## Assessment Of Current And Future Yield Of Lignocellulosic <u>Biomass As</u> A Feedstock For Modeling a Steam Gasifier followed by Hydrogen and Synthetic Natural Gas Production

by

## Avikar Saberwal

to obtain the degree of Master of Science at the Delft University of Technology, to be defended publicly on Friday August 27, 2021 at 14:30 pM. Student number: 5160367 Project duration: November 15, 2020 – August 27, 2021 Thesis committee: Prof. dr. ir. W. de Jong, TU Delft, supervisor Prof. dr. ir. D. Roekaerts, TU Delft Prof. dr. ir. M. Ramdin, TU Delft ir. C. Tsekos. TU Delft, Supervisor

This thesis is confidential and cannot be made public until August 31, 2023.

## Abstract

With issues such as climate change and global warming worsening with each passing day, sustainability has become more important now then ever. The world needs to employ sustainable means of energy in order to overcome the global challenges we are faced with and mitigate the damage already done. Energy from biomass in the form of biofuels is one of the answers to our problem. Biomass is a carbon neutral fuel, and the biofuels produced from treating biomass have the advantage of being readily used in the current energy infrastructure. Lignocellulosic biomass feedstocks are a type of biomass that are available from a variety of sources and do not compete with the food chain. Gasification is a type of thermochemical method for treating biomass, by heating the biomass at temperatures greater than 700°C in the presence of one or more gasifying agents such as air or steam. Gasification of biomass produces a high calorific value gas called syngas which is composed of CO,  $H_2$ ,  $CO_2$  and  $CH_4$ . This syngas has a lot of applications, and can be further processed to form various biofuels.

The aim of this study was to determine the various sources of lignocellulosic biomass available in the European Union, and to estimate their current and future (2050) production potential, in order to meet some of the energy demands of the EU. This study also dealt with creating a kinetic model in ASPEN Plus of a steam gasifier after the Indirectly Heated Bubbling Fluidized Bed Steam Reformer at TU Delft. The model was validated with experimental results obtained from the setup at TU Delft, and evaluated its efficiency. Furthermore, two case studies were undertaken, each to model a process to produce a biofuel, in a biorefinery context. The two kinetic models made were for the production of Synthetic Natural Gas and Hydrogen, both of which have a number of applications in the European context. Finally, a sensitivity analysis was also performed to study the effect of various parameters on each of the models.

The results from the model indicated that the model was validated by the experimental results fairly well, with a maximum relative error of 18% for the primary components. Also, the final product streams from the SNG and the Hydrogen models, were composed of a majority of the desired fuel, and can be used for any desired application once the Nitrogen is removed from them, which was not implemented in the model. Each of the two models have their own merits and demerits, but purely from a process standpoint, it was determined that the SNG model was more attractive as a process due to better efficiency (34.6% for SNG model compared to 20.5% for the Hydrogen model) and lower heat requirements. In the end, the main conclusions of the thesis were drawn and compiled in the form of five research questions, and some recommendations for future work was suggested.

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### List of Symbols and Abbreviations

Symbol/Abbreviation	Parameter	Unit
$\epsilon_0$	stationary bed voidage	-
e	expanded bed voidage	-
λ	Equivalence Ratio	-
$\rho_{bulk}$	Bulk Density	$kg/m^3$
ar	As received	-
CC	Carbon Conversion	%
CGE	Cold Gas Efficiency	%
CSTR	Continuously Stirred Tank Reactor	-
db	dry basis	-
Dgas	Diameter of gasifier	mm
D <sub>hyd</sub>	Hydraulic Diameter	mm
D <sub>in</sub>	Inner Diameter of Gasifier	mm
dmass	Mass deviation	kg
D <sub>rtb</sub>	Diameter of radiant tube burner	mm
Ea	Activation Energy	kJ
EU	European Union	-
FC	Fixed Carbon	%
FCC	Fluidized Catalytic Cracking	-
H <sub>exp</sub>	Expanded Bed height	m
H <sub>fixed</sub>	Stationary bed height	m
HHV	Higher Heating Value	MJ/kg
IEA	International Energy Agency	-
IHBFBSR	Indirectly Heated Bubbling Fluidized Bed Steam Reformer	-
$k_1, k_2$	Driving force coefficients	
$K_1, K_2, K_3$	Adsorption coefficients	
$k_i^0$	Pre-exponential factor of reaction j	
LHHW	Langmuir-Hinshelwood-Hougen-Watson	-
LHV	Lower Heating Value	MJ/kg
LUISA	Land Use Integrated Sus-tainability Assessment modelling platform	-
m <sub>i</sub>	Mass of biomass on i basis	kg
Mi	Mass of j component/fraction	kg
od	oven-dried	-
OE	Overall Efficiency	%
PEM	Proton Exchange Membrane fuel cell	-
PSA	Pressure Swing Adsorption	-
pw	Pyrolytic water	-
R	Universal Gas constant	J/Kmol
r <sub>j</sub>	Rate of reaction j	$mol/m^3 \cdot s$
SNG	Synthetic Natural Gas	-
SRC	Short Rotation Coppice crops	-
Т	Temperature	°Cor K
TPES	Total Primary Energy Supply	-
V <sub>bed</sub>	Volume of bed material	$m^3$
V <sub>CSTR</sub>	Volume of CSTR	$m^3$
V <sub>fluid</sub>	Volume of bed during fluidization	$m^3$
VM	Volatile Matter	%
WGS	Water Gas Shift	-
Y:	Mass Yield of i species	%

#### Table 1: List of Symbols and Abbreviations

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# 1

## Introduction

#### 1.1. Overview

In recent years, humanity has been faced with a lot of challenges, which threatens not only our way of life, but our very existence. Our ever growing population has led to an increased demand for dwindling natural resources, due to which many people on Earth are denied access to basic human needs such as food, fresh water and housing. Climate change is one of the more pertinent issues facing us, due to our heavy reliance on fossil based fuels such as coal, petroleum and natural gas. According to the IEA world energy balances and statistics, as of 2018, more than 81% of the Total Primary Energy Supply (TPES) of the European Union came from fossil fuels [39]. Many visible changes such as melting of polar ice caps, rise in sea level and extreme weather occurrences have forced countries to take certain actions in order to regulate the rising global temperatures.

The Paris Agreement of 2015 was enacted by the United Nations Framework Convention on Climate Change and was signed by 196 parties. The goal of the treaty was to restrict the global temperatures increase to below 2 degrees Celsius, and to try and reach a peak in the greenhouse gas emissions at the earliest, with the long term aim of reaching carbon neutrality by the middle of the century [52]. With this aim in mind, there has been a greater thrust on sustainability and alternate forms of fuels and energy in order to mitigate the ill-effects of climate change. Various sustainable forms of energy exist in the market such as solar, wind and hydro energy which have the potential to generate clean electricity. Other forms of energy such as geothermal provide energy in the form of heat which can be used for industrial and domestic heating purposes. According to the IEA world energy balances and statistics, as of 2018, less than 14% of the Total Primary Energy Supply (TPES) of the European Union came from renewables (hydro, solar, wind and biofuels) [39]. However, electrification of the transport and industrial sectors would require a substantial change in the infrastructure in order to use the clean electricity generated by these sustainable energy sources. Energy from biomass can potentially bridge the gap between the current and future infrastructures, while also providing sustainable energy in the form of heat and electricity.

Biomass refers to a wide range of organic matter derived from plants or animals, and is a very attractive form of sustainable energy. Biomass and the subsequently produced biofuels, have the advantage of being carbon neutral, which implies the amount of carbon dioxide absorbed from the atmosphere during its growth is the same as the amount released when it undergoes treatment, and subsequently combustion. Currently, only 9% of the Total Primary Energy Supply of the EU is provided by biomass and biofuels [39]. Since ancient times, and even today in a lot of rural areas around the world, various biomasses have been used for heating and cooking purposes. Biomass is usually categorized in three generations, based on the origin of the feed-stock. First generation biomass usually includes food crops like sugar and starch crops, and oilseed crops, which are grown for the purpose of producing bioenergy. These, however, usually interfere with food supply, and are thus, not ideal to be used for energy generation. Second generation biomass includes lignocellulosic biomass which is unfit for human consumption, and is often considered waste or discarded. These include forest or wood residues, agricultural waste, etc. The main components of such biomasses are lignin, cellulose and hemicellulose. These crops do not require the same amount of inputs for growing and do not raise as

much alarm over the fuel vs food debate. Third generation biomass include aquatic feedstocks such as algae [60]. As of 2017, the European Union had over 224 biorefineries, off which 181 only processed first generation biomasses, and only 43 were second generation biorefineries which used lignocellulosic biomass and produced a wider range of products [63].

The European Union too has set various short-term and long-term targets for replacing fossil fuels with biofuels and clean electricity sources such as solar and wind energy, coupled with the use of hydrogen for long term storage. The EU targeted the share of biofuels from first generation biomasses to reach 7% of the total energy demand by 2020, and reduce this dependence on food crops by aiming for 3.8% share by 2030. The EU has also set a target to supply 25% of energy to the transportation sector from biofuels made in second generation biorefineries [63]. With these targets in place, the significance of biomass as a leading form of clean and sustainable energy is bound to increase in the future.

Biomass can be converted into usable fuels through a variety of processes which includes extraction, fermentation, anaerobic digestion and thermochemical treatment [61]. Thermochemical treatment of biomass has emerged as a very attractive process as it can deliver energy in the form of solid through torrefaction, liquid through pyrolysis, and gas through syngas. Gasification is a form of thermochemical treatment of biomass at higher temperatures in the presence of one or more gasifying agents, which involves partial oxidation of the biomass, and results in the formation of gaseous products called syngas. The gasifying agents that can be used include air, steam, oxygen, carbon dioxide, or a mixture of them. The product gas, called syngas mostly consists of carbon monoxide, hydrogen, carbon dioxide and methane, and can be used directly as fuel for heating applications, or can be used for further processing to produce chemicals or biofuels [48]. Various gasifiers with different specifications have been used over the last few decades. The type of gasifier considered in this study is an Indirectly Heated Bubbling Fluidised Bed Steam Reformer (IHBFBSR). The entire process of biomass gasification can be modeled using any flowsheeting software, such as ASPEN PLUS, which is the one that has been used here.

#### 1.2. Research Questions

The main aim of using gasification to convert solid biomass into syngas, is to increase its energy density so that it may deliver better efficiency when used as a fuel. Various indicators can be used to evaluate a process and determine its effectiveness. The main aim of this study is to assess the potential yields of lignocellulosic biomass feedstocks in the European Union and to design a process to convert said feedstock into a useful fuel. This study will mostly focus on steam gasification using an indirectly heated bubbling fluidized bed steam reformer.

The main research question for this study is stated as "What is the potential of lignocellulosic biomass in the European Union as a feedstock for energy conversion, and what is the merit of steam gasification in an indirectly heated bubbling fluidized bed gasifier for the production of syngas, and subsequent production of Synthetic Natural Gas and Hydrogen?" In order to answer this main research question, several sub-questions were formulated, which are as follows:

- Which are the main lignocellulosic biomass feedstocks grown and available in the European Union?
- What is the current and future production potential of the available lignocellulosic biomass feedstocks in the European Union, as available in literature?
- How well does the model predict the composition and yield of the gasification products including *CO*, *CO*<sub>2</sub>, *CH*<sub>4</sub>, *H*<sub>2</sub>, *N*<sub>2</sub>, *H*<sub>2</sub>*O* and tar, and also the carbon conversion, cold gas efficiency and the overall efficiency of the gasification model?
- What are the final product compositions and efficiencies for the SNG and the Hydrogen models, and which one would be more attractive to produce?
- What is the effect of varying secondary air and the steam to biomass ratio on the performance of the steam gasification model, and also the SNG and Hydrogen models?

#### **1.3. Thesis Outline**

This section discusses the outline of the thesis. Chapter 2 introduces the different biomass feedstocks, their composition and their production potential right now and in the future. It also introduces the theory behind gasification of biomass and the various steps the biomass undergoes during the process. Chapter 3 describes the design choices for the model made to simulate the indirectly heated bubbling fluidized bed steam reformer. Some of the aspects include splitting the pyrolysis process from gasification, kinetic modeling of the gasification process, tar reduction strategies, etc. It also elucidates the procedure to model the SNG model and the Hydrogen model. Chapter 4 discusses the results and discussion of the simulations, the validation of the model with experimental results, the mass and energy balance of the models and also the sensitivity analysis for different parameters used in the model. Finally, Chapter 5 lists the conclusions drawn from the study, and also suggests scope for future work.

## 2

## Literature Review

#### 2.1. Biomass Feedstocks

Biomass constitutes a wide range of organic matter that can be used in various ways for energy conversion. Second generataion biomass or lignocellulosic biomass have gained a lot of attention as a viable feedstock for energy generation, compared to first generation biomass which tend to interfere with the food supply. Lignocellulosic biomass do not raise as much alarm over the food versus fuel debate, and have the potential to be grown even on discarded land. Lignocellulosic biomass can be broadly categorized into two types: woody biomass and non-woody biomass, both with different physical and chemical properties. Woody biomass has been mainly used for heat and energy purposes for centuries, and is still preferred over non-woody biomass. This is primarily because of the lower heating value of non-woody biomass, compared to woody biomass. Other reasons include unfavourable properties such as vast differences in particle size, moisture content, bulk density, etc [77]. However, there is still a lot of potential from certain non-woody biomass sources to meet energy demands.

#### 2.1.1. Forest and Wood Residues

Woody biomass consists of actual wood from purpose grown trees such as polar, pine, willow, etc, that can be used in the form of firewood, wood pellets, wood briquettes, etc, provided proper management of forest resources is undertaken simultaneously. However, it also consists of forestry residues, that are taken from the directly from the forest and are unaltered by chemical treatment. This includes logging residues or slash, stumps, stemwood and small diameter trees, that are not suitable for wood industry purposes, but are considered good enough fuel resources [5]. Another important source is wood wastes from wood based industries, that includes bark from trees, sawdust, shavings, black liquor, etc. Since these are produced mostly in industrial facilities, collection and subsequent reuse is fairly simple. 43% of land in the European Union is covered with forests, which corresponds to nearly 182 million hectares, as of 2019, and is the primary source of most woody biomass [28]. However, not all forests are accessible for felling and industrial or energy purposes due to various environmental restrictions.

For the purpose of this study, the only woody biomass considered was wood waste and forest residue. Various estimates have been reported on the amount of wood waste generated in the EU 28 every year (including UK). Researchers from Poland made a theoretical estimate for the amount of wood waste generated as a byproduct of various wood based industries such as sawmills, pulp and paper, etc, and available for energy generation, but also from municipal waste and construction sites. They took into account factors such as previously known wood industry waste data, forest area available for wood supply and felling rates in different countries, ecological restrictions and competitive uses, to reach a total value of 79.17 Million tonnes [51]. Other researchers have also made estimates of how much sawdust and other by-products are created from sawmills, and report around 32 million tonnes [19]. Various researchers have also projected the generation of wood wastes, a few decades into the future. Searle et al. projected all potentially available wood waste to 2030, by taking into account the EU's efforts in reducing waste generation and reached an estimate of 43.5 million tonnes per year[62]. However, according to Eurostat, arguably one of the most reliable statistical

sources, the amount of wood waste in the EU in 2016 was 48.46 million tonnes [21].

Forest residues are not as widely used for energy conversion as wood wastes in most EU countries but offer a tremendous potential, provided various incentives are provided. Researchers have tried to make numerous estimates for the amount of forest residues in various countries. One report approximated the amount of forest residues to around 11.5-13.5 million tonnes per year (the article reported the volume of residues in  $m^3$ , which was converted to tonnes for uniformity, by taking an average value of density of 0.5 tonnes/ $m^3$ [62]) [41]. Other researchers have also estimated the amount of forest residue in EU to approximately 40 million tonnes [19]. Searle et al. also calculated the amount of forest residue based on FAOSTAT data, and analysed the data to reach an estimate of 80.7 million tonnes in 2011 [62]. Thorenz et. al. did an analysis on the potential of bark from coniferous and broadleaf trees and estimated an amount of 15 million tonnes. They showed that coniferous bark, prominently spruce and pine, had more potential than broadleaf bark due to their large-scale availability, comparatively lower costs and homogeneity [6]. The Food and Agricultural Organisation of the United Nations provides yearly statistics for such residues and gave an estimate of 25.17 million tonnes (50.34 million  $m^3$ ) per year in 2019 [29], and is also the most recent data available. The forest residues and subsequently wood wastes are most widely found in countries like Finland, Germany, Sweden, Spain, France and Italy which have the highest forest cover area in the EU, and consequently are responsible for the majority of wood supply to industries and for energy generation [19, 28, 41].

#### 2.1.2. Agricultural Residues

Non-woody biomass, on the other hand consists of agricultural residues, dedicated energy crops, domestic and industrial municipal waste, and animal waste. Agriculture in the EU is carried out on a very large scale with nearly 173 million hectares of farm land of varying sizes, which corresponds to roughly 39% of the total land area in the EU. Agricultural activity in the EU includes growth of cereal crops, oil seed crops and sugar and starchy crops as the major contributors, with smaller contributions from fruit and vegetable farming [28]. Agricultural residues can be collected from two major sources. The residues may come from agricultural-industrial processing plants, and include wastes such as sugarcane bagasse, cotton wastes, olive cakes, nutshells, sunflower husks, etc [77]. The other source, which is a much bigger contributor to biomass supply in the EU is crop residues directly from the fields, that are left behind after harvest or pruning. These include cereal straws, corn or maize stover, rice straw, oil seed straw residues, etc. The main agricultural residue with the maximum potential is straw, which can be defined as the residue left behind in the field after the grains have been harvested, and includes majority of the leaves and stems [59]. The straw can be collected by machines in the form of bales for storage and transportation.

However, the exact amounts of crop residues available for energy purposes are hard to estimate due to the many factors which influence their collection and use. The amount of residues generated after harvest depend on weather conditions, crop rotation, soil conditions and fertility, and seed types [6, 59]. Other factors that determine the amount of crop residues that can be made available for energy purposes are the competing uses such as animal bedding and fodder, composting, building, cooking fuel, etc. One of the main competing uses is to balance the quality of topsoil or humus by tilling or burning, which determines the sustainable level of straw or residue removal [6, 59]. Still other factors include supply chains issues such as distance between production and consumption, storage, timings of supply, etc [32]. Despite these factors, various researchers have made estimates on the crop residues which may be potentially available for energy conversion. Bakker et. al. reported that if all factors are accounted for, between 25 and 35% of straw may be available for energy generation on average [59]. Garcia et. al. did a more elaborate estimate by creating a statistically generated empirical model using residue to crop ratio data and crop yields from literature upto 2015 for certain cereal, oil seed and sugar and starchy crops. They concluded that nearly 419 million tonnes of crop residues are generated every year in the EU for the mentioned categories, with cereals contributing the majority towards it, followed by oil seeds, and sugar and starchy crops respectively. According to their estimate wheat, rapeseed, maize and barley contribute more than 80% of the total residue production, which amounts to roughly 347 million tonnes. Wheat was found to be the crop which accounted for most of the residue production in EU due to the large area in which it was sown, but maize had the highest residue production yield per hectare [32]. Searle et. al. did a similar analysis for 12 crops which are most produced in the EU as of 2011, and estimated a total crop residue production of 367 million tonnes. They took into account the amount of residue that must retained in the fields, and that must be set aside for competing uses, and estimated that about 122 million tonnes of the total can be made available for energy conversion. They also made projections for future availability of crop residues, and estimated 393 million tonnes total residues off which 131 million tonnes will be available for energy purposes in 2020, and 417 million tonnes total residues off which 139 million tonnes will be available for energy purposes in 2030 [62]. Thorenze et. al. also did a similar analysis, but came up with a more conservative estimate for the theoretical potential of 390 million tonnes of crop residues, of which only 29 million tonnes was retrieved from fields for energy purposes. They suggested that the entire agricultural business sector be established as a constant provider of feedstock material to run the bioenergy based economy in order to fulfil and utilize this potential, by incentivizing farmers to view the residues as a product off which they can generate extra profits [6].

Figure 2.1 visualises a summary of the production potentials of forest residues, wood wastes and agricultural residues. The figure shows the theoretical potential ranges for all three of the biomass feedstocks, and also the actual current production quantity of forest residue and wood wastes, along with the estimate for the amount of agricultural residues that could theoretically be used for energy generation purposes. Determining the potential of these biomass feedstocks on an energy basis is difficult since most of these projections were made for many different types of feedstocks, all with different properties and heating values. However, on an average, using HHV values of 0.32toe/t, 0.36toe/t and 0.35toe/t for forest residues, wood wastes and agricultural residues respectively [1], an estimate can be made for the potential in energy terms. Forest residues can potentially contribute 3.68-25.8Gtoe/yr of energy, wood wastes between 11.52-28.5Gtoe/yr and agricultural residues between 10.2-48.7Gtoe/yr. According to the IEA, in 2018 the Total Final Consumption in the EU28 was around 1400Gtoe/yr [39]. Combining the three feedstocks, this corresponds to roughly 2-7% of the total energy demand of the EU.



Figure 2.1: Summary of Production Potential for Forest Residues, Wood Wastes and Agricultural Residues

#### 2.1.3. Dedicated Energy Crops

Apart from agricultural residues, the other main source of biomass, which has not been fully exploited yet, but has the potential to provide majority of the feedstock to run the bioeconomy is dedicated energy crops. "Dedicated energy crops can be defined as crops that are unsuitable for human or animal consumption and are grown for the purpose of producing biomass for energy in an agricultural rather than forestry context"

[17]. Dedicated energy crops, however, do not always conform to this one definition, and often include various crops that also compete with the food chain, such as cereals like maize and sorghum, and oil seeds like rapeseeds. For the purpose of this project, however, dedicated energy crops only refer to lignocellulosic biomass that do not compete with the food chain. These are essentially divided into two types: herbacious and woody energy crops. Herbacious energy crops include perennial grasses such as miscanthus, reed canary grass, switchgrass, giant reed, etc, and do not require to be replanted after every harvest, which can happen every year. Herbacious energy crops can be regrown from the same roots for around 15 years, without having to replant them [17]. Woody energy crops, on the other hand, mostly consist of short rotation coppice (SRC) crop varieties. SRC crops refer to perennial crops that have a fast growth pace and yield a large amount of woody biomass when harvested every 2 to 5 years [44]. They can be harvested for a period of 25 years without replantation [17]. The most common SRC crop varieties include willow, poplar and eucalyptus. Dedicated energy crops are a very attractive form of biomass, since they require very few inputs, grow all year round at a fast pace, do not have a large impact on the environment (low greenhouse gas emmissions) due to less input of chemicals, and help mitigate climate change [21, 25, 44].

Despite the tremendous potential energy crops present, their cultivation and use in the European Union has been negligible. To come up with an exact number for the current production quantity of energy crops is extremely challenging for a number of reasons. Since there are a number of definitions for energy crops, very often researchers include oil seeds, sugar and starch crops, and maize in the energy crop category as well, which makes it difficult to differentiate between the lignocellulosic crops and food crops. Most countries in the EU do not have existent energy crop plantations, and the countries which have reported said plantations are mostly experimental patches for case studies. A lot of researchers report the potential yields for a lot of energy crops, which is usually a range, since the yields differ from year to year. Most papers and reports only report the amount of land area available currently, and future projections for potential land area availability. Due to these reasons it is hard to determine the exact potential of dedicated energy crops in the EU. For the purpose of this project, it was decided to come up with an approximate estimate of the current and future production quantities using said yields and land area projections. In order to do so, certain assumptions were made for the sake of homogeneity and consistency, which are listed below.

- All herbacious crops, like miscanthus and reed canary grass, were grouped under the same category. Similarly all SRC crops, like willow and poplar were grouped under the same category.
- The harvest cycle for herbaceous crops was assumed to be every 1 year [17], while that for SRC crops was assumed to be every 2 years [25].
- Most reports and papers reported yields on a dry basis. However, for the yields reported for fresh crops, the moisture in SRC crops was assumed to be 50% as the reported moisture levels for willow and poplar are between 42-65% [25, 54]. The moisture levels for herbaceous crops was assumed to be 40%, as the moisture level for miscanthus is reported to be between 30-60% at the time of harvest, at different cutting times, and under different weather conditions [46].

The yields for energy crops have been reported by various researchers and organisations, and are generally found to have a lot of variation due to many factors like soil conditions, weather conditions, crop variety used, etc. One report by some researchers in Finland reported the yield for willow and poplar to be between 6-20 tonnes dm/ha/yr, and the yield for reed canary grass to be between 4-10 tonnes dm/ha/yr [54]. Shepherd et. al. studied the yields of juvenile and mature miscanthus plants in commercial fields by taking into account various factors that affects their growth, and modeled commercial yields as well, by considering all factors. They found that the maximum variation in yield of miscanthus plants was between 6-15 tonnes/ha/yr, but the average was between 9-12 tonnes/ha/yr. They also showed that the yields of the miscanthus plants only increased with age [7]. IEA Bioenergy released a report, which presented the fresh yields of energy crops. After normalization, the yield for herbaceous crops was reported to be between 6-18 tonnes/ha/yr, and that for SRC crops was between 5-7.5 tonnes/ha/yr [9]. Wickam et. al. reported average commercial yields of SRC crops willow and poplar to be between 8-10 odtonnes/ha/yr. However, they also mentioned that under certain special conditions, and with better breeding practices in the future upto 15-25 odtonnes/ha/yr can be possible [44]. Dimitriou et. al. also presented fresh yields for willow and poplar, along with a range for the harvest cycle of 1-6 years. After normalization, the yields were found to be in the range of 5-15 tonnes/ha/yr can be possible [44].

#### dm/ha/yr [25].

The land area currently under cultivation for dedicated energy crops in the EU has not been properly documented and various estimates and projections are available for the same. In a report by IEA Bioenergy, two estimates were presented by two different studies for the amount of land area that can be potentially available in the EU by the year 2030. de Wit and Faaij estimated a total of 66 million ha of arable land along with an additional 24 million ha of pasture land to be potentially available, after accounting for the land to be set aside for food production, urban expansion and nature conservation. EEA came up with a land area of 25 million ha, by factoring in certain environmentally considerate practices and a more strict selection of land for cultivating energy crops [9]. Castillo et. al. projected the cultivation of energy crops in various European countries, starting from 2020 upto 2050. The model they employed is called LUISA (Land Use Integrated Sustainability Assessment modelling platform) which is able to simulate land use patterns for growth of energy crops by taking into account various factors such as pH, temperature, soil conditions, contamination, land degradation, etc. Their model also assumed some transfer of land meant for food crops to land for energy crops, along with cultivating land which has been degraded due to high salinity, erosion and contamination. Their model predicted that various countries such as Poland, France, Germany, etc would dedicate substantial amounts of land area for cultivation of energy crops. According to their model, 4.73 million ha of land would be available in 2020, and 13.55 million ha by 2050. They also concluded that the European average for land dedicated to energy crops would be around 3.2% and 7.5% in 2020 and 2050, respectively, of total available land [17]. Chudziak et. al. also reported that approximately 8 million ha of land would be released for the cultivation of energy crops between 2004 and 2020 [19]. For the current production of energy crops in the EU, the only reported data has been provided by Bioenergy Europe, which they acknowledged might also be incomplete. They made use of data from various sources such as National Renewable Action Plan Progress Reports, Eurostat data, questionnaires and market estimates, to come up with land area data for SRC crops and herbaceous energy crops being cultivated in all countries in the EU. They estimated that the current cultivated land area under herbaceous energy crops is around 0.053 million ha and that under SRC crops is around 0.064 million ha, which totals up to 0.117 million ha of land [21]. Some publications have also reported an estimate for the potential amount of land currently (as of 2014) available in the EU for the cultivation of energy crops, which is around 1.35 million ha [19].

Based on the available estimates of crop yields and land area availability in literature, the current and future production potentials of energy crops were estimated. The maximum range of crop yields for both herbaceous and SRC crops was found to be between 4-25 tonnes dm/ha/yr. For the current actual cultivated land area approximation by Bioenergy Europe, the production range was found to be between 0.47-2.93 million tonnes/yr. For the current (as of 2014) potential land area availability, the potential production range was estimated to be between 5.4-33.75 million tonnes/yr. For the future production projections, two estimates were made, based on two different degrees of approximations for potential land area availability by 2050. A lower conservative estimate projected the future production of energy crops to be between 54.2-338.75 million tonnes/yr. The other estimate is the maximum possible production potential and is in the range of 360-2250 million tonnes/yr. The future projections are made keeping in mind the current thrust in dedicated energy crop production, and the probable greater dependence on energy from second and third generation biomass sources in the future.

Figure 2.2 shows a summary of the current and future production potential of dedicated energy crops. The production quantity is plotted on a logarithmic scale. The figure shows the current actual and current potential range of production quantity of energy crops. It also shows the lower and maximum possible estimate of production quantity for the future. Assuming a value of 0.36toe/t for the heating value of dedicated energy crops, an estimate can be made for the future potential in energy terms. Dedicated energy crops can provide between 19.5 to 810 Gtoe/yr. This corresponds to approximately 1.4 to 57% of the total energy needs of the EU.

#### 2.2. Biomass Organic Constituents

Lignocellulosic biomass is primarily composed of three main components, namely cellulose, hemicellulose and lignin.



Figure 2.2: Summary of Current and Future Production Potential for Dedicated Energy Crops

Cellulose is the compound that forms the main component of cell wall in plants, and is the world's most abundant bio-polymer. It is composed of a straight chain of C6 glucose monomers connected to each other by  $\beta$  1,4- glycocidic linkages. Cellulose makes up between 40 and 50% of the biomass, when measured on a dry basis [23]. Figure 2.3 shows the molecular structure of cellulose [23].



Figure 2.3: Molecular Structure of Cellulose [23]

Hemicellulose is a biopolymer made up of C5 and C6 sugars, and acts as a structural framework, connecting cellulose fibres. It accounts for between 25-35% of the biomass, and differs for different biomasses [23]. It is mostly made up of d-xylose, l-arabinose, d-galactose, d-glucose and d-mannose sugars [75]. Figure 2.4 shows the molecular structure of hemicellulose [23].

Lignin is a biopolymer composed of a complex network of aromatic compounds, that provides rigidity to the cell wall in plants. It accounts for between 20-30% of the biomass [23]. It is also responsible for protecting the plants against hydrolysing agents [75]. Figure 2.5 shows the molecular structure of lignin [42].



Figure 2.4: Molecular Structure of Hemicellulose [23]



Figure 2.5: Molecular Structure of Lignin [42]

During certain thermochemical pretreatment, the three polymers undergo degradation at different temperatures, depending on the biomass. Hemicellulose starts degrading extensively around 250 °C, Cellulose from 240°C to 350°C and Lignin between 280°C and 500°C, according to previously done studies [13, 30]. However, different studies do get different results for the decomposition temperatures, depending on the biomass used.

#### 2.3. Biomass Characterization

#### 2.3.1. Proximate Analysis

Proximate analysis is one of the primary analysis used to characterize biomass. It comprises of four measures, namely Moisture content (%), Volatile Matter content (%), Ash content (%) and Fixed Carbon content (%).

Moisture content represents the quantity of free water that is inherently present in the biomass, and is expressed as a percentage of the total biomass weight. It is a significant factor when it comes to not only the processing of biomass, but also its handling, storage and transportation. It is calculated on an as received basis using equation 2.1 [16, 23].

$$Moisture^{ar}(\%) = \frac{m_{ar} - m_{db}}{m_{ar}}$$
(2.1)

Volatile Matter consists of the unstable fractions of the biomass which includes condensable vapours and permanent gases, that is released when the biomass is heated. A higher volatile matter content is favourable for the production of bio-oil from pyrolysis. It is calculated on a dry basis using equation [16, 23].

$$VM^{db}(\%) = \frac{\delta m_{devolatisation}}{m_{db}}$$
(2.2)

Ash content represents the fraction of biomass that is left after complete combustion. It is mostly composed of inorganic components like silica, potassium, aluminium, calcium, etc. It is calculated on a dry basis using equation 2.3 [16, 23].

$$Ash^{db}(\%) = \frac{m_{ash}}{m_{db}}$$
(2.3)

Fixed Carbon content represents the solid combustible fraction of the biomass that is left after all the volatile matter has been removed. It is calculated on a dry basis using equation 2.4 [16, 23].

$$FC^{db}(\%) = 100 - Moisture(\%) - VM^{db}(\%) - Ash^{db}(\%)$$
(2.4)

#### 2.3.2. Ultimate Analysis

Ultimate Analysis, along with proximate analysis is the other primary analysis method used to characterize biomass. It generally indicates the weight percentage of Carbon, Hydrogen, Nitrogen, Oxygen, Sulphur and ash of dry biomass. These weight percents are determined by combusting the biomass and then calculating them from the products evolved [23].

Ultimate Analysis also helps determine two other parameters which are useful to characterize biomass. These parameters are the atomic ratios of Oxygen to Carbon (O/C), and Hydrogen to Carbon (H/C). These atomic ratios indicate a lot of properties of biomass, the chief among them being heating value. The parameters are often plotted on a diagram called the van Krevelen diagram, with H/C plotted on the y-axis and O/C plotted on the x-axis. This diagram can compare the fuel properties of biomass with other fuels like anthracite and peat. Biomass tends to have poorer fuel qualities compared to coal and anthracite because of its high H/C and O/C ratios. Figure 2.6 shows a van krevelen diagram [11].



Figure 2.6: Van Krevelen Diagram [11]

#### 2.3.3. Heating Value

The calorific value or heating value of biomass is an important indicator of the fuel properties of biomass, as it specifies the amount of thermal energy that is released from the biomass when it undergoes complete combustion. The heating value is usually expressed either as Higher Heating Value (HHV) or as Lower heating Value (LHV). The main difference between the two is that LHV does not consider the amount of energy that would be needed to evaporate the water produced during combustion [23]. The HHV of a fuel can be determined either experimentally using a device called bomb calorimeter, or using empirical correlations which employ the results of the ultimate analysis. An example of such a correlation is shown in equation 2.5 [23]. The HHV of most biomasses lies in the range of 18 to 22 MJ/kg. [23]

$$HHV^{db}(MJ/kg) = 34.91 \cdot Y_C + 117.83 \cdot Y_H + 10.05 \cdot Y_S - 1.51 \cdot Y_N - 10.34 \cdot Y_O - 2.11 \cdot Y_{Ash}$$
(2.5)

The LHV on the other hand, is determined from the HHV by correcting for the amount of hydrogen content in the fuel, using equation 4.2. In equation 4.2, the 2.4 MJ/kg is the latent heat of vaporisation of water and 8.9 kg/kg is the stoichiometric ratio of water to hydrogen [23].

$$LHV^{db}(MJ/kg) = HHV - 2.4 \cdot 8.9 \cdot Y_H \tag{2.6}$$

#### 2.4. Biomass Treatment Methods

Due to the high moisture content in biomass, and to improve the fuel properties, biomass feedstocks generally undergo certain treatments in order to convert them into more usable forms, so as to maximise their utility. Various routes exist to convert biomass into different types of products for different uses. Figure 2.7 shows the various biomass conversion routes that exist, and the corresponding products that are formed at the end of each of the processes [16]. The biochemical routes are beyond the scope of this study, so the focus is going to be on the thermochemical routes, specifically pyrolysis and gasification.



Figure 2.7: Different Biomass Conversion Routes and Corresponding Products [16]

#### 2.4.1. Torrefaction

Torrefaction, also called mild pyrolysis, is a thermochemical pretreatment method for biomass, that takes place in an inert nitrogen environment (absence of oxygen) at atmospheric pressure, and between temperatures of 200°C and 300°C. The main steps that take place during torrefaction include drying and removal of water, devolatilization of hemicellulose, and also depolymerization of cellulose and lignin. Three products are formed after torrefaction of biomass, namely torrefied solid char, permanent gases like CO,  $CO_2$ ,  $H_2$  and  $CH_4$ , and a condensable mixture which consists of water, acetic acid, phenols, etc. Among these, the solid char is the primary product, accounting for around 80% of the total biomass input, and comparitively smaller quantities of the liquid and gaseous product [72]. Torrefaction is often employed as a pretreatment method to improve the yields from pyrolysis or gasification.

Torrefaction effects the biomass in a number of ways. The primary purpose of doing torrefaction is to reduce the amount of moisture present in the biomass, and to increase the energy density. It also improves the heating value of the biomass by decreasing the O/c ratio, due to the removal of majority of the water. Another advantage of torrefaction is that it makes the resulting biomass more hydrophobic, which protects it from microbial activity when stored for long periods of time, and in unfavourable conditions. The hydrophobicity is mostly the consequence of the preferential destruction of the hemicellulose structure, which is the most hydrophillic component of biomass. Apart from these advantages, torrefaction also leads to better grindability, which requires less cost and energy for grinding [23].

#### 2.4.2. Hydrothermal Gasification

Hydrothermal gasification, sometimes referred to as wet torrefaction, is a thermochemical treatment of biomass in an aqueous environment. Hydrothermal gasification takes place at very high temperatures and pressures, where water starts approaching its critical point, and acts as a supercritical media. Water acts as supercritical water around temperatures of 600°C and 30MPa [23]. Hydrothermal gasification is employed specifically for biomass feedstocks with high moisture content like sewage sludge, which would otherwise have to be dried for thermal gasification. A catalyst may or may not be used, depending on the temperature and final product desired. The main products formed at the end of the process include  $H_2$ , CO,  $CO_2$ ,  $CH_4$ , and smaller amounts of char and tar. It has been determined experimentally, that hydrothermal gasification at low temperatures of around 500°C favours the production of a methane rich gas, while that at higher temperatures above 600°C favours the formation of a hydrogen rich gas [11, 23].

Hydrothermal gasification has many advantages when compared to thermal gasification. The process works very well for wet biomass feedstocks, which is evident by the higher thermal efficiencies of close to 70% which are achieved, compared to thermal gasification. Another advantage is the low tar formation, due to the good dissolution of the tar components in the media, which leads to ease of reforming of the tar components. Even the amount of char produced is lower, which leads to less energy loss. Carbon dioxide, which needs to removed from the product gases in case of thermal gasification, is easily separated in case of hydrothermal gasification due to higher solubility of  $CO_2$  in pressurised water. Another important advantage is that the product gases are easily separated automatically from the media which may contain char or tar particles [11].

#### 2.4.3. Pyrolysis

Pyrolysis is another thermochemical treatment of biomass in the presence of an inert environment, i.e, an absence of oxidising agents. It is typically carried out in the temperature range of 300-650°C, and at atmospheric pressure [11]. Pyrolysis also yields three major products, namely solid char, permanent gases and a condensable liquid product, often referred to as bio-oil. When the pyrolysis process is carried out at higher temperatures for a very short duration of time and at a higher heating rate, in order to maximise the output of the bio-oil, the process is called fast pyrolysis. On the other hand, if pyrolysis is carried out at lower temperatures in order to get more of the solid char product, the process is called slow pyrolysis [23]. Pyrolysis is also regarded as one of the preliminary steps in biomass gasification process.

The char produced is a carbonaceous product, which mostly consists of carbon and ash. For simplicity, it is often modelled as solid carbon [11]. The gaseous products consist of non-condensable components which includes  $H_2$ , CO,  $CO_2$  and  $CH_4$ , along with very small quantities of lighter hydrocarbons. However, the main

product of interest from pyrolysis is the liquid bio-oil. It is mostly composed of pyrolytic water, and a mixture of organic compounds which includes carboxylic acids, aldehydes, ketones, sugars, aromatic compounds like phenols and other oxygenated compounds [11, 37]. Another product formed from pyrolysis is called tar. Tars are often seen as a part of the bio-oil, since they are also condensable compounds, that are mostly composed of aromatic compounds [27]. The pyrolysis products are primarily a product of the depolymerisation and decomposition of the organic biomass components, i.e., hemicellulose, cellulose and lignin [23]. At higher temperatures, several secondary reactions may also take place which can include, tar cracking, oxidation, reforming, etc.

#### 2.4.4. Gasification

Gasification is a thermochemical conversion technique which involves partial oxidation of a feedstock at high temperatures in the presence of an oxidising agent. Gasification is usually carried out in the temperature range of 700-1500°C and under pressures ranging from atmospheric pressure upto 7MPa. Various oxidising agents can be used, such as oxygen, air, steam, carbon dioxide, or a mixture of two of them, most often oxygen and steam [23]. The limited oxygen provided to the gasifier, allows some combustion of the feedstock, in order to produce heat for the gasification process, since gasification is an endothermic process. If the agent used is steam, the product gas produced is more rich in Hydrogen [11]. Gasification technology was originally used to gasify coal, but has been used to gasify solid biomass feedstocks, as well liquid products derived from biomass such as bio-oil.

The products generated at the end of biomass gasification mainly consists of  $H_2$ , CO,  $CO_2$  and  $CH_4$ , along with other other undesired tar compounds, and if air was the gasifying agent, a fair amount of  $N_2$ . This uncleaned gas is referred to as producer gas, and after it undergoes certain cleaning treatment, it is called syngas, which mostly consists of CO and  $H_2$ , and can be used to synthesize a host of hydrocarbon products in biore-fineries.

The mechanism which biomass follows during the entire gasification process can be quite complex, and is often sequentially described through the following sub-processes: [11, 23, 77]

- Drying: This is the first step when the biomass feed enters the gasifier and receives heat from the surroundings. Above 100°C, the biomass starts to lose the loosely bound water.
- Pyrolysis or Devolatilization: This step occurs when the temperature of the biomass reaches a high enough value, for the main organic constituents to start thermally decomposing. The products of this step are char, long chain hydrocarbon volatiles in the form of tar and small amounts of non-condensable gases.
- Secondary Tar Reactions: During this step, the tars undergo various reactions due to the heat, to lead to the formation of smaller and lighter hydrocarbons, which will undergo reactions with the gasifying agents in the next step.
- Gasification Reactions: In this step, the products of the previous steps, i.e, char and tars, undergo further homogenous and heterogenous reactions with the gasifying agents and with the other gases, such as oxidation and reforming reactions and also others like Boudouard and water gas shift reactions, to form more of the final product gases.

There are no clear boundaries between the above mentioned steps, and often most steps overlap and occur simultaneously. Table 2.1 lists the main typical reactions which occur during the entire gasification process. The tar reactions mentioned are just some of the reactions which occur for certain representative compounds to give an idea, as well as general tar compound reactions.

Biomass Gasification is also dependent on a number of parameters, which play a significant role on the product composition and the efficiency of the process. Some of the parameters and their influence on the process, are listed below:

• Temperature: Temperature plays an important role in determining the quality and output of products, and is also different for different types of feedstocks. Higher temperatures are considered better for im-

Reaction	Reaction Name	Reaction Equation	Reference
R1	Boudouard Reaction	$C + CO_2 \longrightarrow 2CO$	[36]
Primary Components Oxidation			
R2	Char Oxidation	$\alpha C + O_2 \longrightarrow 2(\alpha - 1) CO + (2 - \alpha) CO_2$	[56]
R3	H <sub>2</sub> Oxidation	$H_2 + 0.5 O_2 \longrightarrow H_2 O$	[33]
R4	CO Oxidation	$CO + 0.5O_2 \longrightarrow CO_2$	[33]
R5	CH <sub>4</sub> Oxidation	$CH_4 + 0.5O_2 \longrightarrow CO + 2H_2$	[33]
	Pi	rimary Components Steam Reforming	
R6	Water Gas	$C + H_2O \longrightarrow CO + H_2$	[36]
R7	Water Gas Shift Reaction	$CO + H_2O \longrightarrow CO_2 + H_2$	[78]
R8	CH <sub>4</sub> Reforming	$CH_4 + H_2O \longrightarrow CO + 3H_2$	[36]
		Tar Components Oxidation	
R9	$C_6H_6$ Oxidation	$C_6H_6 + 3O_2 \longrightarrow 6CO + 3H_2$	[56]
R10	$C_7 H_8$ Oxidation	$C_7H_8 + 3.5O_2 \longrightarrow 7CO + 4H_2$	[66, 68]
R11	$C_{10}H_8$ Oxidation	$C_{10}H_8 + 7O_2 \longrightarrow 10CO + 4H_2O$	[66, 68]
R12	Tar Oxidation	$C_nH_m + 0.5 nO_2 \longrightarrow nCO + 0.5 mH_2$	[12]
		Tar Components Reforming	
R13	$C_6H_6$ Reforming	$C_6H_6 + 2H_2O \longrightarrow 1.5C + 2.5CH_4 + 2CO$	[66, 68]
R14	$C_7 H_8$ Reforming	$2C_7H_8 + 21H_2O \longrightarrow 7CO_2 + 29H_2 + 7CO$	[66, 68]
R15	$C_6 H_6 O$ Reforming	$C_6H_6O + 3H_2O \longrightarrow 2CO + CO_2 + 2.95CH_4 + 0.05C + 0.1H_2$	[66, 68]
R16	Tar Reforming	$C_nH_m + nH_2O \longrightarrow (n + m/2)H_2 + nCO$	[11]
Tar Components Thermal Cracking			
R17	$C_6H_6O$ Cracking	$C_{6}H_{6}O \longrightarrow CO + 0.4C_{10}H_{8} + 0.15C_{6}H_{6} + 0.1CH_{4} + 0.75H_{2}$	[12, 66, 68]
R18	$C_{10}H_8$ Cracking	$C_{10}H_8 \longrightarrow 7.38C + 0.275C_6H_6 + 0.97CH_4 + 2.235H_2$	[66, 68]

Table 2.1: Typical Reactions that occur during Gasification of Biomass

proving char and tar decomposition reactions, which leads to a greater quantity of product gases. However, higher temperatures are achieved through greater oxidation reactions, which reduces the heating value of the final product, and also lowers the thermal efficiency of the process [69].

• Equivalence Ratio: Equivalence Ratio ( $\lambda$ ) is the ratio between supplied air to fuel ratio and stoichiometric air to fuel ratio on a dry ash free basis. Equation 2.7 shows the formula to calculate said parameter [23]. The value of  $\lambda$  can determine the type of process that takes place. A value of  $\lambda = 1$  corresponds to complete combustion. On the other hand, a value of  $\lambda = 0$  corresponds to pyrolysis. For gasification to take place, the value of  $\lambda$  should be between 0 and 1. Equivalence ratio is closely related to the temperature, since a higher equivalence ratio, which leads to more oxidation reactions and increases the temperature inside the gasifier, also leads to more tar decomposition and  $CO_2$  to be produced, which lowers the heating value of the product gas, and vice versa [23, 69].

$$\lambda = \frac{O_2 supplied / fuel supplied}{StoichiometricO_2 required / fuel input}$$
(2.7)

• Steam to Biomass Ratio: Steam to Biomass ratio can be defined either as the ratio of mass flow rate of steam to mass flow rate of biomass, or as the ratio of mass flow rate of steam plus the mass flow rate of the moisture in the biomass to the mass flow rate of biomass [23]. A higher steam to biomass ratio, upto a certain value, usually leads to higher gas yields, and in particular higher  $H_2$  yields. A higher calorific value syngas is also achieved due to more water gas shift reactions and reforming reactions [69].

#### 2.5. Biomass Gasifier Technologies

Over the years, many gasifier technologies have been developed to improve upon existing tecnologies, in order to make the process more efficient, and the final product better in quality. The three broad gasifier types considered here are Fixed Bed gasifiers, Fluidized Bed Gasifiers, and Entrained Flow Gasifiers. Each of these types differ from each other in various aspects as discussed below.

#### 2.5.1. Fixed Bed Gasifiers

Fixed Bed gasifiers, or Moving Bed Gasifiers when a moving grid was employed instead of a fixed grid, are the first kind of gasifiers put to use for small scale gasification needs, upto a few MW. These are typically used inn conjunction with other gas engines for fulfilling energy demands. The three main fixed bed gasifier configurations used are Downdraft, Updraft and Crossdraft gasifiers [23].

Downdraft gasifiers operate in a cocurrent configuration, in which the biomass and gasifying agent move in the same direction. These are simple and reliable, and produce a final product with low tar concentrations. However, they also require small particle size and low moisture feed, and produce syngas at high temperature [23, 69]. Updraft gasifiers operate in a countercurrent configuration, in which the biomass and gasifying agent move in opposite directions. These are also simple and relatively cheap gasfiers which can handle more moisture in the biomass, but the syngas produced has to undergo a lot of clean-up due to the high tar concentrations [23, 69]. Cross-draft gasifiers involve a perpendicular flow of the fuel and gasifying agent, and is mostly used for charcoal [23]. It has also been noted that these are not competitive with other technologies any more [69]. Figure 2.8 shows a schematic depiction of the above mentioned gasifiers. The figure also shows different temperature zones in each of the gasifiers, where the fuel undergoes different reactions.



Figure 2.8: Updraft (left), Downdraft (middle) and Cross-draft (right) configurations of Fixed Bed Gasifiers [23]

#### 2.5.2. Fluidised Bed Gasifiers

Fluidised Bed Gasifiers were designed in order to scale up production of syngas to around 100MW. They involve an inert or catalyst bed, which needs to have small particle size in order to allow better heat and mass transfer, to be suspended in a fluidized state using a gasifying agent which enters from the bottom of the gasifier. The temperature across all sections of the gasifier is more or less homogeneous, which is why distinct zones do not exist as in fixed bed gasifiers. These gasifiers typically operate in the temperature range of 700-900°C and between pressures of 0 and 7MPa. Due to the relatively lower temperature of operation, the final syngas tends to have some amount of tar, which must be removed in the downstream gas cleaning. They are mainly of two types, Bubbling Fluidized Bed and Circulating Fluidized Bed Gasifiers. Various other designs have also been commercialised which may involve multiple stages, interconnections, etc [23, 69].

A Bubbling Fluidized Bed Gasifier typically consists of two sections, the bedzone and the freeboard. The gasifying agent enters the bed region at an intermeditae gas velocity of 0.5-2 m/s forming bubbles within the reactor, such that majority of the bed material stays within the bedzone. Most of the heterogenous gasification reactions take place in the bedzone, whereas some reactions such as the cracking and reforming reactions, which are mostly in the gas phase, take place in the freeboard region. It also has a good carbon conversion and flexibility in terms of feedstock characteristics, and load [23, 48].

A Circulating Fluidized Bed Gasifier is so named because the gasifying agent enters the gasifier at very high velocities of around 5-10m/s, which leads to a large amount of the solid to be entrained with the products. It comprises of a cyclone connected to it, in order to separate and recycle the solids back to the gasifier for optimal conversion. This gasifier also reports high carbon conversion and good flexibility in load, but also lower residence times [23, 48]. Figure 2.9 shows the two configurations of fluidized bed gasifiers [23].



Figure 2.9: Bubbling (left) and Circulating (right) Fluidized Bed Gasifiers [23]

#### 2.5.3. Entrained Flow Gasifiers

Entrained Flow Gasifiers were initially used for gasification of coal, but have since been used to gasify biomass as well due to the fact that they can be designed to operate at a very large scale, upwards of 100 MW. The fuel and gasifying agent mostly enter the gasifier co-currently. Since these gasifiers typically require feeds to be in the form of a powder or slurry, using biomass became challenging due to the high moisture content. The biomass is usually ground to a fine powder or an intermediary torrefaction step is executed to reduce moisture and bulk density, or a pyrolysis step is executed to convert the biomass into bio-oil and gas [23, 48, 69].

These gasifiers are usually operated at a high temperature range of 1200-1500°C and pressure range of 25-30 bar, which lends them a huge advantage of having very low tar concentrations in the final product gas. These are also considered very flexible in the type of fuel and operation parameters, and are also reported to have good carbon conversion. However, it requires high volumes of gasifying agents, which is mostly oxygen, and sometimes a mixture of steam and oxygen, which increases the operation costs. Despite these drawbacks, entrained flow gasifiers have been successfully used in various commercial projects, most notable being by Shell, Texaco, Mitsubushi Heavy Industries, etc [23, 48, 69].

#### 2.6. Biomass Gas Cleaning

The product gas from the gasification process contains a considerable amount of impurities, and must undergo certain downstream processing in order to become suitable for the production of other chemicals and products. The quantity of unwanted substances may differ for different gasifier types, biomass varieties and operating conditions, but the kind of impurities is more or less the same for all. The impurities which are contained in the raw syngas include mostly particulate matter, unconverted tar, nitrogen compounds like ammonia, sulphur compounds like hydrogen sulphide, chlorine compounds like hydrochloric acid, etc. These impurities must be removed upto the minimum requirement for different end uses [8, 23].

Various gas cleaning technologies exist for different impurities. Gas cleaning techniques can be broadly classified into hot gas cleaning and cold gas cleaning. When the product gas from gasification is cleaned post cooling, or cooled and cleaned simultaneously, the cleaning method used is referred to as cold gas cleaning. On the other hand, hot gas cleaning refers to either the filtration of gas to remove impurities above 260°C, or the conversion of tar to gas. Other sub classifications can also be made based on the mode of operation [8].

Particulate matter can be present in the product gas due to ash particles, bed material particles and due to carbonaceous materials. Various technologies exist for the removal of such particulate matter, which operate in different temperature ranges. Some of them are cyclone separators, electrostatic filter scrubbers, rotating particle separators, baghouse filters, ceramic and metallic filters, etc. Each of them removes particles above a certain diameter only [23].

Tars during gasification can be minimised if the operating conditions of the gasifier such as temperature and equivalence ratio are chosen optimally. Other ways to reduce tars during gasification includes using catalytic bed material additives such as olivines, limestones and dolomite, or by using monoliths with catalysts. Still other ways could be do carry out steam reforming or catalytic cracking or placing fixed bed gasifiers, downstream of the main gasification reactor. Some pilot plants have also employed absorbers to separate tar from the syngas, with varying levels of success [8, 23].

Sulphur capture can be carried out using catalysts as for tar removal, but also using various metal oxide sorbents such as zinc oxide or copper oxide downstream of the gasifier [23]. Chlorine molecules can be removed using additives like limestone or dolomite, but also by cooling the gas to less than 600°C, thus allowing for the chlorine molecules to condense to solid particles, and later being removed by solid separators. Nitrogen compounds can be removed by using similar catalysts as for tar removal [23].

The sequence of removing or converting most of these contaminants may vary based on type of gas cleaning methods employed and their operating conditions. The particulate matter and solids are usually removed first since they are also recycled sometimes. The tars can be removed later as long as the temperature stays above the dew point of the tars, which is around 300 to 350°C [50]. Other contaminants may be removed depending on the temperature or if one compound interferes with the removal of another.

#### 2.7. Syngas End Uses

Biomass on its own faces a number of challenges to be used for varied applications. However, converting biomass to clean syngas, opens up a number of possibilities in terms of immediate use, and further production of chemicals and fuels, without any drawbacks from the original biomass composition. Some of the products that clean syngas can be used to produce include electricity and heat, chemicals like methanol and ammonia, and biofuels like synthetic natural gas and Fischer-Tropsch synthesis products [23, 48].

#### 2.7.1. Electricity and Heat

Once the syngas has been processed to be within the required limits of impurities like tar and particulate matter, it may undergo combustion by itself or with other fuels, to produce heat and power. The combustion can take place in steam boilers, gas turbines or internal combustion engines, each with different efficiencies and requirements. Other methods include high temperature fuel cells like Solid Oxide fuel cells to produce electricity through the chemical conversion route instead of combustion. This process has the maximum reported efficiency of around 40%, but needs syngas with very low to none impurities [48].

#### 2.7.2. Fischer-Tropsch Synthesis for Production of Hydrocarbon Fuels

Fischer-Tropsch synthesis refers to a number of reactions through which syngas components CO and  $H_2$  are converted into hydrocarbons at high pressures and temperatures, usually in the presence of a catalyst. It is particularly attractive as a technology, due to its maturity and it being very flexible towards the use of many times of biomass feedstock. Equation 2.8 shows the general overall reaction for Fischer-Tropsch synthesis, n is an integer. An n value of 1 corresponds to methane [23, 48].

$$nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$$
(2.8)

Fischer-Tropsch synthesis is usually carried out in the temperature range of 480-620K and pressures of 10-60 bar. Low temperatures of around 500K are preferred since higher temperatures leads to uncontrollable reaction rates and heat release, due to the reaction being highly exothermic, which makes it hard to cool and ensure safety. Also, high temperatures favours the production of less favourable compounds such as methane. The catalyst used for high temperature synthesis (480-530K) is iron, which favours the production of hydrocarbons which correspond to gasoline ( $C_4 - C_{12}$ ). On the other hand, the catalyst used for low temperature synthesis (580-620K) is cobalt, which favours the production of long chain hydrocarbons which corresponds to diesel. The reactor type preferred for high temperature synthesis is fluidized bed reactors, while that for low temperature synthesis is multitubular packed bed reactors and slurry bubble columns [23].

#### 2.7.3. Bioethanol

Bioethanol can be produced from syngas using two routes. The first route is through syngas fermentation using acetogenic bacteria. These anaerobic bacteria convert the *CO* and  $H_2$  into acetyl-CoA, which is then converted to ethanol via acetaldehyde. The second route is through thermochemical catalytic conversion of syngas. The most effective catalyst used is Rhodium based, but others such as copper based catalyst are also used with promoters to favour the production of C2 alcohols. Equation 2.9 shows the main reaction for alcohol production, where n is an integer which lies between 1 and 8, and a value of 2 corresponds to ethanol. This reaction is typically carried out in the temperature range of 833-858°C, so as to ensure maximum production of  $C_2 - C_3$  alcohols, instead of undesired by-products [48].

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + OH + (n-1)H_2O$$
(2.9)

#### 2.7.4. Synthetic Natural Gas

Synthetic Natural Gas or substitute natural gas refers to methane produced by thermochemical treatment, similar to Fischer-Tropsch synthesis, as opposed to that produced by anaerobic digestion. This product from syngas is considered advantageous since it can directly be fed into the existing natural gas infrastructure after the required specifications are met. Equation 2.10 shows the main methanation reaction which takes place in the reactor, and is also very exothermic in nature.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$
 (2.10)

This synthesis takes place at slightly higher temperatures compared to Fischer-Tropsch synthesis of around 520-770K and pressures of 20-70 bar, so as to ensure maximum production of methane. A Nickel or Nickel-Alumina based catalyst is generally used for this synthesis. It usually takes place in adiabatic fixed bed reactors in series or fluidized bed reactors. Other systems such as those employing membrane technology have also been used [23, 48].

#### 2.7.5. Methanol

Syngas can also be processed to form methanol, which is an important chemical used as an intermediate for the production of a number of high value chemicals, or can also be used as a fuel. Equation 2.11 shows the reaction for syngas to methanol, and is also exothermic in nature [23].

It is most desirable to carry out the reaction at high temperature and low pressure, so as to maximise the product, by shifting the equilibrium to the right. Usually this synthesis take place in the temperature range of 490 to 560 K and pressure range of 50 to 100 bar. The catalyst most often used is Cu/ZnO/Al2O3 based catalyst, as it ensures a high selectivity for methanol. It is used in a adiabatic reactor with the catalyst bed, but other reactor types are also employed. Methanol can be further converted into chemicals such as formaldehyde or dimethyl ether, but also fuels like hydrocarbons which correspond to gasoline. Methanol can also be used for the production of olefins, which may also be attractive based on the use. Another novel way to use methanol is to convert it into hydrogen using steam reforming, for use in fuel cells in cars [23].
# 3

# **Process Model Development**

This chapter discusses the process model development of the gasification section and its validation, and the subsequent downstream gas cleaning. It also describes the further model development for the chosen biore-finery products namely Synthetic Natural Gas and Hydrogen, both of which have numerous applications in the energy industry.

# 3.1. Gasification Model

## 3.1.1. Overview

The gasification process can be modelled as an Equilibrium model or as a Kinetic model. An Equilibrium model involves determining the equilibrium compositions of the gasification products by using a Gibbs reactor which minimises the Gibbs free energy of the gasification process. This type of model may or may not also involve specifying the stoichiometry and equilibrium constants of the reactions. A Kinetic model on the other hand takes into account the hydrodynamics of the gasifier along with the chemical conversions, to provide the product composition at any specific time. There are some merits to both approaches of modeling, however, a kinetic model is considered more accurate and realistic. While an equilibrium does not require the specification of gasifier design, however, it assumes that complete equilibrium between reactants and products is achieved. In reality, for low temperature gasification, full equilibrium is often not achieved, which is why only kinetic models can make an accurate enough estimation of the gasification products' composition [11, 15].

Due to the reasons discussed above, it was decided to model the gasification process as a Kinetic model. The gasification model has been designed based on the reactor setup of the Indirectly heated Bubbling Fluidised Bed Steam Reformer, present at the Delft University of Technology. A schematic diagram of the gasifier with its dimensions is shown in Appendix A. The software used to model the process was ASPEN Plus, which is a chemical process simulator software, and is used for designing models and flowsheets. Each step of the process has been modelled as a separate block, each with its own inputs.

The pyrolysis step of the gasification process has been separated from the gasification reactions, and modelled as such. The gasifier itself has been modelled as two separate sections, the Bedzone and the Freeboard. The primary gasifying agent considered is steam, and the biomass used for gasification is miscanthus.

#### 3.1.2. Basis of Design

The aim of the developed gasification model was to predict the composition of the product syngas to validate the model with the experimental results. The chosen scale was that of the experimental setup at TU Delft, which required an input of 8kg/hr of biomass feedstock. Using this input, the models developed for SNG and Hydrogen production, were aimed at maximising the yield and also the efficiency of the model. The syngas from the gasification model was also cleaned to remove or convert all contaminants namely tar,  $NH_3$ ,  $H_2S$ and HCl, so as to obtain a final product which could be used for any application. The aim of the final SNG model was to obtain a product gas which was composed majorly of methane (with little to no water and nitrogen to be removed), and that of the Hydrogen model was to obtain a product gas composed majorly of Hydrogen (with little to no CO,  $CO_2$  and water, and nitrogen to be removed). Nitrogen removal for both models would depend on the application for which it is used, but in order to obtain a concentrated stream of Methane or Hydrogen, majority of the nitrogen will have to be removed. Even though an economic analysis was not performed in this study, the size of the equipment and wastage streams were aimed to be reduced or reused as much as possible.

#### **3.1.3. Biomass Feedstock**

The biomass feedstocks chosen for the model were wood and miscanthus, as the experimental results were available for both. The wood used for the experiments was sourced from forest residues in the Netherlands, while the Miscanthus was grown specifically as an energy crop and sourced from Germany. Both feedstocks were available in dried and pelletized form, so no pre-treatment operation was required in the model.

In ASPEN Plus, biomass needs to be input as a non-conventional component and is characterized by its proximate and ultimate analysis results. The biomass was input into the model at room temperature and at-mospheric pressure, and at a flow rate of 8 kg/hr. Table 3.1 shows the proximate and ultimate analysis results for both biomass feedstocks.

Analysis	Wood
Proximate Analysis	
Moisture Content (%)	$5.57 \pm 0.11$
Ash Content (%)	$0.46 \pm 0.12$
Volatile Matter Content (%)	$79.90\pm0.81$
Fixed Carbon Content (%)	14.07
Ultimate Analysis	
Carbon (%)	$47.88 \pm 0.08$
Hydrogen (%)	$6.44 \pm 0.07$
Oxygen (%)	$45.62\pm0.02$
Nitorgen (%)	$0.0 \pm \pm 0.01$
Sulphur (%)	$0.010 \pm 0.001$
LHV (MJ/kg)	19.50

Table 3.1.	Provimate and	Ultimate	Analysis	results f	or Wood
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#### 3.1.4. Pyrolysis

As mentioned above, the pyrolysis step of the gasification process was separated from the subsequent steps, and modelled as such. The composition of products from the pyrolysis step is based on the results of the pyroprobe experiments conducted at TU Delft, and documented in Maarten Kwakkenbos's Thesis [45].

The assumptions made for the pyrolysis step are listed below:

- All biomass particles were homogeneous in nature. This assumption was made in order to ensure that all biomass particles behaved identically.
- The temperature across the reactor and across each particle was the same. This was to make sure that the temperature in the reactor was homogeneous and no dead spots were present.
- Except the biomass decomposition into the products, no other reactions take place within the reactor. This assumption was made since the product yields were based on experimental data from pyrolysis experiments and not gasification.
- The entire biomass entering the reactor is converted into the products, leaving no unreacted biomass.

#### **Pyrolysis Products**

The biomass dissociates into a number of products during pyrolysis, due to the breakdown of the organic constituents present in the biomass, namely hemicellulose, cellulose and lignin. The different products from the experiments were measured for each experiment conducted at different temperatures, and then approximated using regression analysis, to obtain devolatilization curves for each component yield. The curves were generated using a fourth degree polynomial in Matlab, and take the form as shown in equation C.1, where i is the particular component. Appendix C lists the coefficients for each of the component mass yields, for both biomass feedstocks.

$$M_i = aT^4 + bT^3 + cT^2 + dT + e (3.1)$$

The main solid component is char which is a black carbon substance, and is apppoximated by the difference between the solid component and the ash, ashown in equation 3.2. It has been chosen to model the char as the conventional solid component Carbon (Graphite). The other solid component present is the ash, which is obtained from the proximate analysis on an as received basis, and is modelled as a non-conventional solid component, similar to the biomass.

$$M_{char} = M_{solid} - M_{ash} \tag{3.2}$$

The liquid component from pyrolysis mainly consists of pyrolytic water and tars, which are heavier hydrocarbons. However, approximately 10-20% of the mass from the pyroprobe experiments could not be accounted for. A possible reason for this could be the inability of the entire condensabale fraction of the vapours to condense, resulting in lower than the exact amount of liquids. An analysis for the reasons that cause this discrepancy in the mass balance closure can be found in [70]. For this reason, it is assumed that the unaccounted for mass is part of the liquid fraction. This mass deviation is added to the measured liquid fraction, thus yielding the total amount of liquids. This has been shown in equation 3.3.

$$M_{total-liquids} = M_{measured-liquid} + M_{dmass}$$
(3.3)

The amount of pyrolytic water is determined using a correlation as a function of temperature, from another research work [4], and is shown in equation 3.4. The total water present in the final product is a sum of the pyrolytic water and the moisture inherently present in the biomass, which is known from the proximate analysis. Apart from the water, tars make up the rest of the liquid fraction, and is calculated as shown in equation 3.5.

$$M_{pw} = 5.157 \cdot 10^5 \cdot T^2 - 1.186 \cdot 10^1 \cdot T + 84.91 \tag{3.4}$$

$$M_{tar} = M_{total-liquids} - M_{pw} - M_{moisture} \tag{3.5}$$

Phenol was chosen to be the representative tar compound. According to the results of the pyroprobe experiments as shown in [71], Phenol is the most abundant tar component after the pyrolysis step, and is thus a reasonable representation of the tar composition. Initially, the tar fraction was represented by four compounds namely, benzene, toluene, phenol and naphthalene, in order to obtain a more accurate representation of primary, secondary and tertiary tar components. However, during the validation of the model, it turned out that ASPEN PLUS was overestimating the amount of tars left in the product gas, as compared to the experimental results. Thus, it was decided to model the tars as a single component.

The gas fraction was entirely composed of CO,  $CO_2$ ,  $H_2$  and  $CH_4$ . Other gaseous hydrocarbons such as ethane and ethylene, which are typically present in small amounts after gasification, were assumed to be absent. All these equations for determination of mass yields of different components was input as a FORTRAN code in ASPEN Plus, which is shown in Appendix B.

#### 3.1.5. Reactions of Nitrogen, Sulphur and Chlorine Compounds

The composition of biomass, intrinsically contains small amounts of Nitrogen, Sulphur and Chlorine, which happens to react during the gasification process. Even though each of the three elements may form more than one compounds, for the purpose of this study, it was assumed that the Sulphur reacts to form only  $H_2S$ , the Nitrogen reacts to form only  $NH_3$  and the Chlorine reacts to form only HCl. Since these compounds may lead to some fouling, corrosion, catalyst deactivation or environmental damage in the downstream processes, it was assumed that they do not react in the gasifier. The formation of these compounds has been shown in equations 3.6 to 3.8. It was also assumed that the fractional conversion of N, S and Cl was 100%, to ensure that all of them get converted to their hydrogenated forms in their entirety, in order to make it easier to clean them out of the gas in the downstream gas cleaning.

$$N_2 + H_2 \longrightarrow 2NH_3$$
 (3.6)

$$S + H_2 \longrightarrow H_2 S$$
 (3.7)

$$Cl_2 + H_2 \longrightarrow 2HCl$$
 (3.8)

#### 3.1.6. Gasification Reactions

The Gasification model in this work has been designed to simulate steam gasification of biomass, with the addition of some air, in order to produce some heat in the reactor since gasification is an endothermic process, and also to ensure maximum cracking of tar components. For these reasons, it was decided to simulate biomass reactions with both oxygen and steam. The main reactions taking place in the gasifier are oxidation reactions, steam reforming reactions, Boudouard reaction, Water Gas Shift reaction and the tar cracking reactions. The catalytic properties of unreacted char were assumed to not play any role. All reactions are presented in Table 3.2 below.

Reaction	Reaction Name	Reaction Equation	Reference		
R1	Boudouard Reaction	$C + CO_2 \longrightarrow 2CO$	[36]		
		Primary Components Oxidation			
R2	Char Oxidation	$\alpha C + O_2 \longrightarrow 2(\alpha - 1) CO + (2 - \alpha) CO_2$	[56]		
R3	$H_2$ Oxidation	$H_2 + 0.5 O_2 \longrightarrow H_2 O$	[33]		
R4	CO Oxidation	$CO + 0.5O_2 \longrightarrow CO_2$	[33]		
R5	CH <sub>4</sub> Oxidation	$CH_4 + 0.5O_2 \longrightarrow CO + 2H_2$	[33]		
	Pi	imary Components Steam Reforming			
R6	Water Gas	$C + H_2O \longrightarrow CO + H_2$	[36]		
R7	Water Gas Shift Reaction	$CO + H_2O \longleftrightarrow CO_2 + H_2$	[78]		
R8	CH <sub>4</sub> Reforming	$CH_4 + H_2O \longrightarrow CO + 3H_2$	[36]		
	<u>`</u>	Tar Components Oxidation			
R9	$C_6H_6$ Oxidation	$C_6H_6 + 3O_2 \longrightarrow 6CO + 3H_2$	[56]		
R10	$C_{10}H_8$ Oxidation	$C_{10}H_8 + 7O_2 \longrightarrow 10CO + 4H_2O$	[66, 68]		
	Tar Components Reforming				
R11	$C_6H_6$ Reforming	$C_6H_6 + 2H_2O \longrightarrow 1.5C + 2.5CH_4 + 2CO$	[66, 68]		
R12	$C_6 H_6 O$ Reforming	$C_6H_6O + 3H_2O \longrightarrow 2CO + CO_2 + 2.95CH_4 + 0.05C + 0.1H_2$	[66, 68]		
Tar Components Thermal Cracking					
R13	$C_6 H_6 O$ Cracking	$C_6H_6O \longrightarrow CO + 0.4C_{10}H_8 + 0.15C_6H_6 + 0.1CH_4 + 0.75H_2$	[12, 66, 68]		
R14	$C_{10}H_8$ Cracking	$C_{10}H_8 \longrightarrow 10C + 4H_2$	[53, 58]		

Table 3.2: All Reactions Considered for Gasification of Biomass

The kinetics for the gasification reactions were taken from literature and were chosen based on similar conditions for the gasification process. The kinetics chosen from literature are either in the form of the powerlaw equation, or in the form of Langmuir-Hinshelwood-Hougen-Watson (LHHW) equation. The general form of the powerlaw kinetics for a reaction 3.9, is shown in equation 3.10. The general form of the LHHW kinetics for the same reaction 3.9, is shown in equations 3.11 and 3.12, the only difference being one of the reactants (Q in this case) would be in the solid phase. The kinetic parameters for all the reactions listed above are shown in Appendix D.

$$pP + qQ \longrightarrow rR + sS \tag{3.9}$$

$$r_j = k_j^0 \cdot exp(\frac{-E_a}{RT}) \cdot [P]^p \cdot [Q]^q$$
(3.10)

$$r_j = \frac{[KineticTerm][DrivingForceTerm]}{[AdsorptionTerm]}$$
(3.11)

$$r_j = \frac{k_j^0 \cdot exp(\frac{-E_a}{RT}) \cdot (k_1(\Pi C_i^{n_i}) - k_2(\Pi C_l^{n_i}))}{1 + K_1[P]^p + K_2[R]^r + K_3[S]^s}$$
(3.12)

3.1.7. Bedzone



Figure 3.1: Schematic Diagram of the Gasifier Modelled in ASPEN Plus

Figure 3.1 shows the schematic diagram of the Gasifier modelled in the ASPEN Plus flowsheet. The Gasifier has been modelled as a Bedzone and a Freeboard, with the Bedzone being modelled by a CSTR in the AS-PEN Plus flowsheet. The Bedzone ideally, is a well mixed zone with a uniform temperature distribution. It is also assumed that the CSTR operates under isothermal conditions and at steady state. The temperature in the CSTR has been chosen based on the temperature recorded during gasification experiments, and is set at 711.3°C. The pressure is set at atmospheric pressure.

The bed material used to model the bedzone is Corundum, which is a crystalline form of Aluminium Oxide  $(Al_2O_3)$ . The form of Corundum used for the model is  $F_046$ , which has an average particle size of  $500\mu m$ , a real density of 3950  $kg/m^3$  and a bulk density of 1636  $kg/m^3$ . The bed material is non-catalytic in nature and has no influence on the kinetics of the reactions taking place.

It is assumed that the CSTR models the volume of the reactor above the actual bed material. The volume of the CSTR is thus the volume of the vapour phase around the bed material. Since the gasifier also includes the radiant tube burner, the hydraulic diameter was considered for calculation of the CSTR volume, as shown in equation 3.13. The value of  $D_{gas}$  is 346mm and that of  $D_{rtb}$  is 150mm.

$$D_{hyd} = \sqrt{D_{gas}^2 - D_{rtb}^2}$$
(3.13)

The value of  $D_{hyd}$  was calculated to be 311.8mm. The mass of bed material considered to be in the gasifier was 75kg. The height of the stationary bed, when no gasifying agents are present, was calculated using equation 3.14.

$$H_{fixed} = \frac{m_{bed}}{\rho_{bulk} \cdot 0.25 \cdot \pi \cdot D_{hvd}^2}$$
(3.14)

The stationary bed height was calculated to be 0.6m. For corundum, there is very little information available in literature for its behaviour during fluidization. Instead, in order to calculate the expanded bed height during fluidization, the voidage of a general FCC catalyst was considered. Rapagna et. al. [57] considered the effect of temperature on fluidization for said material. They observed that the stationary bed voidage for the material is 0.4, and during fluidization and at a temperature of around 800°C, the expanded bed voidage was 0.5. These values were considered in order to calculate the expanded bed height, as shown in equation 3.15.

$$H_{exp} = H_{fixed} \cdot \frac{1 - \epsilon_0}{1 - \epsilon} \tag{3.15}$$

The expanded bed height was calculated to be 0.72m. The total volume of the bedzone during fluidization was calculated using equation 3.16. The volume of the bed material in the gasifier was calculated using equation 3.17.

$$V_{fluid} = H_{exp} \cdot 0.25 \cdot \pi \cdot D_{hyd}^2 \tag{3.16}$$

$$V_{bed} = \frac{m_{bed}}{\rho_{real}} \tag{3.17}$$

The volume of the vapour phase above the bed can be obtained by subtracting the volume of the bed from the total volume of the bedzone at fluidization, as shown in equation 3.18. This is the final volume of the CSTR that was specified in the ASPEN Plus flowsheet, and was calculated to be 36.06l.

$$V_{CSTR} = V_{fluid} - V_{bed} \tag{3.18}$$

It was decided that all reactions mentioned in table 3.2 take place in the bedzone. According to Basu [11], the oxidation reactions take place first, quickly followed by the reforming and cracking reactions. Thus, it made sense to model all reactions in the bedzone.

#### 3.1.8. Freeboard

The freeboard of the Gasifier was modelled in ASPEN Plus as two RPLUG reactors. The freeboard is considered to have mostly gas phase present and compared to the bedzone, much shorter residence times. Another assumption was that no axial mixing takes place in the freeboard. It is also assumed that both the RPLUG reactors operate under isothermal conditions and at steady state. The temperature in the RPLUG reactors has been chosen based on the temperature recorded during gasification experiments, and is set at 783°C for the first one, and 863°C for the second one. The pressure is set at atmospheric pressure in both.

The reason behind modelling the freeboard as two RPLUG reactors, was to account for the addition of secondary air into the gasifier. Since the secondary air enters the gasifier, around half way through the freeboard as shown in 3.1, it was assumed that secondary air only reacts above the point where it is added, due to the assumption that no axial mixing takes place. Secondary air is mainly added in order to facilitate the maximum cracking of tars as possible. The amount of secondary air added was 4kg/hr.

The diameter of the freeboard varies along the length of the reactor due to the physical dimensions, and also because of the presence of the radiant tube burner, as shown in 3.1. Table 3.3 shows the variation of diameter of all unit operations used to model the gasifier, with height. The total height of the gasifier is 2.454m, the height of the CSTR is 0.720m, the height of Freeboard 1 is 0.804m and the height of Freeboard 2 is 0.93m.

Reactor Section	Height	Height (mm)	Relative Height	<i>D<sub>in</sub></i> ( <b>mm</b> )	$D_{rtb}$ (mm)	$D_{hyd}$ (mm)
CSTR	H1	0	0	346	150	311.8
	H2	600	0.833	346	150	311.8
	H3	720	1	346	150	311.8
Freeboard 1	H3	720	0	346	150	311.8
	H4	1068	0.433	346	150	311.8
	H5	1206	0.6045	382.2	150	351.5
	H6	1453	0.912	447	0	447
	H7	1524	1	447	0	447
Freeboard 2	H7	1524	0	447	0	447
	H8	1704	0.1935	447	100	435.67
	H9	2454	1	447	100	435.67

Table 3.3: Variation of Freeboard Diameter with Height

In order to model the reactions in both the RPLUG reactors, an assumption was made for the reactions involving char. The initial assumption made was that no char reactions would take place in the freeboard and only gaseous reactions would take place, as done in [36, 47]. However, this assumption was amended in order to consider the minute solid particles that are carried into the freeboard in the form of fines. It was assumed that 1% of the char would be carried over into the freeboard as fines and would react to form products. This was done by changing the pre-exponential factor of the reactions involving char, to 1% of their original values. The value 1% was determined using a trial and error method by validating the char conversion with the experimental values.

#### **3.1.9. Gasification Model Flowsheet**



Figure 3.2: Gasification Model ASPEN Plus Flowsheet

Figure 3.2 shows the ASPEN Plus flowsheet of the complete kinetic Gasification Model. The model uses air and steam as the gasifying agents. Nitrogen is added in order to prevent any blocking and obstruction of the measuring equipment (pressure transmitters) within the gasifier, and also to prevent any back-flow of product gas in the feeding system. All three agents are preheated before entering the CSTR. The biomass enters the RYield reactor where it decomposes into the pyrolysis products, based on the mass yields entered in the CAL calculator block. The products then enter an RSTOIC reactor where the N, S and Cl get converted into their hydrogenated forms as mentioned in section 4.1.4. Following this, all the products along with the gasifying agents enter the CSTR and then Freeboard 1. The products from Freeboard 1 are mixed with a secondary stream of air and Nitrogen, and then enter Freeboard 2. The gasification products are then mixed with another stream of Nitrogen, and enter an ideal solid separator which models a cyclone separator. It is assumed that all the solid components, which consists of unreacted char and ash, are removed from the product gas stream. Table 3.4 summarises all the blocks in the gasification model flowsheet.

Block Type	Block Name	Description		
RYIELD	RYIELD	This reactor models the decomposition of the biomass into conven- tional components, based on known mass yields. The reactor operates at a temperature of 711.3°C and at atmospheric pressure.		
CALCULATOR	CAL	This Calculator block specifies the mass yields of the products from the pyrolysis products. The correlations for the mass yields are input in a FORTRAN Code.		
RSTOIC	NS-SEP	This reactor models the conversion of N to $NH_3$ , S to $H_2S$ and Cl to $HCl$ , using some hydrogen from the pyrolysis as a reactant. It is assumed that all of the N, S and Cl gets converted, and that the $NH_3$ , $H_2S$ and $HCl$ are inert.		
SEPARATOR	SEP1	This component separator completely separates the gaseous and solid pyrolysis products. The Gas stream consists of all gaseous components including the inert and tar components. The Char stream consists of the char and ash.		
RCSTR	OX-CSTR	This reactor models the bedzone of the gasifier. The volume of the re- actor was set at 36.06l. The reactor operates at a temperature of 711.3°C and at atmospheric pressure. It models all the oxidation, reforming and cracking reactions of the primary components and tars.		
RPLUG	FRBRD 1	This reactor models the first half of the freeboard, with a height of 0.804m. The reactor operates at a temperature of 783°C and at atmospheric pressure. It models all the oxidation, reforming and cracking reactions, and assumes only 1% of the char reacts in the form of fines.		
	FRBRD 2	<ul> <li>reactions, and assumes only 1% of the char reacts in the form of fines.</li> <li>This reactor models the second half of the freeboard, with a height of 0.93m. The reactor operates at a temperature of 863°C and at atmospheric pressure. It models all the oxidation, reforming and cracking reactions, and assumes only 1% of the char reacts in the form of fines.</li> </ul>		
MIXER	B5	This mixer mixes all the gasifying agents together, before being preheated.		
	MIX-PROD	This mixer mixes the gasification products exiting the Freeboard with a nitrogen stream, before entering the solid separator. The Nitrogen is addded in order to prevent any obstruction in the cyclone separator.		
HEATER	B6	This heater preheats the gasifying agents upto a temperature of 441°C. The amount of heat supplied to this heater is 10.5kW.		
SEPARATOR	SOL-SEP	This ideal solid separator is used to model a cyclone separator, which removes all the solid components (unreacted char and ash) from the product gas. It is assumed that this separator all the solids from the product gas.		

#### Table 3.4: Summary of all Blocks in the Gasification Model Flowhseet

# 3.2. Gas Cleaning

Syngas from a gasifier often cannot be used for a lot of applications without any treatment due to the presence of various impurities. The impurities which might include particulate matter, unconverted tar, etc. must be removed through certain downstream cleaning. The undesired components from the gasification model in this study include tar,  $H_2S$ ,  $NH_3$  and HCl. Different methods and process conditions are employed in order to remove each of these impurities as discussed in this section.

# 3.2.1. Tar Conversion

Tar can be converted or removed using different processes. Wet gas cleaning has been employed for the removal of tar, using absorption. Absorption of tar using Bio-oil or Bio-diesel, as in the popular OLGA process of ECN [34], has been widely accepted and used. However, tar removal using an absorption and stripping unit can be expensive due to the energy consumption, and material costs. Also, instead of removing the tar in the syngas, it can be converted in order to produce more of the desired products.

For this reason, in this study, it was decided to convert the tar through the use of a catalyst. The most common and effective catalyst used for gasification is dolomite  $(CaMg(CO_3)_2)$  which is a mineral combposed of calcium and magnesium carbonate. Another reason why dolomite was used, was to decompose the ammonia, as explained in the next subsection. In a lot of studies in literature [43], dolomite is first calcined by heating at temperatures above 900°C. Calcined dolomite has been proven to have better catalytic properties, due to the presence of higher surface area. Calcined dolomite is represented by the formula CaO.MgO. In this study calcined dolomite was used to convert the tar into syngas. The amount of dolomite required was taken from [64], which was about 0.0015kg/hr, and it can be regenerated and recycled.

The process of tar conversion was modelled in ASPEN Plus using a stoichiometric reactor at a temperature of 800°C and atmospheric pressure, and was placed right after the CSTR in the gasification section. The idea behind this, was to simulate dolomite as the bed material, instead of corundum, in order to enhance tar conversion. Corundum was used in the gasification model in order to validate the model with experimental results. However, using a catalyst such as dolomite as the bed material would have ensured all tar got converted, and would also eliminate the need for downstream gas cleaning for removal of tar. In this study it was assumed that the dolomite only influences the reaction of tar, and no change in kinetics of other reactions takes place. Also, it was observed that the assumed representative tar component, Phenol, gets almost entirely cracked and reformed into Benzene and Naphthalene in the bedzone. The tar left in the syngas after the original gasification model was only in the form of Benzene. In order to remove the remaining benzene, it was assumed that dolomite only leads to the reaction of benzene, with a conversion of 100%, and not Phenol or Napthalene. The secondary air in the freeboard ensures the remaining Phenol, Napthalene and Benzene get cracked, thus, leaving no tars in the final syngas.

Various mechanisms have been suggested in literature, for how dolomite carries out tar conversion. The most common mechanisms are the reforming of benzene with steam or carbon dioxide. In this study, it was decided to simulate the steam reforming of benzene in the RSTOIC reactor, as elaborated in [64]. The suggested mechanism involves the adsorption of benzene and water on the surface of dolomite where the reaction takes place. The reaction for steam reforming of benzene is shown in equation 3.19.

$$C_6H_6 + 6H_2O \longrightarrow 6CO + 9H_2 \tag{3.19}$$

#### **3.2.2.** Ammonia (*NH*<sub>3</sub>) Conversion

As explained in the previous section,  $NH_3$  was an inert component, that was still present in the syngas exiting the gasifier, and needed to be removed. Dolomite has been proven very effective in converting the ammonia present in syngas. This was another reason for employing dolomite for converting tar, since it could be used for ammonia conversion as well, which reduces the overall cost of the process.

It was decided to carry out the conversion of ammonia in the same RSTOIC reactor as the tar conversion. According to [14], dolomite can effectively convert upto 95% of the ammonia in syngas when operated around a temperature of 800°C. For this reason, it was assumed that 95% of the ammonia gets converted in the reactor. The conversion of ammonia over dolomite takes place according to equation 3.20.

$$2 \operatorname{NH}_3 \longrightarrow \operatorname{N}_2 + 3 \operatorname{H}_2$$
 (3.20)

#### **3.2.3. Hydrogen Sulphide** (*H*<sub>2</sub>*S*) **Removal**

Hydrogen Sulphide is another inert present in syngas that must be removed through a downstream process. The most widely used and effective method to remove  $H_2S$  is using a metal oxide. The most commonly used metal oxide is Zinc Oxide (*ZnO*), due its high efficiency in  $H_2S$  removal, less affinity to form side products and low cost [22]. Other metal oxides often used include copper oxide, manganese oxide, lead oxide, etc. *ZnO* reacts with  $H_2S$  according to the reaction in equation 3.21.

$$ZnO + H_2S \longrightarrow ZnS + H_2O$$
 (3.21)

It was decided to use a stoichiometric reactor to model the reaction. The temperature was set at 400°C and pressure at atmospheric pressure. It was also assumed that all of the  $H_2S$  gets reacted with the ZnO and gets removed from the syngas. The amount of ZnO required for the reaction was determined stoichiometrically to react with all of the  $H_2S$ , and was determined to be 0.003 kg. However, according to literature, ZnO has a maximum loading capacity between 25-40% [22]. For this reason, it was assumed that the required amount of ZnO for complete removal of the  $H_2S$  was 0.01kg.

#### **3.2.4. Hydrochloric Acid** (*HCl*) Removal

HCl is another inert that may be present in syngas, and must be removed for downstream applications. Similar to  $H_2S$  removal, HCl is also removed using ZnO, which uses chemisorption to remove the gas. Other metal oxides often used include calcium oxide, magnesium oxide, etc. ZnO reacts with HCl according to the reaction in equation 3.22 [22].

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$
 (3.22)

Similar to the implementation of  $H_2S$  removal, it was decided to model the above reaction using a stoichiometric reactor. The temperature was set at 125°C and pressure at atmospheric pressure. It was also assumed that all of the HCl gets reacted with the ZnO and gets removed from the syngas. For the biomass used in this study, the ultimate analysis did not indicate the presence of any Chlorine in it. However, it was decided to implement HCl removal as part of the gas cleaning, since other biomass often have small amounts of Chlorine present in them. The amount of ZnO required for the reaction was assumed to be 0.01 kg for the same amount of HCl as the  $H_2S$ , but must be tweeked depending on the amount of HCl present in the syngas.

#### 3.2.5. Gas Cleaning Model Flowsheet



Figure 3.3: Gas Cleaning Model ASPEN Plus Flowsheet

Figure 3.3 shows the ASPEN Plus flowsheet of the entire gasification and gas cleaning model. As explained in section 4.2.1, the tar and ammonia cleaning dolomite reactor was placed right after the CSTR simulating the bedzone. The solid separator following that was to separate the dolomite in order to regenerate and recycle. After the cyclone separator, the desuphurization reactor was placed followed by another solid separator to remove the ZnS and the unreacted ZnO. Since the desulphurization reactor was operated at a higher temperature, the dechlorination reactor was placed after it, following which was another solid separator to remove the  $ZnCl_2$  and the unreacted ZnO. Table 3.5 summarises all the blocks in the gas cleaning model flowsheet.

Block Type	Block Name	Description
JF		<b>F</b>
RSTOIC	CLEAN	This stoichiometric reactor models tar, in the form of benzene, and am-
		monia removal from the syngas. Dolomite catalyses the steam reform-
		ing of benzene and the dissociation of ammonia. The reactor operates
		at 800°C and atmospheric pressure. The fractional conversion of ben-
		zene was assumed to be 100% and that of ammonia to be 95%.
	DESULPH	This stoichiometric reactor models the chemisorption of $H_2S$ from syn-
		gas onto $ZnO$ . The reactor operates at 400°C and atmospheric pres-
		sure. The fractional conversion of $H_2S$ was assumed to be 100%.
	DECHLOR	This stoichiometric reactor models the chemisorption of $H_C l$ from syn-
		gas onto $ZnO$ . The reactor operates at 125°C and atmospheric pres-
		sure. The fractional conversion of <i>HCl</i> was assumed to be 100%.
SEAPARATOR	SEP2	This solid separator was used to separate the dolomite from the prod-
		uct gas. It was assumed that 100% of the dolomite is removed from the
		outgoing gas.
	SEP4	This solid separator was used to separate the $ZnS$ and the unreacted
		ZnO from the product gas. It was assumed that 100% of the solids were
		removed from the outgoing gas.
	SEP5	This solid separator was used to separate the $ZnCl_2$ and the unreacted
		ZnO from the product gas. It was assumed that 100% of the solids were
		removed from the outgoing gas.

Table 3.5: Summary of all Blocks in the Gas Cleaning Model Flowhseet

# 3.3. Case Study 1: Synthetic Natural Gas

This study considered the production of two final downstream products. The first product considered was Synthetic Natural Gas (SNG). SNG is an essential part of the European energy infrastructure, and is used for a number of purposes. Natural gas is used in the EU in gas fired power plants, for domestic heating, etc. Another advantage of choosing SNG as the final product, is that it can directly be fed into the existing natural gas pipelines. In the coming years, the supply of natural gas is going to be more important as the demand will continue to go up, due to the phasing out of coal plants. Even the domestic production of natural gas is expected to decline a little in the coming years, thus, increasing the dependence on imports [55]. For these reasons, the production of synthetic natural gas from syngas, can potentially be a good decision.

## **3.3.1. Methanation Process**

Clean syngas mainly consists of carbon monoxide, carbon dioxide, methane, hydrogen, water and nitrogen. In order to increase the concentration of methane, the CO and  $CO_2$  need to be converted into methane. The reactions involved in the methanation of the two gases are shown in equations 3.23 and 3.24. However, due to the presence of steam and the fact that most catalysts which catalyse the methanation of CO and  $CO_2$  also catalyse other reactions, one side reaction which takes place in the reactor is the Water Gas Shift reaction as shown in equation 3.25.

$$CO + 3H_2 \longleftrightarrow CH_4 + H_2O$$
 (3.23)

$$CO_2 + 4H_2 \longleftrightarrow CH_4 + 2H_2O$$
 (3.24)

$$CO + H_2O \longleftrightarrow CO_2 + H_2$$
 (3.25)

Various studies have been done to determine the kinetics of the two reactions using different catalysts and process conditions. The kinetics used in this study for the three reactions, are all in the form of the Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics, and were taken from literature. The methanation reactions are both catalysed using a nickel based catalyst. The kinetic parameters for the *CO* methanation and the water gas shift reaction were taken from [67, 74], and that for  $CO_2$  methanation were taken from [3, 74]. It was also noted that both sets of kinetics were applicable for a range of temperatures. The kinetics are listed in Appendix E.

It was decided to model the above reactions in an RPLUG reactor, in the presence of a catalyst, since all the reactants and products are in the gaseous phase, and the RPLUG reactor was assumed to model a fluidized bed reactor, which is one of the types of reactors commonly used for methanation. The reactor was made to operate at a temperature of  $550^{\circ}$ C and atmospheric pressure [73]. The dimensions of the reactor were decided using a trial and error method, by reducing the dimensions until the same conversion was achieved. The final dimensions of length and diameter were both 100mm. A similar approach was used to determine the amount of catalyst required in the reactor to ensure the maximum conversion of CO and  $CO_2$ . The final catalyst loading was determined to 0.01kg. The bed voidage was set at 0.46, which is what most commercial catalyst configurations employ [73].

One observation made was that the amount of hydrogen generated in the gasification process, and present in the syngas, was insufficient to completely carry out the methanation of CO and  $CO_2$ . For this reason it was decided to input hydrogen into the reactor using a supplemetary stream. The mass flow rate of the hydrogen was determined through a trial and error method, by increasing the hydrogen flow rate until all the CO and  $CO_2$  was converted. The hydrogen flow rate was determined to be 1.43kg/hr (202.63MJ/hr). Other studies have also shown the need for a supplementary hydrogen stream to carry out the complete methanation of CO and  $CO_2$  [73].

#### 3.3.2. Water Removal

After the methanation process, the product gas consisted of methane, nitrogen and water. The water must be removed before the methane can be used for downstream purposes. It was decided to use a flash drum to remove the water. The gas from the methanation reactor enters the flash drum, where it is quickly quenched to a temperature of 20°C and remains at atmospheric pressure. This sudden quenching, condenses most of the steam in the gas, and is then removed.

#### 3.3.3. SNG Model Flowsheet



Figure 3.4: Synthetic Natural Gas Model ASPEN Plus Flowsheet

Figure 3.4 shows the ASPEN Plus flowsheet of the entire gasification, gas cleaning and SNG production model. The hydrogen stream is preheated using the heat from the stream exiting the desulphurization reactor. The preheated hydrogen is mixed with the product gas exiting the gas cleaning section in a mixer and enters a heat exchanger where the gas is further preheated before entering the methanation reactor where the CO and  $CO_2$  are converted into  $CH_4$ . The product gas from the methanation reactor then enters the flash drum, where the water is removed to yield a final product stream consisting of SNG and Nitrogen. The Nitrogen separation from SNG is a potentially difficult process, due to the similarity in properties. However, the said separation can be carried out using molecular sieves and pressure swing adsorption [18], but has not been implemented in this study. The amount of Nitrogen to be removed from the final product gas would depend on the application for which it is used. If it is injected into the natural gas pipeline in the EU, it can contain upto 15-20% Nitrogen [2]. The water exiting the flash drum can also be easily recycled to create steam for the gasification process. However, ASPEN Plus requires the recycle stream to be identical, but in this model the condensation and separation of water results in very small (ppm levels) amounts of methane and nitrogen to be dissolved in the water, due to which ASPEN Plus does not allow recycling. Table 3.6 summarises all the blocks in the Synthesis Gas model flowsheet.

Block Type	Block Name	Description
MIXER	MIX2	This mixer models the mixing of the supplementary Hydrogen stream
		with the product gas stream exiting the gas cleaning section, which is
		then directed to the methanation reactor.
RPLUG	METH	This reactor models the catalytic methanation reactions of <i>CO</i> and
		<i>CO</i> <sub>2</sub> , and also the side reaction water gas shift. The reactor operates
		at a temperature of 550°C and atmospheric pressure. The catalyst
		loading was 0.01kg and bed voidage was 0.46. The hydrogen supplied
		was sufficient to convert all of the $CO$ and $CO_2$ into $CH_4$ .
FLASH2	H2OREM	This flash drum quenches the product gas to 20°C in order to remove
		the water from the desired SNG.
HEAT EXCHANGER	HX1	This heat exchanger was used in order to cool down the hot gas com-
		ing from the gasifier at a temperature of 800°C to 400°C, and to heat
		up the agents going to the methanation reactor from a temperature of
		207.1°C to 518.7°C. The exchanger operates in a counter-current op-
		eration, and was modelled using the Shortcut method and in Design
		mode.
	HX2	This heat exchanger was used in order to cool down the hot gas com-
		ing from the desulphurization reactor at a temperature of 400°C to
		225°C, and to heat up the supplementary Hydrogen stream going to
		the methanation reactor from a temperature of 25°C to 355.5°C. The
		exchanger operates in a counter-current operation, and was mod-
		elled using the Shortcut method and in Design mode.

#### Table 3.6: Summary of all Blocks in the SNG Model Flowhseet

# 3.4. Case Study 2: Hydrogen

This study considered the production of two final downstream products. The second product considered was Hydrogen. Hydrogen is an extremely important chemical, which has a multitude of applications. Hydrogen is considered to be the primary method of long-term energy storage, and also for energy transportation as an energy carrier, in the future. Hydrogen is also considered as a renewable fuel for future modes of transport, through the use of fuel cells, thereby reducing the dependence on fossil fuels. Hydrogen as a fuel is also environmentally favourable due to the production of no harmful pollutants, thus, making it extremely attractive as a future resource. However, the current production of Hydrogen is still low, thus, making it a potentially good choice for a product made from syngas.

After the syngas has been cleaned, it consists of CO,  $CO_2$ ,  $H_2$ ,  $CH_4$ ,  $H_2O$  and  $N_2$ . Off these, the CO and  $CH_4$  can be reformed using steam to yield Hydrogen and  $CO_2$ . However, a large amount of  $CO_2$  is left behind which must be removed. The other components which will have to be removed, similar to the SNG model are Nitrogen and Water.

#### 3.4.1. Methane Reforming

The methane generated during gasification, even though a small amount, can be converted using steam reforming to form Hydrogen. The reaction involved in the steam reforming of  $CH_4$  is shown in equation 3.26. The reaction itself takes place in the presence of a catalyst, which is a Nickel based catalyst, as used in industrial settings [40]. The kinetics considered for the reaction in this study, were in the form of Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics, and were taken from literature [40, 65]. The Kinetic parameters for the reaction are listed in Appendix F.

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2$$
 (3.26)

It was decided to model the above reaction in an RPLUG reactor, in the presence of a catalyst. The reactor

was made to operate at a temperature of 700°C and atmospheric pressure [40]. The dimensions of the reactor were decided using a trial and error method, by reducing the dimensions until the same conversion was achieved. The final dimensions of length and diameter were both 100mm. A similar approach was used to determine the amount of catalyst required in the reactor to ensure the maximum conversion of *CO* and *CO*<sub>2</sub>. The final catalyst loading was determined to 0.01kg. The bed voidage was assumed to be 0.5, similar to the value used for the methanation reactor in the previous section.

#### 3.4.2. Water Gas Shift

After the Methane Reforming reactor, and combined with the product from the gasifier, there is a fair bit of *CO* present in the gas, which needs to be converted to Hydrogen. This is done using the water gas shift reaction, which is shown in equation 3.27. The reaction also takes place in the presence of a catalyst, which is a Nickel based catalyst. The kinetics considered for the reaction in this study, were in the form of Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics, and were taken from literature [67, 74]. The Kinetic parameters for the reaction are listed in Appendix E.

$$CO + H_2O \longrightarrow CO_2 + H_2 \tag{3.27}$$

It was decided to model the above reaction in an RPLUG reactor, in the presence of a catalyst. The reactor was made to operate at a temperature of 180°C and atmospheric pressure [40]. The dimensions of the reactor were decided using the same approach as for the methane reforming reactor, and were finalised to be a length and diameter of 100mm. The same approach was used to determine the amount of catalyst required in the reactor and the final catalyst loading was determined to 0.01kg. The bed voidage was assumed to be 0.5, similar to the value used for the methane reforming reactor in the previous section.

#### 3.4.3. Carbon Dioxide Removal

Carbon dioxide is an undesired product present in syngas, that only lowers the quality of the gas, and must thus, be removed. After the methane reforming and water gas shift reactors, the product gas contains a large amount of  $CO_2$ , which needs to be removed. Various methods have been described in literature for the removal or separation of  $CO_2$  such as pressure swing adsorption and solvent based absorption. In this study,  $CO_2$  capture using Calcium Oxide (*CaO*) was considered. *CaO* is an inexpensive and commonly available raw material making it suitable for this application[38]. *CaO* has also been used in conjunction with the gas gasification process, due to its tar cracking properties, and also to simultaneously capture  $CO_2$  [24]. The *CaO* can also be recycled to maximise its usage. The reaction involved in the capture of  $CO_2$  using *CaO* is shown in equation 3.28.

$$CaO + CO_2 \longrightarrow CaCO_3$$
 (3.28)

It was decided to model the above reaction in a stoichiometric RSTOIC reactor. The reactor was made to operate at a temperature of 650°C and atmospheric pressure. It was assumed that all of the  $CO_2$  gets removed from the gas with the CaO, and the thus formed  $CaCO_3$  is removed using an ideal solid separator which models a cyclone separator. In order to achieve this, the amount of CaO required was determined stoichiometrically to be 16.05kg/hr. Even though this is a fairly large amount of CaO, the entire  $CaCO_3$  generated can be easily regenerated back to CaO by calcining at a high temperature of around 900°C, and then recycled back to the reactor [24]. This was not modelled in this study though.

#### 3.4.4. Water Removal

After the carbon dioxide has been removed from the gas, the product gas consisted of hydrogen, nitrogen and water. The water must be removed before the hydrogen can be used for downstream purposes. It was decided to use a flash drum to remove the water, similar to the SNG model. The gas from the carbon dioxide capture reactor enters the flash drum, where it is quickly quenched to a temperature of 20°C and remains at atmospheric pressure. This sudden quenching, condenses most of the steam in the gas, and is then removed.

#### 3.4.5. Hydrogen Model Flowsheet



Figure 3.5: Hydrogen Model ASPEN Plus Flowsheet

Figure 3.5 shows the ASPEN Plus flowsheet of the entire gasification, gas cleaning and Hydrogen production model. The gas exiting the gas cleaning section is preheated before entering the Methane reforming reactor, where steam reforming of  $CH_4$  takes place to form CO. The gas then enters a heat exchanger where it is cooled down before entering the Water Gas Shift reactor, where the CO is converted to  $H_2$  and  $CO_2$ . The gas exiting the water gas shift reactor is then heated up using the product gas stream exiting the gasifier section, before entering the  $CO_2$  removal reactor, where the  $CO_2$  is made to react with CaO to form  $CaCO_3$ . The  $CaCO_3$  is then removed from the product gas in a solid separator, after which the gas enters a flash drum, where the water is removed to yield a final product stream consisting of Hydrogen and Nitrogen. Nitrogen separation from Hydrogen is a difficult process, and often expensive and energy intensive. However, some processes available in literature effectively separate the two gases, using membrane separation technology [26]. This has, however, not been implemented in the model in this study. The amount of water exiting the flash drum is relatively smaller, compared to the SNG model. However, it can be recycled to form part of the steam required for the gasification process. ASPEN Plus does not allow the recycle of this water because of the presence of very small amounts (ppm levels) of hydrogen and nitrogen dissolved in the water, and so was not implemented in this study. Table 3.7 summarises all the blocks in the Synthesis Gas model flowsheet.

Block Type	Block Name	Description
RPLUG	METH-REF	This reactor models the catalytic steam reforming of $CH_4$ to form $H_2$ and $CO$ . The reactor operates at a temperature of 700°C and atmospheric pressure. The catalyst loading was 0.01kg and bed voidage was 0.5
	WGS	This reactor models the catalytic water gas shift reaction to convert the $CO$ into $H_2$ and $CO_2$ . The reactor operates at a temperature of 180°C and atmospheric pressure. The catalyst loading was 0.01kg and bed voidage was 0.5.
RSTOIC	CO2-REM	This reactor models the removal of $CO_2$ from the product gas using <i>CaO</i> . The reactor operates at a temperature of 650°C and atmospheric pressure. The fractional conversion of <i>HCl</i> was assumed to be 100%.
SEPARATOR	SEP6	This solid separator was used to separate the $CaCO_3$ and the unre- acted $CaO$ from the product gas. It was assumed that 100% of the solids were removed from the outgoing gas.
FLASH2	H2OREM	This flash drum quenches the product gas to 20°C in order to remove the water from the desired Hydrogen gas.
COOLER	B13	This cooler was employed to cool down the gas coming from the desulphurization reactor from a temperature of 400°C to 125°C.
HEAT EXCHANGER	HX1	This heat exchanger was used in order to cool down the hot gas com- ing from the gasifier at a temperature of 800°C to 400°C, and to heat up the gas exiting the water gas shift reactor from a temperature of 180°C to 616.9°C. The exchanger operates in a counter-current op- eration, and was modelled using the Shortcut method and in Design mode.
	HX2	This heat exchanger was used in order to cool down the hot gas com- ing from the methane reforming reactor at a temperature of 700°C to 180°C, and to heat up the product gas going to the methane reform- ing reactor from a temperature of 125°C to 670.9°C. The exchanger operates in a counter-current operation, and was modelled using the Shortcut method and in Design mode.

Table 3.7: Summary of all Blocks in the Hydrogen Model Flowhseet

# 4

# **Results and Discussion**

This chapter discusses the validation of the gasification model with the experimental results. It then elucidates the main results derived from the models. The chapter also covers the mass and heat balance of the models. Finally, a sensitivity analysis was done in order to observe the effects various parameters have on the results of the model.

# 4.1. Gasification Model Validation

The gasification model explained in the previous chapter, was implemented for wood, for which the experimental data from the gasification experiments done on the IHBFBSR, was available. The operating parameters for which the model was validated are shown in table 4.1.

Parameter	Value	Unit
Reactor Temperature	Bedzone - 711.3	°C
	Freeboard 1 - 783	
	Freeboard 2 - 863	
Reactor Pressure	1	atm
Biomass Flow rate	8	kg/hr
Primary Air Flow Rate	1.9	kg/hr
Primary Nitrogen Flow Rate	4.81	kg/hr
Steam Flow Rate	8.7	kg/hr
Secondary Air Flow Rate	4	kg/hr
Secondary Nitrogen Flow Rate	0.7	kg/hr
Equivalence Ratio	0.04	-
Steam to Biomass Ratio	1.2	-

Table 4.1: Operating Parameters Considered for the Validation of the Gasification Model

## 4.1.1. Primary Component Volume Percentages

Figure 4.1 shows the yields of the primary components, namely CO,  $CO_2$ ,  $H_2$  and  $CH_4$ , from both the model and the experiments. The values for the primary components are presented on a dry nitrogen free basis, for ease of comparison, and were calculated by normalizing the sum of the four components to 100%. As can be seen from the figure, the model is validated by the experimental values fairly well. The CO and  $CO_2$  are slightly overestimated by the model, while the  $H_2$  is underestimated. The amount of  $CH_4$  for both the model and experiment are almost the same. The maximum absolute error observed for the primary components, on the basis of volume percentage, was 4.8 for Hydrogen. The relative errors for CO,  $CO_2$ ,  $H_2$  and  $CH_4$  are -17.8, -5.6, 10.9 and 3.05 respectively. However, considering that there may be some experimental errors, all



Figure 4.1: Primary Component Volume Percentages for Gasification of Wood for Model Validation

values are within a reasonable margin. Even though different models in literature have different operating conditions and type of biomass used, it has been noted that the errors for most are between 10-70%. The relative errors for the primary components observed in this study are all lower than the average value of errors observed in different studies in literature [80]. These errors may be due to various reasons, such as differences in conditions under which the kinetics taken from literature were determined, measurement errors, overlap of the pyrolysis and gasification processes, mass balance errors from experiments etc.

#### 4.1.2. Nitrogen, Water and Tar Volume Percentages

Figure 4.2 shows the yields of  $N_2$ ,  $H_2O$  and Tars from both the model and the experiments, on a logarithmic scale, in order to present all three components on the same graph. Nitrogen has been presented on a dry tar free basis for the ease of comparison, while the tar has been presented on a dry basis. Water is presented on the raw basis. The estimate of Nitrogen from the model is lower than that observed in the experiment, with a relative error of 16.85%. This underestimation is probably because the total gas yield of the primary components from the model is higher than that observed in the experiment.

The biggest deviation off all components is observed for water. Water is underestimated in the model quite a bit, with a relative error of 59.53%. There may be a few reasons for this underestimation. Firstly, the amount of water calculated from the experiment is probably overestimated. Experimental determination of water is potentially difficult, which may cause such deviations. It was also observed that the hydrogen and oxygen balances from the experiments were 57% and 60% respectively, which might also be a reason for this deviation. Secondly, the determination of pyrolytic water in this study was done using an emperical correlation from literature, which is bound to be different from the actual water produced in the gasifier considered in this study, are more influential than what happens physically.

Finally, the tar components estimated in the model, are only slightly higher than what is observed in the experiment, but are in the same range. The calculated relative error between the model and experiment is 100%, but the absolute error is only -0.11. In actuality, the relative error appears so big because of the extremely small amounts of tar present in the gas. The tar from the model is 0.22%, while that determined from the experiment is 0.11%, on a dry basis. From the model it was observed that all of the Phenol gets cracked



Figure 4.2: Nitrogen, Water and Tar Volume Percentages for Gasification of Wood for Model Validation

or reformed, mostly in the bedzone, into Naphthalene and Benzene. The Naphthalene also gets oxidized or cracked in its entirety. The tar left in the gas is in the form of Benzene. Even though, by definition, Benzene is not considered tar, it is still counted as a tar component in a lot of studies, since it is a product of the decomposition and cracking of several other tar compounds [66]. It should also be noted that in this study, Phenol was the only tar component used to represent the tar fraction, which is possibly why the tar yield is so well estimated by the model. However, in reality, many tar components exist in the tar fraction, thereby making it extremely difficult to accurately predict and simulate the composition of the tar and subsequently the tar yield.

#### 4.1.3. Carbon Conversion, Cold Gas Efficiency and Overall Efficiency

Carbon Conversion, Cold Gas Efficiency and Overall Efficiency are three important parameters to judge the efficiency of the model. The Carbon Conversion is calculated using the char residue left in the product gas, and the amount of carbon present in the feed, as shown in equation 4.1. Cold Gas Efficiency is calculated using the flow rate and the Lower Heating Value (LHV) of the product gas and the biomass feed, ashown in equation 4.3. The LHV of the gas is calculated using equation 4.2 [76, 80]. The overall efficiency is calculated in a similar way, except the denominator also includes the energy input to the preheaters and the gasifier, as shown in equation 4.4. The heat input to both the preheaters and the gasifier were known from the experiment, and were 10.5kW and 32kW, respectively.

$$CC(\%) = 1 - \frac{m_{C,residue}}{m_{C,feed}}$$
(4.1)

$$LHV(MJ/Nm^{3}) = CO \cdot 12.636 + H_{2} \cdot 10.798 + CH_{4} \cdot 35.818$$
(4.2)

$$CGE(\%) = \frac{m_{prodgas} \cdot LHV_{prodgas}}{m_{biomass} \cdot biomass}$$
(4.3)

$$OE(\%) = \frac{m_{prodgas} \cdot LHV_{prodgas}}{m_{biomass} \cdot biomass + P_{preheaters} + P_{gasifier}}$$
(4.4)



Figure 4.3: Carbon Coversion, Cold Gas Efficiency and Overall Efficiency for Gasification of Wood for Model Validation

Figure 4.3 shows the Carbon Conversion and the Cold Gas Efficiency of both the model and the experiment. As can be seen in the figure, the carbon conversion of the model is in very good agreement with that from the experiment, with an absolute error of 0.82. The relative error between the two is 0.98%. The Cold Gas efficiency, on the other hand, for the model is lower than that of the experiment, with an absolute error of 17.33, and relative error of 31.33%. The Overall efficiency is also underestimated for the model, with an absolute error of 7.13, and relative error of 27.11%. This underestimation is due to a lower flow rate of the product gases, and not because of the LHV. The LHV of the product gas was calculated to be  $4.64 MJ/Nm^3$ , which is very close to that calculated for the experiment which is  $4.86 MJ/Nm^3$ . The calculations for the estimation of the product gas yield for the experiments were made assuming the closure of the N2 balance of the experiments. That could lead to an overestimation of the product gas from the experiments, which would also explain the discrepancy.

# 4.2. Synthetic Natural Gas Model Results

The SNG model results displayed in this section was implemented for wood, as explained in the previous chapter. The operating parameters for the gasification section were the same as shown in table 4.1. The operating parameters for the SNG section are shown in table 4.2.

Table 4.2: Operating Parameters Considered for the SNG Model

Parameter	Value	Unit
Methanation Reactor Temperature	550	°C
Methanation Reactor Pressure	1	atm
Catalyst Loading	0.01	kg/hr
Bed Voidage	0.46	-
Supplementary Hydrogen Flow Rate	1.43	kg/hr



Figure 4.4: Final SNG Stream Composition

Figure 4.4 shows the composition of the final SNG product stream from the model. As can be seen from the figure, all the *CO* and *CO*2 gets converted in the reactor to form  $CH_4$ . Majority of the water present in the gas is removed in the flash drum, the remainder forming just 0.7% of the product gas. With the Nitrogen included, the amount of  $CH_4$  present in the gas formed 42% of the total, with the remaining 57% being Nitrogen. However, once the Nitrogen is removed from the gas using techniques mentioned in the previous chapter, the gas would be comprised almost entirely of SNG. According to [2], the gas consumed in Europe should contain more than 80% methane, with the other being light hydrocarbons, carbon dioxide, nitrogen, etc. Thus, once the nitrogen is removed from the product gas in this work, the gas should be fit for consumption.





Figure 4.5 shows the cold gas efficiency and the overall efficiency of the SNG process model. As can be seen from the figure, both the efficiencies of the SNG model are higher than that of the gasification model. This can be attributed to two reasons, the first being that no external energy was required to be supplied to the gas cleaning operations and the methanation reactor, due to all of them being exothermic in nature. The second reason is that the final gas composition did not have any other components, such as  $CO_2$  (apart from  $N_2$ ), that reduced the heating value of the product gas. The LHV of the product gas was calculated to be  $15MJ/Nm^3$ , which is significantly higher than the LHV of the product gas from the gasification process, which was around  $4.64 MJ/Nm^3$ . Similar values for the CGE and OE were also observed in other studies for gasification and methanation of coal and biomass [10].

# 4.3. Hydrogen Model Results

The Hydrogen model results displayed in this section was implemented for wood, as explained in the previous chapter. The operating parameters for the gasification section were the same as shown in table 4.1. The operating parameters for the Hydrogen section are shown in table 4.3.

Parameter	Value	Unit
Methane Reforming Reactor Temperature	700	°C
Methane Reforming Reactor Pressure	1	atm
Water Gas Shift Reactor Temperature	180	°C
Water Gas Shift Reactor Pressure	1	atm
Catalyst Loading	0.01	kg/hr
Bed Voidage	0.5	-
Carbon Dioxide Removal Reactor Temperature	700	°C
Carbon Dioxide Removal Reactor Pressure	1	atm
Calcium Oxide Flow Rate	16.05	kg/hr

Table 4.3: Operating Parameters Considered for the Hydrogen Model



Figure 4.6: Final Hydrogen Stream Composition

Figure 4.6 shows the composition of the final Hydrogen product stream from the model. As can be seen from the figure, all of the  $CH_4$  and nearly all of the CO in the syngas from the gasification process were converted to form  $H_2$  and  $CO_2$ . The reaction of  $CO_2$  with the CaO also ensured that all of the  $CO_2$  was removed from the product gas. Majority of the water present in the gas is removed in the flash drum, the remainder forming just 0.6% of the product gas. With the Nitrogen included, the amount of  $H_2$  present in the gas formed a little more than 53% of the total, with the remaining 45% being Nitrogen. However, once the Nitrogen is removed from the gas using techniques mentioned in the previous chapter, the gas would be comprised almost entirely of Hydrogen. According to [31], for hydrogen to be used in a Proton Exchange Membrane (PEM) type fuel cell, which is a popular application for hydrogen to produce energy, the amount of CO in the gas must be less than 20 ppm, as CO is a significant poison to the process. Thus, for the hydrogen to be successfully utilized, the CO needs to be removed. This may be achieved by employing Pressure Swing Adsorption (PSA) which has been reported to be effective in achieving a hydrogen stream with 99.9999% hydrogen [79]. However, for other applications in different industries, the hydrogen product stream from the model, after Nitrogen removal, should be sufficient.

Figure 4.7 shows the cold gas efficiency and the overall efficiency of the Hydrogen process model. As can be seen fro the figure, the efficiency of the entire hydrogen model is very similar to the gasification model, despite the fact that majority of the gas is composed of hydrogen. This is because some external heat, roughly 3kW was required to be supplied to the methane reforming reactor, and was included in the calculation of the overall efficiency. The LHV of the product gas was calculated to be  $5.82MJ/Nm^3$ , which is higher than the LHV of the product gas from the gasification process, which was around  $4.64 MJ/Nm^3$ . Similar values for efficiency of a gasification and hydrogen production model have been reported in literature [20].



Figure 4.7: Cold Gas Effiency (%) and Overall Efficiency (%) of the Hydrogen Model

# 4.4. Sensitivity Analysis

Sensitivity analysis is an important tool to analyse the effects of various parameters on the performance of the model. In this study, the sensitivity analysis was performed by varying two parameters and studying their effects on the gasification process, and also the SNG and Hydrogen processes. The chosen parameters were Secondary Air and Steam to Biomass Ratio. The influence of Primary Air was not considered as it greatly influences the temperature of the bedzone and the freeboard, which is only determined experimentally.

#### 4.4.1. Variation of Secondary Air

The secondary air in the model was varied from a value of 0kg/hr to 8kg/hr. The value of primary air was kept constant at 1.9kg/hr, and so was the steam flow rate at 8.7kg/hr. All other operating parameters as mentioned in table 4.1 were unchanged. It was assumed that since the secondary air only enters in the top half of the freeboard, its influence on local temperature was negligible. Also, due to the fact that heat is mainly provided from the burners, which operate at a certain set point, the increase of the amount of air does not have much of an effect on the local temperature. The temperature in the gasifier was set for a corresponding value of secondary air of 4 kg/hr, which is the mean value of the secondary air variation values. All values for component yields in the graphs that follow, were presented on an as received or raw gas basis, for ease of comparison.

Figure 4.8 shows the impact of variation of secondary air on the product gas component yields from the gasification model. Increasing the flow of secondary air in the gasifier leads to a greater concentration of oxygen and nitrogen. The decreasing trend of CO and  $H_2$  can be explained by the fact more oxidation reactions take place leading to the production of  $CO_2$  and  $H_2O$  respectively. However, the yields of  $CO_2$  and  $H_2O$  in the gas remain more or less at the same level. This can be explained due to the relatively same levels of increase of dilution of the gas with  $N_2$  and the corresponding increase of  $CO_2$  and  $H_2O$  due to the increasing oxidation reactions. The increase of  $CO_2$  and  $H_2O$  would be observed on a dry nitrogen free basis. The yield of  $CH_4$  was also observed to show a decreasing trend which can be explained by the increase of oxidation reaction and dilution with  $N_2$ . The main reason behind injecting secondary air into the gasifier was to promote tar cracking. However, the tar reduced from 0.3% at 0kg/hr of secondary air to 0.2% at 2kg/hr and constant thereafter.



Figure 4.8: Impact of Variation of Secondary Air on the Product Gas Component Yields from the Gasification Model

Figure 4.9 shows the impact of variation of secondary air on the Carbon Conversion, Cold Gas Efficiency and Overall Efficiency of the Gasification Model. As can be seen from the figure, the carbon conversion efficiency stays almost the same as the secondary air is increased. However, the carbon conversion should increase at least a little with increasing secondary air due to the occurrence of more oxidation reaction, as is observed for the 6kg/hr secondary air. The Cold Gas Efficiency and the Overall Efficiency are both observed to show a decreasing trend with an increase in secondary air. This is because of the decreasing levels of *CO* and  $H_2$ , which contribute to most of the heating value of the gas, and also because of increasing flow of  $N_2$  in the gas. The LHV of the product gas was found to decrease from a value of  $6MJ/Nm^3$  at 0kg/hr to  $3.6MJ/Nm^3$  at 8kg/hr. It was observed in the experiments, that the LHV of the product gas decreased from 6.4 at 0kg/hr to  $4MJ/Nm^3$  at 8kg/hr, which is similar to the values observed from the model.

For the gasification model, it can be concluded that a low value of secondary air of 2kg/hr would be sufficient to reduce the tar concentration as much as it reduces. Beyond this point the quality of the product gas reduces dramatically, with significant dilution with nitrogen which would have to removed for downstream applications. The efficiency of the process also reduces significantly which makes it much less attractive as a process. Similar results were also obtained in experimental demonstrations in literature [35].

Figure 4.10 shows the impact of variation of secondary air on the product gas component yields from the SNG model. The sensitivity analysis was performed using the operating parameters as mentioned in table 4.2. As can be seen from the figure, increasing the secondary air leads to significant dilution of the gas with  $N_2$ , which will eventually have to be removed. Because of the increase in  $N_2$ , the concentration of  $CH_4$  in the product gas decreases, as the amount of secondary air increases. It was also observed that for secondary air upto 4kg/hr all of the CO and  $CO_2$  in the gas undergo methanation to form  $CH_4$ . Also there is a greater amount of  $H_2$  in the product gas from gasification which reduces the amount of supplementary  $H_2$  required for the complete methanation of CO and  $CO_2$ , as is justified by the downward trend of  $H_2$  in the gas from 0kg/hr to 4kg/hr of secondary air. However, for secondary air values of 6kg/hr and 8kg/hr, the amount of CO and  $CO_2$  in the gas little, indicating the need for more supplementary hydrogen to ensure complete methanation of CO and  $CO_2$ . The amount of water in the gas was constant at 0.7%.



Figure 4.9: Impact of Variation of Secondary Air on the Carbon Conversion, Cold Gas Efficiency and Overall Efficiency of the Gasification Model



Figure 4.11: Impact of Variation of Secondary Air on the Cold Gas Efficiency and Overall Efficiency of the SNG Model

Figure 4.11 shows the impact of variation of secondary air on the Cold Gas Efficiency and Overall Efficiency of the SNG Model. As can be seen from the figure, an increase in secondary air from 0kg/hr to 2kg/hr leads to a slight increase in efficiency. This is probably because of the fact that the excess  $CO_2$  produced from the oxidation reactions in the gasifier also undergo methanation, thereby increasing the flow rate of  $CH_4$ , which is relatively more than the increase in flow of  $N_2$ . As the secondary air was increased further from 4kg/hr to 8kg/hr, a decreasing trend for the efficiencies was observed, which was due to the falling heating value of the gas. The LHV of the product gas was found to decrease from a value of  $16.9MJ/Nm^3$  at 0kg/hr to  $12.3MJ/Nm^3$  at 8kg/hr.



Figure 4.10: Impact of Variation of Secondary Air on the Product Gas Component Yields from the SNG Model

For the SNG model, it can be concluded that a value of secondary air more than 2kg/hr would not be suitable. The process yields the maximum  $CH_4$  at 2kg/hr, and also has the highest efficiency. Beyond this point, the gas is greatly diluted with  $N_2$ , which will require more energy and resources to remove. The efficiency of the process is also reduced significantly making it less viable.



Figure 4.12: Impact of Variation of Secondary Air on the Product Gas Component Yields from the Hydrogen Model

Figure 4.12 shows the impact of variation of secondary air on the product gas component yields from the Hydrogen model. The sensitivity analysis was performed using the operating parameters as mentioned in table

4.3. As can be seen from the figure, increasing the amount of secondary air led to an increase in the concentration of  $N_2$ , and a consequent decrease in the concentration of  $H_2$  in the product gas. It was also observed that the amount of *CO* in the gas also reduced marginally from 1% at 0kg/hr to 0.2% at 8kg/hr. This decrease is mostly probably due to the dilution of the gas with  $N_2$  and less because of an increase in *CO* conversion in the water gas shift reactor. Another observation made was that the amount of  $CO_2$  in the gas marginally increased from 0% at 4kg/hr to 0.3% at 8kg/hr, indicating the need for more *CaO* in the carbon dioxide removal reactor. The amount of water in the product gas was constant at 0.6%.



Figure 4.13: Impact of Variation of Secondary Air on the Cold Gas Efficiency and Overall Efficiency of the Hydrogen Model

Figure 4.13 shows the impact of variation of secondary air on the Cold Gas Efficiency and Overall Efficiency of the Hydrogen Model. As can be seen from the figure, both the efficiencies follow a decreasing trend as the secondary air was increased. The decreasing efficiency can be attributed to the dilution of the product gas with  $N_2$ , resulting in a fall in the heating vale of the gas. The LHV of the product gas was found to decrease from a value of  $6.8MJ/Nm^3$  at 0kg/hr to  $4.6MJ/Nm^3$  at 8kg/hr. The reason for the slight increase in efficiency from 6kg/hr to 8kg/hr could not be determined exactly, but might possibly be due to the increase in flow rate of the product gas. For the hydrogen model as well, it can be concluded that a lower amount of secondary air is favourable to obtain a higher concentration of hydrogen in the product gas, and also higher efficiencies from the process. All the results for the sensitivity analysis of secondary air are shown in Appendix G.

#### 4.4.2. Variation of Steam to Biomass Ratio

The steam to biomass ratio in the model was varied from a value of 0.6 to 1.8, which corresponds to a steam flow rate of 4.36kg/hr to 13.96kg/hr respectively. The steam to biomass ratio was calculated by taking into account the moisture content in the biomass. The value of primary air was kept constant at 1.9kg/hr, and so was the secondary air at 4kg/hr. All other operating parameters as mentioned in table 4.1 were unchanged. All values for component yields in the graphs that follow, were presented on an as received or raw gas basis, for ease of comparison.



Figure 4.14: Impact of Variation of Steam to Biomass Ratio on the Product Gas Component Yields from the Gasification Model

Figure 4.14 shows the impact of variation of steam to biomass ratio on the product gas component yields from the gasification model. As can be seen from the figure, increasing the flow rate of steam entering the gasifier leads to an increase in the amount of the water content in the final product gas. This increase indicates that the amount of steam being fed to the reactor is more than what is being consumed for the reforming reactions. The figure also shows that the concentration of *CO* in the gas decreases and that of  $H_2$  and  $CO_2$ increases as the steam to biomass ratio increases. This is similar to what has been observed in other studies as well [36].  $CH_4$  remains more or less constant with increasing steam to biomass ratio. The decrease in *CO* and increase in  $H_2$  and  $CO_2$  can be explained by the possible occurrence of more number of reforming reactions, in particular water gas shift reaction. However, the stable nature of  $CH_4$  was not expected, since other studies report a decreasing trend of  $CH_4$  as well [36]. It is possible that the methane reforming reaction reached an equilibrium, which would explain the stability of the  $CH_4$  concentration in the product gas. Due to the increase in steam flow rate, the concentration of  $N_2$  in the gas decreases considerably as the steam to biomass ratio increases. The amount of tar in the gas also decreases from 0.3% at 0.6 to 0.1% at 1.8 steam to biomass ratio. This could be due to a greater number of reforming reactions taking place in the gasifier, or due to the dilution of the gas with  $H_2O$ .



Figure 4.15: Impact of Variation of Steam to Biomass Ratio on the Carbon Conversion, Cold Gas Efficiency and Overall Efficiency of the Gasification Model

Figure 4.15 shows the impact of variation of steam to biomass ratio on the Carbon Conversion, Cold Gas Efficiency and Overall Efficiency of the Gasification Model. As can be seen from the figure, the carbon conversion efficiency increases with an increase in the steam to biomass ratio. This is due to more char getting gasified due to the extra steam supplied to the gasifier. The cold gas efficiency and the overall efficiency were also observed to increase with an increase in steam to biomass ratio. This increase can be attributed to the increase in flow rate of the product gas, particularly  $H_2$ , and the overall increasing heat value of the gas. A similar increase in efficiency was also observed by other researchers [49]. The LHV of the product gas was found to increase from a value of  $4.5MJ/Nm^3$  at 0.6 to  $4.7MJ/Nm^3$  at 1.8 steam to biomass ratio. Due to the opposite trends observed for *CO* and  $H_2$  with increasing steam to biomass ratio, the optimum value would depend on the final downstream application of the gas.



Figure 4.16: Impact of Variation of Steam to Biomass Ratio on the Product Gas Component Yields from the SNG Model

Figure 4.16 shows the impact of variation of steam to biomass ratio on the product gas component yields from the SNG model. The sensitivity analysis was performed using the operating parameters as mentioned in table 4.2. As can be seen from the figure, increasing the steam to biomass ratio from 0.6 to 1.2, led to an increase in the concentration of  $CH_4$  in the product gas. However, after 1.2, the concentration of  $CH_4$  did not increase further and remained constant. The concentration of  $H_2$  in the gas was observed to decrease from 0.6 to 1.2, indicating the presence of excess  $H_2$  in the gas. However, from 1.4 to 1.8  $H_2$  increased slightly in the product gas, which might be due to the attainment of equilibrium, which would also justify the slight increase in  $CO_2$  concentration in the gas, and the fact that the  $CH_4$  remained constant thereafter.  $N_2$  also remained constant for the most part, with only a marginal decrease from 0.6 to 1.8. CO was not present throughout and the concentration of  $H_2O$  in the gas was constant at 0.7%.

Figure 4.17 shows the impact of variation of steam to biomass ratio on the Cold Gas Efficiency and Overall Efficiency of the SNG Model.As can be seen from the figure, the cold gas efficiency and the overall efficiency of the model increased significantly as the steam to biomass ratio was increased from 0.6 to 1.2. However, after 1.2, both the CGE and the OE remained constant with increasing steam flow. This can be explained by the fact that the concentration of  $CH_4$  in the gas, and consequently the LHV of the gas, was constant after 1.2. All the excess water in the gas was removed in the flash drum, which also ensured that the flow rate of the gas remained more or less constant. The LHV of the product gas was found to increase from a value of  $13.6MJ/Nm^3$  at 0.6 to  $15MJ/Nm^3$  at 1.2, and constant thereafter. For the SNG model, the optimum value of steam to biomass ratio can be concluded to be 1.2, since beyond this value, almost no change is observed in the  $CH_4$  concentration and the efficiencies, and also because a greater amount of energy and resources would have to be employed to remove the excess water from the product gas.



Figure 4.17: Impact of Variation of Steam to Biomass Ratio on the Cold Gas Efficiency and Overall Efficiency of the SNG Model



Figure 4.18: Impact of Variation of Steam to Biomass Ratio on the Product Gas Component Yields from the Hydrogen Model

Figure 4.18 shows the impact of variation of steam to biomass ratio on the product gas component yields from the Hydrogen model. The sensitivity analysis was performed using the operating parameters as mentioned in table 4.3. The figure shows the concentration of  $H_2$  increased considerably from 0.6 to 1, after which the increase was very moderate. It was also observed that *CO* in the gas reduced drastically from 0.6 to 1, and remained close to 0% thereafter. The presence of a considerable amount of *CO* in the product gas at 0.6 and 0.8 suggests an inadequate amount of water in the gas for the water gas shift reaction to take place. This decrease also explains the increase in  $H_2$  in the product gas. It can also be seen that the  $CO_2$  in the gas increased a little from 1.4 to 1.8, probably due to the increase in the water gas shift reaction. The increase in  $CO_2$  also indicates that a greater amount of *CaO* is required in order to remove all of the  $CO_2$  from the gas. The amount of  $N_2$ 

in the gas also increases a little fro 0.6 to 0.8, due to the fall in *CO*, but shows a constantly decreasing trend therafter, due to the increase in  $H_2$ . The amount of  $CH_4$  remained 0 throughout and the concentration of water was constant at 0.6%.



Figure 4.19: Impact of Variation of Steam to Biomass Ratio on the Cold Gas Efficiency and Overall Efficiency of the Hydrogen Model

Figure 4.19 shows the impact of variation of steam to biomass ratio on the Cold Gas Efficiency and Overall Efficiency of the Hydrogen Model. As can be seen from the figure, both the cold gas efficiency and the overall efficiency of the model increases significantly with increasing steam to biomass ratio. This can be explained by the increasing concentration of  $H_2$  in the gas, which also increases the heating value of the product gas. The excess steam also leads to a greater amount of char undergoing gasification, which increases the flow rate of the product gas. The LHV of the product gas was found to decrease marginally from a value of  $6.3MJ/Nm^3$  at 0.6 to  $6MJ/Nm^3$  at 1.2. This slight decrease is due to the increase in  $CO_2$  in the product gas, which suggests that the increasing efficiency is solely due to the increasing flow rate. For the Hydrogen model, the optimum value can be concluded to be either 1.2 or 1.4, since beyond this value the increase in  $H_2$  is very low, but would require more resources for  $CO_2$  and  $H_2O$  removal. All the results for the sensitivity analysis of steam to biomass ratio are shown in Appendix H.

# 4.5. Mass Balance

The mass balance was done for the gasification model, the SNG model and the Hydrogen model, in order to account for the mass flow rates of all the input and output flow streams. Table 4.4 shows the mass balance for the gasification model. As can be seen from the table, the mass balance for the gasification model does not close upto 100%. The mass balance restrictions for the simulated reactors were eased a little in order to ensure the model converged. The observed relative error in the mass balance was 7.63%. This is considerably lower than what was observed for the experiments which was around 22.83%. It is possible that this error is due to reaction kinetics. Various studies use correction factors in the kinetic parameters in order to correct mass balance errors. However, no correction factors were considered in this study, and can be looked into in future works.

Gasification Model				
Input Mass Flow Rate (kg/hr) Output Mass Flow Rate (kg/hr)				
Bi	iomass	Biomass		
Wood	8	Wood	0	
Gasific	ation Agents	Gasificati	on Products	
Steam	8.7	СО	2.87	
Air 1	1.9	CO2	6.05	
Air 2	4	CH4	0.53	
Nitrogen 1	4.807	H2	0.36	
Nitrogen 2	0.7	N2	11.08	
Nitrogen 3	1.05	H20	5.25	
		Benzene	0.1	
		Phenol	0	
		Naphthalene	0	
		NH3	0.01	
		H2S	0.001	
		Char	0.645	
		Ash	0.051	
Total	29.15	Total	26.92	

Table 4.4: Mass Balance for the Gasification Model

Table 4.5 shows the mass balance for the SNG model. As can be seen from the table, the mass balance closed almost completely, with a relative error of just 0.9%.
SNG Model					
Input Mass Flow Rat	e (kg/hr)	Output Mass Flow Rate (kg/hr)			
Biomass		Biomass			
Wood	8	Wood	0		
Gasification Age	ents	Gasificatio	on Products		
Steam	8.7	CO	3.04		
Air 1	1.9	CO2	6.06		
Air 2	4	CH4	0.56		
Nitrogen 1	4.81	H2	0.37		
Nitrogen 2	0.7	N2	11.08		
Nitrogen 3	1.05	H20	5.12		
Dolomite	0.0015	Benzene	0		
		Phenol	0		
		Naphthalene	0		
		NH3	0		
		H2S	0.001		
		Char	0.64		
		Ash	0.051		
		Dolomite	0.0015		
Total	29.15	Total	26.93		
Desulphurization I	Reactor	Desulphurization Reactor			
ZnO	0.01	ZnO	0.007		
		ZnS	0.003		
Dechlorination R	eactor	Dechlorina	tion Reactor		
ZnO	0.01	ZnO	0.01		
Methanation	1	Metha	anation		
СО	3.04	CO	0		
CO2	6.06	CO2	0		
CH4	0.56	CH4	4.63		
H2	0.37	H2	0		
N2	11.08	N2	11.08		
H20	5.12	H20 Gas	0.24		
Supplementary H2	1.43	H2O FD	11.98		
Total	27.665	Total	27.93		

Table 4.5: Mass Balance for the SNG Model

Table 4.6 shows the mass balance for the Hydrogen model. As can be seen from the table, the mass balance closed almost completely, with a relative error of just 0.3%.

Hydrogen Model				
Input Mass	Flow Rate (kg/hr)	Output Mass Flow Rate (kg/hr)		
B	iomass	Biomass		
Wood	8	Wood	0	
Gasific	ation Agents	Gasification Products		
Steam	8.7	СО	3.04	
Air 1	1.9	CO2	6.06	
Air 2	4	CH4	0.56	
Nitrogen 1	4.81	H2	0.37	
Nitrogen 2	0.7	N2	11.08	
Nitrogen 3	1.05	H20	5.12	
Dolomite	0.0015	Benzene	0	
		Phenol	0	
		Naphthalene	0	
		NH3	0	
		H2S	0.001	
		Char	0.64	
		Ash	0.051	
		Dolomite	0.0015	
Total	29.15	Total	26.93	
Desulphu	rization Reactor	Desulphuriz	zation Reactor	
ZnO	0.01	ZnO	0.007	
		ZnS	0.003	
Dechlori	nation Reactor	Dechlorina	ation Reactor	
ZnO	0.01	ZnO	0.01	
Hydr	Hydrogenation		genation	
CO	3.04	СО	0.11	
CO2	6.06	CO2	0	
CH4	0.56	CH4	0	
H2	0.37	H2	0.93	
N2	11.08	N2	11.08	
H20	5.12	H20 Gas	0.30	
CaO	16.05	H2O FD	1.37	
		CaO	0.027	
		CaCO3	28.6	
Total	42.285	Total	42.422	

Table 4.6: Mass Balance for the SNG Model

#### 4.6. Energy Balance

The energy balance was carried out for the SNG model and the Hydrogen model. For the gasification model, it was known from the experiments conducted, how much heat is supplied to the preheaters, and how much heat is required for the gasifier. For this reason, no specefic heat balance for the gasification section was carried out.

Table 4.7 shows the energy balance for the entire SNG model. The table clearly shows that most of the heat being supplied to the preheaters is not utilized and gets lost, which leads to a loss of efficiency. It was known from the experiments that the gasifier requires a heat input of 32kW. The aim of performing the energy balance, was to determine if some of this heat requirement for the gasifier can be met by some of the downstream processes. The methanation reactor, being exothermic in nature, creates roughly 14kW of heat, which must be removed from the reactor using a system like a cooling jacket. If some part of this heat can be used to heat up a thermal fluid, it can be used to provide some of the heat requirement for the gasifier. The flash drum also releases a significant amount of heat which can be captured and used for heating the gasifier. The heat exchangers were used to cool down and heat up certain streams in the flowsheet, so as to prevent the use of

SNG Model									
Heat Input (kW)Heat Utilized (kW)Heat Loss/Output (kW)									
Preheater	10.5	2.21	8.29						
Gasifier	32	32	0						
<b>Methanation Reactor</b>	0		14.1						
Flash Drum	0		16						
HX1		5.24							
HX2		1.9							

#### Table 4.7: Energy Balance for the SNG Model

Table 4.8: Energy Balance for the Hydrogen Model

Hydrogen Model								
Heat Input (kW) Heat Utilized (kW) Heat Loss/Output (kW)								
Preheater	10.5	2.21	8.29					
Gasifier	32	32	0					
<b>Methane Reforming Reactor</b>		3.2	0					
Water Gas Shift Reactor	0		1.87					
CO2 Removal Reactor	0		10.92					
Flash Drum	0		6					
Cooler B13	0		2.95					
HX1		5.24						
HX2		5.86						

heaters and coolers, ad also to reduce the heat duty of the processes.

Table 4.7 shows the energy balance for the entire SNG model. The energy balance of the preheater and the gasifier is same as the SNG model. As can be seen from the table, the methane reforming reactor requires some heat to be input into it. This heat can be met by the heat released by the cooler, which are almost equal. The heat being released from the exothermic water gas shift and  $CO_2$  removal reactor can be used to provide some of the heat required by the gasifier. Similar to the SNG model, the flash drum also releases some heat, although much less than what is observed for the SNG model, due to lower water content in the gas, and can also be used for heating the gasifier or for generating steam. The heat exchangers also perform a similar fucntion as in the SNG model.

## 5

#### Conclusions

This study looked into assessing the different types of biomass feedstocks grown and available in the European Union, which can potentially be used for energy generation. The production potential of the different possible feedstocks was also determined for the current period and for a future timeline (2050) using data for yields and land availability from various reliable sources in literature, such as FAOSTAT and Eurostat. Following this, it was decided to model a steam gasifier based on the Indirectly Heated Bubbling Fluidized Bed Steam Reformer at TU Delft. The model was created using ASPEN Plus, and was a kinetic model for air-steam gasification. The model was validated using the experimental results obtained from the setup at TU Delft. The product syngas from the gasification model, was also used as a feedstock to create 2 different biofuels as in a biorefinery. A gas cleaning model was created to rid the syngas of impurities such as tar,  $H_2S$  and  $NH_3$ , following which two kinetic models were created, one to simulate the production of Synthetic Natural Gas and the other for production of Hydrogen gas, both of which are important fuels, with a number of applications. The main conclusions derived from the model were elaborated by answering the research questions formulated at the beginning of this thesis.

#### **5.1.** Answers to Research Questions

#### Which are the main lignocellulosic biomass feedstocks grown and available in the European Union?

Various lignocellulosic biomass feedstocks available in the European Union were identified in this study. The first one was Forest Residues and Wood wastes. Forest residues include pieces of wood that are taken directly from the forest floor without going through any chemical processing. Wood wastes are those which are obtained from wood processing industries in the form of bark, shavings, etc. The second feedstock is Agricultural residues, which are non woody biomasses in the form of crop residues that are obtained from fields after harvest. The final type of feedstock is Dedicated Energy crops, which are crops specially grown for the purpose of generating energy in an agricultural context. These are of two types, Herbaceous crops which include perrenial grasses like miscanthus and reed canary grass, and Short Rotation Coppice (SRC) crop varieties that are perrenial crops like willow and poplar, and are woody in nature. These feedstocks together have the potential to contribute a big chunk of the energy requirements of the European Union.

#### What is the current and future production potential of the available lignocellulosic biomass feedstocks in the European Union, as available in literature?

Various estimates, both theoretical and actual, are available in literature for the availability and production potential of the mentioned lignocellulosic biomass feedstocks. Table 5.1 summarises the current and future potential of all selected lignocellulosic biomass feedstocks.

Feedstock		Theoretical Potential (million	Actual Potential (million
		tonnes/yr)	tonnes/yr)
Forest Residue		11.5 - 80.7	25.17 (2019)
Wood Waste		32 - 79.17	48.46 (2016)
Agricultural		367 - 419	29 - 139
Residue			
Dedicated Energy	Current	5 4 33 75 (2014)	0.47 2.93 (2019)
Crops	Current	5.4 - 55.75 (2014)	0.47 - 2.33 (2013)
	Future	54.2 - 338.75 (lower conservative estimate)	
	(2050)	360 - 2250 (maximum possible estimate)	

Table 5.1: Summary of all Selected Lignocellulosic Biomass Feedstock Current and Future Potentials

### How well does the model predict the composition and yield of the gasification products including CO, $CO_2$ , $CH_4$ , $H_2$ , $N_2$ , $H_2O$ and tar, and also the carbon conversion, cold gas efficiency and the overall efficiency of the gasification model?

The Gasification model was validated for wood as the biomass feedstock, using operating conditions as mentioned in table 4.1. The model was validated by the experimental results fairly well, with a relative error for CO,  $CO_2$ ,  $CH_4$  and  $H_2$  between -17.81%, -5.63%, 3.05% and 10.93% respectively, on a dry nitrogen free basis. These errors were found to be lower than the average validation errors as found in literature. The  $N_2$  was also close enough with a relative error of 16.85%. The biggest deviation off all components was observed for water, with a relative error of 59.53%. The tar was also observed to be in the same range as the experiments, only slightly higher. However, this good validation for tar content was because of the use of only Phenol as the representative tar compound, and may differ when a more detailed approach for defining tar components is used. The Carbon Conversion efficiency was found to be very close to the experimental results, with a relative error of less than 1%. The Cold Gas Efficiency and Overall Efficiency were found to be lower than what was determined experimentally, with relative errors of 31.3% and 27.1% respectively.

#### What are the final product compositions and efficiencies for the SNG and the Hydrogen models, and which one would be more attractive to produce?

The kinetic models for the production of Synthetic Natural Gas and Hydrogen from syngas also gave interesting results. The SNG product stream was composed of 42% CH<sub>4</sub>, 57.4% N<sub>2</sub> and a very small amount of water around 0.7%. Once the Nitrogen is removed from the product gas, leaving between 15-20%  $N_2$ , the SNG can be used for energy applications by plugging into the Natural Gas pipleine in Europe. The Cold Gas efficiency of the model was estimated to be around 68.5% and the Overall efficiency around 34.6%. The Hydrogen model, on the other hand, had a final product stream which was composed of 53.3% H<sub>2</sub>, 45.6% N<sub>2</sub>, a very small amount of water around 0.6%, and an even smaller amount of CO around 0.5%. The product gas from the model will need to go some further processing in order to remove the traces of CO in the gas, and the  $N_2$  for it to be fit to use in a PEM fuel cell. The Cold Gas efficiency of the model was estimated to be around 42.1% and the Overall efficiency around 20.5%. Both models have their merits and demerits. The SNG model was found to have a larger fraction of  $N_2$  which will have to be removed, and requires a significant amount of supplementary  $H_2$ . However, it requires very few other heat inputs, and had a much higher efficiency, compared to the Hydrogen model. On the other hand, the Hydrogen model had a relatively lower amount of  $N_2$  in the gas, but had traces of unconverted CO, which will have to be removed, and also required inputs in terms of CaO to remove the  $CO_2$  from the gas. The methane reforming reactor also required some extra heat input, in addition to the gasifier. Based on these factors, and solely from a process point of view, and not economically, the SNG model seems more viable due to a much higher efficiency and less strict usage constraints. However, from an economic standpoint, it is possible that the supplementary  $H_2$  leads to a very expensive process, making it less attractive, and that the Hydrogen process model turns out to be more economically viable if used for purposes other than fuel cells. This can be looked into in future works.

What is the effect of varying secondary air and the steam to biomass ratio on the performance of the steam gasification model, and also the SNG and Hydrogen models?

A sensitivity analysis was carried out for two parameters, namely secondary air and steam to biomass ratio. Secondary air was varied from a value of 0kg/hr to 8kg/hr. Increasing the secondary air led to a decrease in the yields of CO,  $H_2O$  and  $CH_4$ , while a sharp increase was observed for  $N_2$ . The amount of  $CO_2$  and  $H_2O$  were found to remain the same. Tar conversion, which was the main reason for injecting secondary air into the gasifier, was found to decrease from 0kg/hr to 2kg/hr, and then remained constant indicating that 2kg/hr was sufficient. The Carbon conversion remained constant, while the Cold Gas efficiency and Overall efficiency decreased with increasing secondary air. For the SNG model, it was observed that an increase in secondary air led to an increase in  $N_2$  and a consequent decrease in  $CH_4$ . It was also noted that a lesser amount of supplementary hydrogen was required for 0kg/hr and 2kg/hr, while more hydrogen was required for 6kg/hr and 8kg/hr of secondary air. The efficiencies of the model also peaked at 2kg/hr, and decrease in  $H_2$ . The amount of  $CO_2$  was higher for lower values of secondary air. It was also noted that the amount of  $CO_2$  was higher for higher values of secondary air. For both models, a lower value of secondary air of 2kg/hr seemed optimum.

The Steam to Biomass ratio was varied from a value of 0.6 to 1.8. Increasing the steam to biomass ratio led to a decrease in *CO* and  $N_2$  and an increase in  $H_2$ ,  $CO_2$  and  $H_2O$ . The  $CH_4$  concentration remained constant throughout, while the tar decreased slightly with increasing steam flow rate. The carbon conversion, cold gas efficiency and the overall efficiency were all found to increase with increasing steam to biomass ratio. For the SNG model, increasing the steam to biomass ratio, increased the  $CH_4$  uptil 1.2, and then remained constant thereafter.  $N_2$  was also found to be constant throughout. It was also noted that more supplementary hydrogen was required for steam to biomass ratio lower than 1.2, and the methanation reactions, reached an equilibrium after 1.4. The efficiencies also increased till 1.2, and remained stable thereafter. The optimum ratio for the SNG model would be 1.2, since very little to no change is observed after this point. For the Hydrogen model, increasing the steam to biomass ratio led to a sharp increase in  $H_2$  till 1.0, and only a marginal increase thereafter. The  $N_2$  also reduced continuously. Some *CO* remained in the gas for steam to biomass ratios of 0.6 to 1. It was also noted that more *CaO* was required for complete removal of  $CO_2$  from 1.4 to 1.8. The efficiencies of the model increased with an increase in steam to biomass ratio. The optimum value of the ratio for the hydrogen model should be 1.2 or 1.4 since beyond this value the increase in  $H_2$  is very low, but would require more resources for  $CO_2$  and  $H_2O$  removal.

#### **5.2. Recommendations for Future Work**

The model made in this study was simple in some respects, and some more complexity can be added to it. Some possible recommendations for future work are described in this section. The char was modeled as pure carbon, but in reality the char contains some amount of hydrogen and oxygen, and can be implemented. The effect of fluidization was not considered in this study, and the study of bubble size and fluidization velocity along with temperature can be studies in order to get a deeper understanding of the process. The tar composition from pyrolysis should be looked into, in order to determine the detailed yields of some of the major compounds. Another improvement to the model can be to determine the amount of pyrolytic water generated during the process to get a more detailed idea. The kinetic parameters for the different reactions can be determined for the process conditions specific to this study. The catalytic properties of unreacted char can also be studied and implemented. The cyclone separator in this study was modelled as an ideal separator. The particle size distribution of the biomass can also be integrated and a cyclone separator can be modelled for greater complexity. The gasification process can also be modelled using Dolomite as bed material, which would improve the tar cracking and the final product composition. Tar cleaning can also be simulated using an absorption and stripper system to determine its effectiveness in gas cleaning. All the processes in this model were carried out at atmospheric pressure. The pressure can be varied to see how much that changes the product composition and performance. An economic evaluation for the gasification model, SNG model and Hydrogen model should be carried out to determine the economic viability. Finally, the scale up of the designed models can be looked into, by taking into account the locations of plants and supply of the feedstocks from different places in Europe. A network of biomass supply chain should be put into place for effective energy conversion. To begin with a pilot plant setup could be installed to demonstrate a TRL 5-6 level, with a scale of about 100 kg/hr of biomass, to demonstrate the system's readiness.

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## A

**Gasifier Dimensions** 





### B

### FORTRAN Code in ASPEN Plus for Implementing Pyrolysis Curves

 $H2 = -1.2083330E - 10^{*}T^{**}4 + 5.0611670E - 07^{*}T^{**}3 + -7.8676770E - 04^{*}T^{**}2 + 5.3905650E - 01^{*}T - 1.3753190E + 02$ CO2 = -1.4250000E - 09\*T\*\*4 + 5.9211000E - 06\*T\*\*3 + -9.1564079E - 03\*T\*\*2 + 6.2556923E + 00\*T - 1.5900540E + 03\*T\*\*2 + 0.2556923E + 00\*T - 0.256923E + 0.256922E + 0.256922E + 0.256922E + 0.256922E + 0.25692E + 0.2569E + 0.2568E + 0.2 $CO = -3.6083333E - 09^{*}T^{**}4 + 1.4490300E - 05^{*}T^{**}3 - 2.1573920E - 02^{*}T^{**}2 + + 1.4162384E + 01^{*}T - 3.4650211E + 03^{*}T^{*}2 + 0.4162384E + 0.416284E + 0.416284E + 0.416284E + 0.41644E +$  $CH4 = -6.7916670E - 10^{*}T^{**4} + 2.7391500E - 06^{*}T^{**3} - 4.0928670E - 03^{*}T^{**2} + + 2.6940660E + 00^{*}T - 6.6055220E + 02$ SOLID = 2.6416667E - 09\*T\*\*4 - 1.1349700E - 05\*T\*\*3 + 1.8419703E - 02\*T\*\*2 + -1.3438756E + 01\*T + 3.7509808E + 03E + 0 $LIQUID = 5.7458333E - 09*T^{**4} - 2.2760283E - 05*T^{**3} + + 3.3234326E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205559E + 01*T + 5.0234410E + 03E - 02*T^{**2} - 2.1205555E - 02*T^{**2} - 2.1205555E - 02*T^{**2} - 2.1205555E - 02*T^{**2} - 02*T^$ N2 = 0.06S = 0.01 CL2 = 0ASH = 0.49 O2 = 0CHAR = SOLID - ASH PW = 5.157E-05\*T\*\*2 - 11.86E-02\*T + 84.91 MOIST = 5.57DMASS = 100 - CO - H2 - CO2 - CH4 - LIQUID - SOLID - N2 - S LIQUIDS = LIQUID + DMASS H2O = PW + MOISTPHENOL = LIQUIDS - H2O TCSTR = TTSTOIC = T

## C

### Devolatilization Curves Coefficients

The table C.1 belowbelow shows the coefficients for the devolatilization curves obtained for each f the biomass feedstocks from the Pyro Probe experiments. Equation C.1 shows the form each of the curves take as a fourth degree polynomial, where i is the particular component.

$$Y_i = aT^4 + bT^3 + cT^2 + dT + e$$
(C.1)

Wood					
Component	а	b	с	d	e
Solid	+2.6416667E-09	-1.1349700E-05	+1.8419703E-02	-1.3438756E+01	+3.7509808E+03
Liquid	+5.7458333E-09	-2.2760283E-05	+3.3234326E-02	-2.1205559E+01	+5.0234410E+03
H <sub>2</sub>	-1.2083330E-10	+5.0611670E-07	-7.8676770E-04	+5.3905650E-01	-1.3753190E+02
СО	-3.6083333E-09	+1.4490300E-05	-2.1573920E-02	+1.4162384E+01	-3.4650211E+03
CH <sub>4</sub>	-6.7916670E-10	+2.7391500E-06	-4.0928670E-03	+2.6940660E+00	-6.6055220E+02
CO <sub>2</sub>	-1.4250000E-09	+5.9211000E-06	-9.1564079E-03	+6.2556923E+00	-1.5900540E+03

Table C.1: Devolatilization Curves Coefficients

### D Gasification Kinetics

Reaction	Reaction Name	Reaction Kinetics	Reference			
R1	Boudouard Reaction	$r_1 = k_1 \cdot P_{CO_2}^{0.31}(N/m^2)$ $k_1 = 1.12 \cdot 10^8 \cdot exp(\frac{-245014}{BT})$	[53]			
	Primary Components Oxidation					
R2	Char Oxidation	$r_{2} = k_{2} \cdot F_{2} \cdot C_{O_{2}}$ $k_{2} = 595.7 \cdot T \cdot exp(\frac{-149440}{RT})$ $F_{2} = \frac{6}{d_{p}} \text{ where } d_{p} = 0.006m$ $\alpha = \frac{1+2 \cdot f_{x}}{1+f_{x}} \text{ with } f_{x} = 4.72 \cdot 10^{-3} \cdot exp(\frac{37737}{RT})$	[56]			
R3	H <sub>2</sub> Oxidation	$r_{3} = k_{3} \cdot C_{H_{2}} \cdot C_{O_{2}}$ $k_{3} = 1.08 \cdot 10^{13} \cdot exp(\frac{-125525}{RT})$	[33]			
R4	CO Oxidation	$r_4 = k_4 \cdot C_{CO} \cdot C_{O_2}^{0.3} \cdot C_{H_2O}^{0.5}$ $k_4 = 4.78 \cdot 10^8 \cdot exp(\frac{-66900}{BT})$	[33]			
R5	CH <sub>4</sub> Oxidation	$r_{5} = k_{5} \cdot C_{CH_{4}}^{0.5} \cdot C_{O_{2}}^{1.25}$ $k_{5} = 4.4 \cdot 10^{11} \cdot exp(\frac{-126000}{BT})$	[33]			
	Primary Co	omponents Steam Reforming				
R6	Water Gas	$r_{6} = k_{6} \cdot C_{C} \cdot C_{H_{2}O}$ $k_{6} = 3.6 \cdot 10^{12} \cdot exp(\frac{-310000}{BT})$	[66, 68]			
R7	Water Gas Shift Reaction	$r_{7} = k_{7} \cdot C_{CO} \cdot C_{H_{2}O} - \frac{C_{CO_{2}} \cdot C_{H_{2}}}{k_{eq}}$ $k_{7} = 2778 \cdot exp(\frac{-12560}{RT})$ $k_{eq} = 0.022 \cdot exp(\frac{34730}{RT})$	[56]			
R8	CH <sub>4</sub> Reforming	$r_8 = k_8 \cdot C_{CH_4} \cdot C_{H_2O} \\ k_8 = 3 \cdot 10^5 \cdot exp(\frac{-125000}{RT})$	[36]			
	Tar (	Components Oxidation	-			
R9	$C_6H_6$ Oxidation	$r_9 = k_9 \cdot C_{C_6H_6} \cdot C_{O_2}$ $k_9 = 1.58 \cdot 10^{15} \cdot exp(\frac{-202641}{RT})$	[56]			
R10	$C_{10}H_8$ Oxidation	$r_{10} = k_{10} \cdot C_{C_{10}H_8}^{0.5} \cdot C_{O_2}^{0}$ $k_{10} = 9.2 \cdot 10^6 \cdot T \cdot exp(\frac{-80000}{RT})$	[66, 68]			
	Tar (	Components Reforming	-			
R11	$C_6H_6$ Reforming	$r_{11} = k_{11} \cdot C_{C_6H_6}^{1.3} \cdot C_{H_2O}^{0.2} \cdot C_{H_2}^{-0.4} \ k_{11} = 3.39 \cdot 10^{16} \cdot exp(rac{-443000}{RT})$	[66, 68]			
R12	$C_6 H_6 O$ Reforming	$r_{12} = k_{12} \cdot C_{C_6H_6O}$ $k_{12} = 1 \cdot 10^8 \cdot exp(\frac{-100000}{RT})$	[66, 68]			
	Tar	Components Cracking				
R13	$C_6H_6O$ Cracking	$r_{13} = k_{13} \cdot C_{C_6H_6O} \\ k_{13} = 1 \cdot 10^7 \cdot exp(\frac{-100000}{RT})$	[12, 66, 68]			
R14	$C_{10}H_8$ Cracking	$r_{14} = k_{14} \cdot C_{C_{10}H_8}$ $k_{14} = 1.13 \cdot 10^6 \cdot exp(\frac{-109000}{RT})$	[53, 58]			

#### Table D.1: Gasification Kinetics

## E

**Methanation Kinetics** 

Reaction Name	Reaction Kinetics	Reference
CO Methanation	$r = \frac{k_1 A_C A_H^2 (P_{C0}^{0.5} P_{H_2} - K_1 \frac{P_{CH_4} P_{H_2O}}{P_{CO} P_{H_2}^2})}{(1 + A_C P_{CO} + A_H P_{H_2O}^{0.5})^3}$ $k_1 = 1.944 \cdot 10^7 \cdot exp(\frac{-103000}{RT})$ $K_1 = 810 \cdot T^{3.03} \cdot exp(\frac{-202300}{RT})$ $A_{C_0} = 1.83 \cdot 10^{-6} P a^{-0.5}, \Delta H_C = -42000 \text{ J/mol}$ $A_{H_0} = 5.06 \cdot 10^{-5} P a^{-0.5}, \Delta H_H = -16000 \text{ J/mol}$	[67, 74]
CO <sub>2</sub> Methanation	$r = \frac{k_2 (P_{CO_2}^{0.5} P_{H_2}^{0.5} - K_2 \frac{P_{CH_4} P_{H_2O}^2}{p_{CO_2}^{0.5} P_{H_2}^{3.5}})}{(1 + A_{OH} \frac{P_{H_2O}}{p_{H_2}^{0.5}} + A_{H_2} P_{H_2O}^{0.5} + A_{mix} P_{CO_2}^{0.5})^2} \\ k_2 = 4.15 \cdot 10^{-10} \cdot exp(\frac{-208200}{RT}) \\ K_2 = 137 \cdot T^{-3.998} \cdot exp(\frac{-158700}{RT}) \\ A_{OH_0} = 1.45 \cdot 10^{-3} P a^{-0.5}, \Delta H_{OH} = 29300 \text{ J/mol} \\ A_{H_{20}} = 1.58 \cdot 10^{-3} P a^{-0.5}, \Delta H_{H_2} = 470 \text{ J/mol} \\ A_{mix_0} = 2.59 \cdot 10^{-3} P a^{-0.5}, \Delta H_{mix} = -9900 \text{ J/mol} \end{cases}$	[3, 74]
Water Gas Shift	$r = \frac{\frac{k_3}{P_{H_2}}(P_{CO}P_{H_2O} - \frac{P_{CO_2}P_{H_2}}{K_3})}{(1 + A_{CO}P_{CO} + A_{H_2}P_{H_2} + A_{CH_4}P_{CH_4} + \frac{A_{H_2O}P_{H_2O}}{P_{H_2}})^2} \\ k_3 = 2.175 \cdot 10^{-2} \cdot exp(\frac{-62000}{RT}) \\ K_3 = 9.01 \cdot 10^{-6} \cdot T^{0.968} \cdot exp(\frac{-43600}{RT}) \\ A_{CO_0} = 8.23 \cdot 10^{-10}Pa^{-1}, \Delta H_{CO} = -70650 \text{ J/mol} \\ A_{H_20} = 6.12 \cdot 10^{-14}Pa^{-1}, \Delta H_{H_2} = -82900 \text{ J/mol} \\ A_{CH_4} = 6.65 \cdot 10^{-9}Pa^{-1}, \Delta H_{CH_4} = -38280 \text{ J/mol} \\ A_{H_{20_0}} = 1.77 \cdot 10^5, \Delta H_{H_{2O}} = 88680 \text{ J/mol} \end{cases}$	[67, 74]

Table E.1: Methanation Kinetics

## F

### Hydrogen Formation Kinetics

Reaction Name	Reaction Kinetics	Reference
<i>CH</i> <sub>4</sub> Reforming	$r = \frac{\frac{k_1}{K_1}(K_1 \frac{P_{CH_4}P_{H_2O}}{P_{H_2}^{2.5}} - P_{CO}P_{H_2}^{0.5})}{(1+K_{CO}P_{CO}+K_{H_2}P_{H_2}+K_{CH_4}P_{CH_4} + \frac{K_{H_2O}P_{H_2O}}{P_{H_2}})^2}$ $k_1 = 3.736 \cdot 10^{14} \cdot exp(\frac{-240100}{P_{H_2}})$ $K_1 = 7.747 \cdot 10^7 \cdot exp(\frac{-220200}{RT})$ $K_{CO_0} = 8.122 \cdot 10^{-10}Pa^{-1}, \Delta H_{CO} = -70650 \text{ J/mol}$ $K_{H_2O} = 6.04 \cdot 10^{-14}Pa^{-1}, \Delta H_{H_2} = -82900 \text{ J/mol}$ $K_{CH_4} = 6.56 \cdot 10^{-9}Pa^{-1}, \Delta H_{CH_4} = -38280 \text{ J/mol}$ $K_{H_2O_0} = 1.77 \cdot 10^5, \Delta H_{H_2O} = -88680 \text{ J/mol}$	[40, 65]
Water Gas Shift	$r = \frac{\frac{k_3}{P_{H_2}}(P_{CO}P_{H_2O} - \frac{P_{CO_2}P_{H_2}}{K_3})}{(1 + A_{CO}P_{CO} + A_{H_2}P_{H_2} + A_{CH_4}P_{CH_4} + \frac{A_{H_2O}P_{H_2O}}{P_{H_2O}})^2}$ $k_3 = 2.175 \cdot 10^{-2} \cdot exp(\frac{-62000}{RT})$ $K_3 = 9.01 \cdot 10^{-6} \cdot T^{0.968} \cdot exp(\frac{-43600}{RT})$ $A_{CO_0} = 8.23 \cdot 10^{-10}Pa^{-1}, \Delta H_{CO} = -70650 \text{ J/mol}$ $A_{H_20} = 6.12 \cdot 10^{-14}Pa^{-1}, \Delta H_{H_2} = -82900 \text{ J/mol}$ $A_{CH_4} = 6.65 \cdot 10^{-9}Pa^{-1}, \Delta H_{CH_4} = -38280 \text{ J/mol}$ $A_{H_{20_0}} = 1.77 \cdot 10^5, \Delta H_{H_2O} = 88680 \text{ J/mol}$	[67, 74]

Table F.1: Hydrogen Formation Kinetics

# G

Sensitivity Analysis Results for Secondary Air

	0 kg/hr	2kg/hr	4kg/hr	6kg/hr	8kg/hr
Char Out (kg/hr)	0.6	0.593	0.645	0.547	0.667
CO %	13.400	11.800	10.800	9.800	9.300
CO2 %	14.300	14.800	14.500	16.400	14.400
H2%	23.200	20.100	18.700	16.100	16.000
CH4 %	5.000	4.600	3.500	1.700	2.000
N2 %	33.7	38.2	41.8	44.5	47.7
H2O %	10.1	10.3	10.4	11.2	10.3
Tar %	0.3	0.22	0.22	0.22	0.22
CC%	83.425	83.619	82.182	84.890	81.575
LHV (MJ/Nm3)	5.989	5.309	4.638	3.586	3.619
CGE%	53.242	43.245	37.97	29.863	29.89
OE%	26.879	21.832	19.17	15.077	15.09
	S	NG Mode	l		
Char Out (kg/hr)	0.609	0.606	0.638	0.501	0.634
CO %	0	0	0	1.5	7.6
CO2 %	0	0	0	2.5	0
H2%	10.9	1.5	0	0	0
CH4 %	44	45.4	41.9	35.1	31.7
N2 %	44.4	52.5	57.4	60.2	60
H2O %	0.7	0.7	0.7	0.7	0.7
CC%	83.177	83.260	82.376	86.160	82.486
LHV (MJ/Nm3)	16.937	16.423	15.01	12.762	12.315
CGE%	71.86	75.67	68.505	52.26	48.82
OE%	36.28	38.2	34.585	26.382	23.42
	Hyd	lrogen Mo	del		
Char Out (kg/hr)	0.609	0.606	0.638	0.501	0.634
CO %	1	0.7	0.5	0.2	0.2
CO2 %	0	0	0	0.7	0.3
H2%	62.3	57.9	53.3	42	44.2
CH4 %	0	0	0	0	0
N2 %	36.1	40.8	45.6	56.5	54.6
H2O %	0.6	0.6	0.6	0.6	0.6
CC%	83.177	83.260	82.376	86.160	82.486
LHV (MJ/Nm3)	6.8535	6.3405	5.818	4.56	4.798
CGE%	52.606	47.887	42.125	24.16	30.84
OE%	25.67	23.365	20.55	11.8	15.06

Table G.1: Sensitivity Analysis Results for Secondary Air

# Η

### Sensitivity Analysis Results for Steam to Biomass Ratio

	0.6	0.8	1	1.2	1.4	1.6	1.8
Char Out (kg/hr)	1.069	0.872	0.73	0.645	0.516	0.436	0.333
CO %	13.8	12.6	11.5	10.8	9.9	9.2	8.7
CO2 %	12.4	13.4	14.1	14.5	15.1	15.3	15.6
H2%	14.3	16.5	17.9	18.7	19.7	20.3	20.7
CH4 %	3.6	3.4	3.5	3.5	3.6	3.7	3.9
N2 %	50.4	46.6	43.6	41.8	39	37.1	35.4
H2O %	5.2	7.2	9.1	10.4	12.6	14.2	15.6
Tar %	0.3	0.3	0.2	0.2	0.2	0.2	0.1
CC%	70.470	75.912	79.834	82.182	85.746	87.956	90.801
LHV (MJ/Nm3)	4.577	4.592	4.640	4.638	4.668	4.680	4.731
CGE%	27.72	30.3	34.823	37.97	43.83	48.2	52.717
OE%	13.99	15.297	17.58	19.17	22.129	24.34	26.614
		SI	NG Mode	1			
Char Out (kg/hr)	1.053	0.859	0.73	0.638	0.502	0.394	0.318
CO %	0	0	0	0	0	0	0
CO2 %	0	0	0	0	0.6	1.5	2.5
H2%	8.1	4.9	4.1	0	0.2	0.8	1.9
CH4 %	35.6	37.9	39	41.9	42	41.8	41.2
N2 %	55.6	56.5	56.3	57.4	56.6	55.2	53.7
H2O %	0.7	0.7	0.7	0.7	0.7	0.7	0.7
CC%	70.912	76.271	79.834	82.376	86.133	89.116	91.215
LHV (MJ/Nm3)	13.626	14.104	14.412	15.01	15.065	15.058	14.962
CGE%	51.826	57.203	60.72	68.505	69.8	70.91	70.81
OE%	26.165	28.88	30.66	34.585	35.24	35.8	35.752
		Hyd	rogen Mo	del			
Char Out (kg/hr)	1.053	0.858	0.727	0.638	0.503	0.394	0.319
CO %	15.4	3.7	0.8	0.5	0.3	0.2	0.2
CO2 %	0	0	0	0	2	3.5	4.5
H2%	40.5	47.8	51.9	53.3	54.4	55.2	55.7
CH4 %	0	0	0	0	0	0	0
N2 %	44.1	48.2	46.6	45.6	42.7	40.4	39
H2O %	0	0.4	0.6	0.6	0.6	0.6	0.6
CC%	70.912	76.298	79.917	82.376	86.105	89.116	91.188
LHV (MJ/Nm3)	6.319	5.629	5.705	5.818	5.912	5.986	6.040
CGE%	29.06	32.095	39.075	42.125	46.83	50.937	53.77
OE%	14.2	15.676	19.085	20.55	22.87	24.88	26.26

Table H.1: Sensitivity Analysis Results for Steam to Biomass Ratio