barriers.

The main challenge for producing fuel from pyrolysis is the upgrading of the bio-oil. Bio-oil is as mentioned in previous chapter, a high vicious, corrosive and chemical unstable liquid due to a high oxygen content (up to 50 wt %). As a result bio-oil is hard to handle and transport making the area of usage for bio-oil limited. In order to convert transportation fuels from bio-oil the unwanted properties has to be reduced through upgrading. This upgrading can either be performed as a separate process downstream of the pyrolysis-reactor using either a two-step hydrotreating process or chemical cracking using a zeolite catalyst. The challenge with the upgrading of bio-oil is the amount of hydrogen needed for this operation and as a result this hydrogen-production either on-site production or by purchase from external source. In order to reduce the cost more R&D is needed for reducing the need for extensive upgrading. This can be achieved by developing more efficient catalyst for hydrotreating in order to improve yields of the desired fuel and producing a bio-oil with a higher quality which needs less upgrading. The latter can be achieved by developing new reactor configuration such as hydro-pyrolysis where the vapors from the pyrolysis-process is undergoes upgrading in the reactor itself [32]. This is a very exciting concept, but is only at demonstration-stage at this time.

Fortum joint-venture project in order to commercialize the production of transportation fuels from woody biomass using pyrolysis is considered by the author the most promising effort in developing this process. This is based on Fortums previous experiences with production of bio-oil on commercial scale and the strong partners involved (UPM and Valmet) together with the incentives needed for R&D provided from the Finnish government and EU. The development seen in Finland the last couple of years is a good example of modernizing and exploring new possibilities in an old and traditional industry which can be used as a model to explore in Norway.

In Norway there have been interest in the production of aviation fuel from woody biomass as a part of a sustainable strategy in the Norwegian aviation industry. A report completed by Ramboll commissioned by Avinor in 2013 investigated the possibility of introducing biofuel as a sustainable alternative in the aviation industry. The motivation for introducing biofuel into the aviation industry is to reduce the CO_2-emission from the industry which on a global scale is responsible for 2% of the global emissions of CO_2 and it's expected to increase as traffic increases.

The conclusion of this report was that new biofuel technology can replace considerable amount of fossil jet fuel and that the current rate of development will make biofuel-pathways such as "Biomass to Liquid"(BtL) using biomass from Norwegian forest both technically and economical feasible by 2020-2025 [49].

The use of gasification and FT-synthesis to convert woody biomass to fuel for aviation purposes is considered by the author as the main drive for the development for BtL(biomass to liquid)-technologies. BtL using woody biomass produces a fuel with a different quality than from pyrolysis (blendstock is produced). The interest for BtL helps drive R&D needed in order to improve the process main problem area which seems to be the gasification of woody biomass. The product-gas from the gasification of woody biomass has a higher amount of impurities (tar, ash, char) when compared to conventional gasification of coal. As a result the product-gas needs extensive cleaning and conditioning which leads to a more complex operation and higher investment costs. The main advantage with this technology is the maturity due to extensive use in other industries and this helps accelerate the development of more efficient technology in order to make BtL more competitive with fossil fuels in aviation. Btl is expected to be fully commercialized within a decade [12, 49].

At this point there seems to be little interest in exploring other suitable markets (agriculture, construction, and shipping) for the commercial production of fuel from woody biomass. This can a good starting for further marked analysis in order to identify the whole marked potential for a biofuel-industry in Norway and a revitalizing of the existing wood industry.

7.2 Economic barriers

The main economic barrier independent of the process-pathway, is the huge investment cost needed to establish a commercial production of fuels from woody biomass. From the economical evaluation (table 4-4 and 5-6) the total investment cost ranges from USD $286 million to USD $457 million for the pyrolysis-pathway and USD $359 million to USD $657 million for the gasification- pathway. In some cases the investment cost and the feedstock cost accounts for almost 90% of the total investments cost [49]. In order to establish a wood-fuel industry the two most important factors to reduce the investment cost is to stimulate more R&D and to establish strong industrious collaboration to continue exploring the possibilities for fuel from woody biomass.

From the economical evaluation pyrolysis could be viable method of producing liquid fuels with a MFSP close to USD $0.48 l/ge compared to a current gasoline price (from refinery not retail) in the US of USD $0.46 l/ge [32, 58]. This can be considered optimistic due lack of data supporting this evaluation. MFSP for the gasification pathway ranges from USD $0.71 l/ge to USD $1.88 l/ge, but the current speed of development towards aviation application will reduce the cost to level where it is competitive with fossil alternatives within a decade [49].

7.3 Discussion summary

Both conversion-pathway faces the same type challenges and it is difficult to evaluated two technologies which operates in different markets, as the gasification-pathway produces fuel with a quality more suitable for aviation purposes. Fuel produced from pyrolysis on the other hand provides a higher yield at lower cost than the gasification-pathway making it more suitable for conventional application. As there are a rapid developing new technologies (Fuel cells, Batteries etc.) for powering cars, there could be a more suitable marked for fuel from woody biomass. An alternative marked could be producing fuel from pyrolysis for use in heavy machinery in construction, agriculture and shipping which is less energy efficient and harder to develop more efficient ways to reduce emissions. Diesel produced from the gasification and subsequent FT-synthesis can also provide fuel for this type of marked as a secondary objective [49]. This opens up for a marked scenario where both technologies can contribute in providing renewable source of fuel and coexist without being in direct competition.

8. Conclusion

The aim of this thesis was to identify the most suitable technology for conversion of woody biomass into biofuels. Overall both pyrolysis and gasification shows potential to establish a future commercial fuel production, but in order to establish an industry there has to be a marked for the product and the product has to be able to compete with existing alternatives. At the current point in time both pathways face much of the same technological and economic challenges limiting the potential for commercial success. As the end-product varies in quality depending on the conversion-technology used, the marked for the respective technologies may not be in direct competition and will instead complement each other as a source of renewable fuel for a suitable marked.

There is also the question how these technologies will operates in today's economic climate and how the development of renewable transportation fuel will be affected by other factors (low oil price, changing climate). This is not within the scope of this thesis, but it illustrates that there is still a need for further studies through marked-analysis and case-studies to see which technology that have the greatest impact on emissions reduction (local and atmospheric) in a suitable marked and still is economical viable.

9. Further Work

Based on this thesis the author recommends further work on this field should be on identifying the interest, current activities and suitable markets in Norway. Some proposals on further work is listed below:

- Case-study related to the planning of a demonstration-plant in Tofte, Norway for the production of fuel from woody biomass. This is at the location of an old pulp production plant (Södra Cell Tofte) and is a joint venture project between Statkraft and Södra [59]. The aim of this case-study could be to identify the most suitable technology to be implemented into the existing infrastructure and to find the optimal capacity of a commercial scale production plant in Tofte.

- Identify other suitable location for commercial production of fuel from woody biomass in Norway.

- A marked analysis in order to identify the interest and potential for fuel from woody biomass.

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