

**Process model of the hydrogen production system
integrated with biomass gasification.**

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Abstract

For a long time, people have been looking for a sustainable replacement for fossil fuels, not only due to depletion of the resources but negative impact on the environment as well. The emissions of carbon dioxide are drastically rising in the energy/heat and transportation sector, forcing international organizations and national governments to implement stricter rules. Hydrogen is a key element in the energy transition considering its versatility in applications, and growing interest in its consumption for short-range transportation and electricity generation.

Hydrogen production through biomass gasification is currently the only deployed technology that is both using a sustainable resource (biomass) and can be applied on a large scale. Nevertheless, the process still requires research and continuous improvement to raise its production efficiency.

The thesis attempted to explore the fields of the end-to-end process of hydrogen production from biomass focusing on biomass gasification and synthesis gas processing. Based on the most feasible and proven technologies, the production process model was composed and described. To validate the model, ChemCAD simulation was performed to study the hydrogen production efficiency based on process parameters documented in the industrial applications. Additionally, the influence of steam to biomass ratio was studied to draft conclusions on the most promising gasification parameters to ensure efficient hydrogen production.

Keywords

Biomass gasification, hydrogen, syngas cleaning, hydrogen economy

Resumo

Há muito tempo, as pessoas buscam a substituição sustentável dos combustíveis fósseis, não apenas pelo esgotamento dos recursos, mas também pelo impacto negativo no meio ambiente. As emissões de dióxido de carbono estão aumentando drasticamente no setor de energia/calor e transporte, forçando organizações internacionais e governos nacionais a implementarem regras mais rígidas. O hidrogênio é um elemento chave na transição energética considerando sua versatilidade em aplicações e crescente interesse em seu consumo para transporte de curto alcance e geração de eletricidade.

A produção de hidrogênio por gaseificação de biomassa é atualmente a única tecnologia implantada que usa recurso sustentável (biomassa) e pode ser aplicada em larga escala. No entanto, o processo ainda requer pesquisas e melhorias contínuas para aumentar sua eficiência produtiva.

A tese procurou explorar os campos do processo de ponta a ponta de produção de hidrogênio a partir de biomassa com foco na gaseificação de biomassa e processamento de gás de síntese. Com base nas tecnologias mais viáveis e comprovadas, o modelo do processo de produção foi composto e descrito. Para validar o modelo, a simulação ChemCAD foi realizada para estudar a eficiência da produção de hidrogênio com base em parâmetros de processo documentados nas aplicações industriais. Além disso, a influência da proporção de vapor para biomassa foi estudada para elaborar conclusões sobre os parâmetros de gaseificação mais promissores para garantir a produção eficiente de hidrogênio.

Palavras-chave

Gaseificação de biomassa, hidrogênio, limpeza de gás de síntese, hidrogênio

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List of Acronym

BFB – bubbling fluidized bed
CGE – Cold Gas Efficiency
CC – Carbon Conversion
EU – European Union
EOR – Enhanced Oil Recovery
GHG – greenhouse gases
Gt – gigatons
GPa – giga Pascal
HHV – higher heating value
HPE – Hydrogen Production Efficiency
IEA – International Energy Agency
IPCC – Intergovernmental Panel on Climate Change
LHV – lower heating value
MEA - monoethanolamine
MEC – microbial electrolysis cell
MDEA – methyl diethanolamine
Mt – megatons
MJ – mega Joules
MSW – municipal solid waste
MWh – megawatt hour
Nm³ – normal cubic meter
PEM – polymer electrolyte membrane
PNS – purple non-sulfur bacteria
PSA – pressure swing adsorption
SGT – SES Gasification Technology
WGS – water gas shift

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Introduction

In the past decade, terms such as “global warming”, “climate change” and “energy transition” have been gaining popularity more than ever. Greta Thunberg, a young Swedish activist has caught the attention of worldwide leaders to alarming climate changes and called for action on raising fossil fuels consumption. As the population is growing, increased energy demand must be met, which leads to the depletion of current energy commodities. The IEA estimated that established oil, gas, and coal reservoirs will be depleted by 2050 (International Energy Agency, 2021). Moreover, the energy production based on fossil fuels is causing significant GHG emissions, which are boosting the negative climate changes such as global warming, rising sea levels, and a higher probability of dangerous weather phenomena. On the 9th of August 2021, United Nations during the climate panel released its most comprehensive assessment of climate change yet. The main key points were:

- It is undeniable that human activity including the exploitation of fossil fuels has led to the warming of the atmosphere, ocean, and land and rapid changes in them,
- Without immediate steps on cutting emissions, the temperature can rise over 3 °C by the end of this century compared to pre-industrial times,
- It is now 2.8 times more likely for severe heat waves to happen and it's going to double with every 0.5 °C temperature rise,
- According to the IPCC's most optimistic scenario, during summertime, the sea ice on the Arctic Ocean's surface would disappear totally at least once by 2050 as the region is warming twice as rapidly as the rest of the globe (Intergovernmental Panel on Climate Change, 2021).

The current pathway to achieving the Paris Agreement on cutting emissions by 2050 was also reviewed and the result showed that with currently implemented actions we are not going to meet emission goals for the next ten years. According to data provided by Climate Watch, greenhouse gas emissions are still rising, reaching all-time-high scores. The electricity and heat sector has risen the most of all contributors emitting nearly 15.6 gigatons of CO₂ equivalent in 2018, double the emissions in 1990. (Climate Watch, 2021) The second most influential sector is transportation with over 8.2 Gt of CO₂ equivalent. The expected growth in both sectors is directly related to higher fossil fuel consumption and therefore GHG emission unless any action is taken to transition to renewable solutions. Moreover, increasing oil and gas prices causing more expensive freight and energy fares are driving the shift to alternative fuels and electrification.

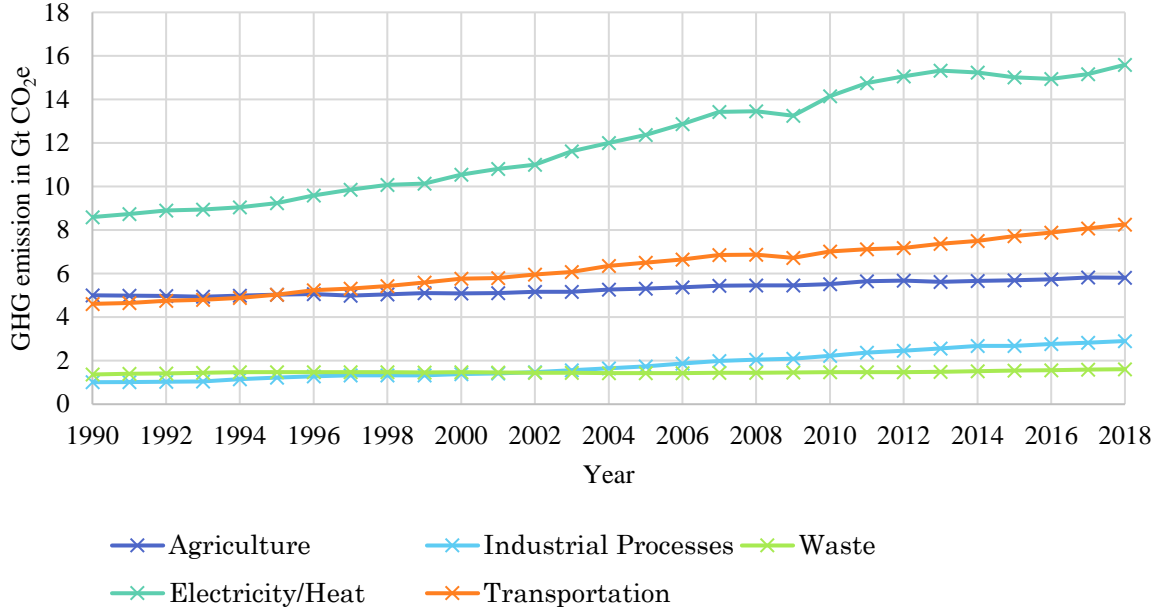


Figure 1. GHG emission in Gt CO₂e over the years (Climate Watch, 2021).

Table 1. GHG emissions in gigatons of CO₂ equivalent per sector over the years (Climate Watch, 2021)

Sector	1990	2000	2010	2018
Agriculture	4.998	5.094	5.515	5.818
Industrial Processes	1.010	1.388	2.223	2.903
Waste	1.364	1.467	1.465	1.607
Electricity/Heat	8.596	10.553	14.151	15.591
Transportation	4.609	5.770	7.012	8.258

The need for sustainable alternatives to fossil fuels has become an urgent matter and concern to most countries and businesses. Governments, as well as the EU, are financially supporting sustainable solutions to boost the innovation and energy transition. In order to achieve the future sustainability goals signed in the Paris Agreement, both the energy sector and transportation need to undergo a radical transformation, where not only electrification should be considered but also the deployment of clean high-energy fuels. (Intergovernmental Panel on Climate Change, 2021) This has brought interest to hydrogen and biofuel production from renewable resources. Clean hydrogen, or green hydrogen production processes are using either syngas sourced from biomass feedstock or renewable energy in electrolyzers to generate fully sustainable hydrogen. The major oil companies are now compromising investments in fossil fuels projects in favor of hydrogen solutions, as well as solar and wind energy projects for renewable energy production. Energy giant Shell announced in November 2021 that has joined forces with Norsk Hydro, a Norwegian hydrogen company to focus on the production and supply of green hydrogen

that would be generated using only renewable electricity. The company also has a partnership with a specialty-vehicle manufacturer to build a hydrogen-powered truck, thus significantly boosting the hydrogen economy in Europe and slowly diversifying its portfolio to achieve the net-zero emissions goal.

Hydrogen is a key element to enable the energy transition in the transportation and freight sector, providing clean energy and fuel sources in a sustainable matter. In order to produce renewable hydrogen, energy derived from solar, wind hydropower, and biomass have to be utilized in the water electrolysis process and only biomass can provide hydrogen in a direct way. Furthermore, biomass is frequently thrown into the environment or used directly to cover daily energy needs where energy efficiency is significantly lower than what might be attained utilizing it with contemporary technologies. As a result, using biomass to generate bio-hydrogen is a viable future technology that protects the environment while also providing a long-term sustainable source of hydrogen fuel. Moreover, the scope and possibilities of extracting hydrogen from biomass are immense and it may be adequate to meet current and future demands for its supply. In order to meet those goals, the commercialization of low-cost and high-efficiency manufacturing technologies needs to be developed.

1.1. The goal, objectives, and scope

The main goal of this master thesis is to develop simple, efficient and sustainable process of hydrogen production using biomass gasification, that could be used for commercial purposed based on economic feasibility. The thesis is based on three main objectives, which are following:

- the first objective is to distinguish influencing factors for hydrogen production,
- the second objective is to present the technological landscape of production process, putting an emphasis on biomass gasification,
- the third objective is to design process model for hydrogen production with chosen technologies based on the literature review and to study the potential for commercial production. The model design, simulation and calibration is conducted in ChemCAD software.

The review of currently know technologies is limited to gasification process, which thermochemical biomass conversion.

2. Hydrogen

As mentioned in the previous chapter, the energy transition process can be enabled by the production of high energy content fuel in a clean and circular way, where bio-hydrogen comes into place. In order to understand its crucial role, the hydrogen properties and specifications will be reviewed.

As the first chemical element in the periodic table, hydrogen is odorless, colorless highly combustible gas that is the fundamental building block for most elements in nature. The hydrogen atoms nucleus consists of a positively charged proton, as well as one unit of negative electrical charge held by an electron. In standard conditions, it is present as a gas of diatomic molecules H_2 where two atoms of hydrogen are connected with a covalent bond (Encyclopedia Britannica, 2020). The summary of the main hydrogen properties is presented in Table 2.

Table 2. Main properties of hydrogen.

Property Description	Value	Unit
Molecular formula	-	H_2
Molecular weight	g/mole	2.016
Density in standard conditions	kg/m ³	0.0838
Density in liquid state	kg/m ³	70.8
HHV and LHV	MJ/kg (liquid)	141.9 and 120
Boiling Point	°C	-252.74
Freezing point	°C	259.18

Table 3. Summary of the energy content of fuels in liquid and gas state. (Scragg, 2009)

Fuel	Energy content mass/ HHV [MJ/kg]	Energy content volume/ HHV [MJ/l]
Petrol	47.4	34.8
LPG	48.8	24.4
LNG	50	23.0
Hydrogen liquid	141.9	11.9
Hydrogen gas	141.9	0.012
Methane gas	50.2	0.039

When compared with currently widely used fuels (Table 3.) pure hydrogen in both gaseous and liquid phases has low energy per unit of volume. Therefore, it should not be considered as a fuel, but rather as a versatile energy carrier that has universal applications across transport, chemicals, and iron and steel production. With a variety of

renewable sources becoming a large part of the electricity generation mix, hydrogen is one of the few that can be used to store large amounts of energy for days, weeks, or months. The range of hydrogen possibilities also includes the ability to transport clean renewable energy from resources to regions with increasing energy demand for thousands of kilometers. However, there are various difficulties in handling, production, and storage of hydrogen, mainly related to flammability, which presents a challenge in hydrogen technology development. (Mazza, 2005).

High promises in hydrogen are related to the decarbonization of the transportation sector where it can be used to power up fuel cell engines or to substitute ordinary fuels with synthetic hydrocarbon fuels when combined with CO₂ (International Energy Agency, 2021). Although there is a plethora of ways to utilize hydrogen, it is only extensively used for ammonia, methanol, and domestic chemical manufacturing (Scragg, 2009). According to the IEA report, global hydrogen demand in 2019 was 75 Mt of H₂, whereas in Sustainable Development Scenario, provided also by IEA, it is estimated to grow up to 520 Mt by 2070. 30% of that would be used as a direct application in cars, trucks, and ships, while 20% of hydrogen use would go to synthetic kerosene production for aviation. The next 10% would be converted into ammonia fuels. All of that combined would cover almost half of the transportation fuel demand in 2070, leading to the decarbonization of this sector.

On the production side, currently, the hydrogen production routes are mainly based on fossil feedstock. In 2019 pure hydrogen was obtained in three quarters from natural gas and the next quarter from coal, the rest mainly from oil. Only 4% of world hydrogen production is coming from renewable sources (Deason, 2010). Due to that, through hydrogen production 800 Mt of CO₂ was emitted, accounting for approximately 2% of global CO₂ emissions from the energy sector (International Energy Agency, 2021). This limitation is mainly caused by the cost of mature technologies for hydrogen production. As indicated by IEA, currently there are only two adopted technologies for hydrogen production: electrolysis and natural gas reforming (left side on Figure 2). Looking at the application side, there are much more ways for hydrogen utilization, due to mature ammonia production technology but over 60% of stated ways of hydrogen use are either in the demonstration or prototype phase (right side on Figure 2). Therefore, meeting the sustainability goals is highly dependent on the development rate of technologies for both production and utilization. This has been mentioned in 1973 by Gregory when the term

“hydrogen economy” was used for the first time. The article mentioned hydrogen as a future fuel for transport and energy carrier for storage.

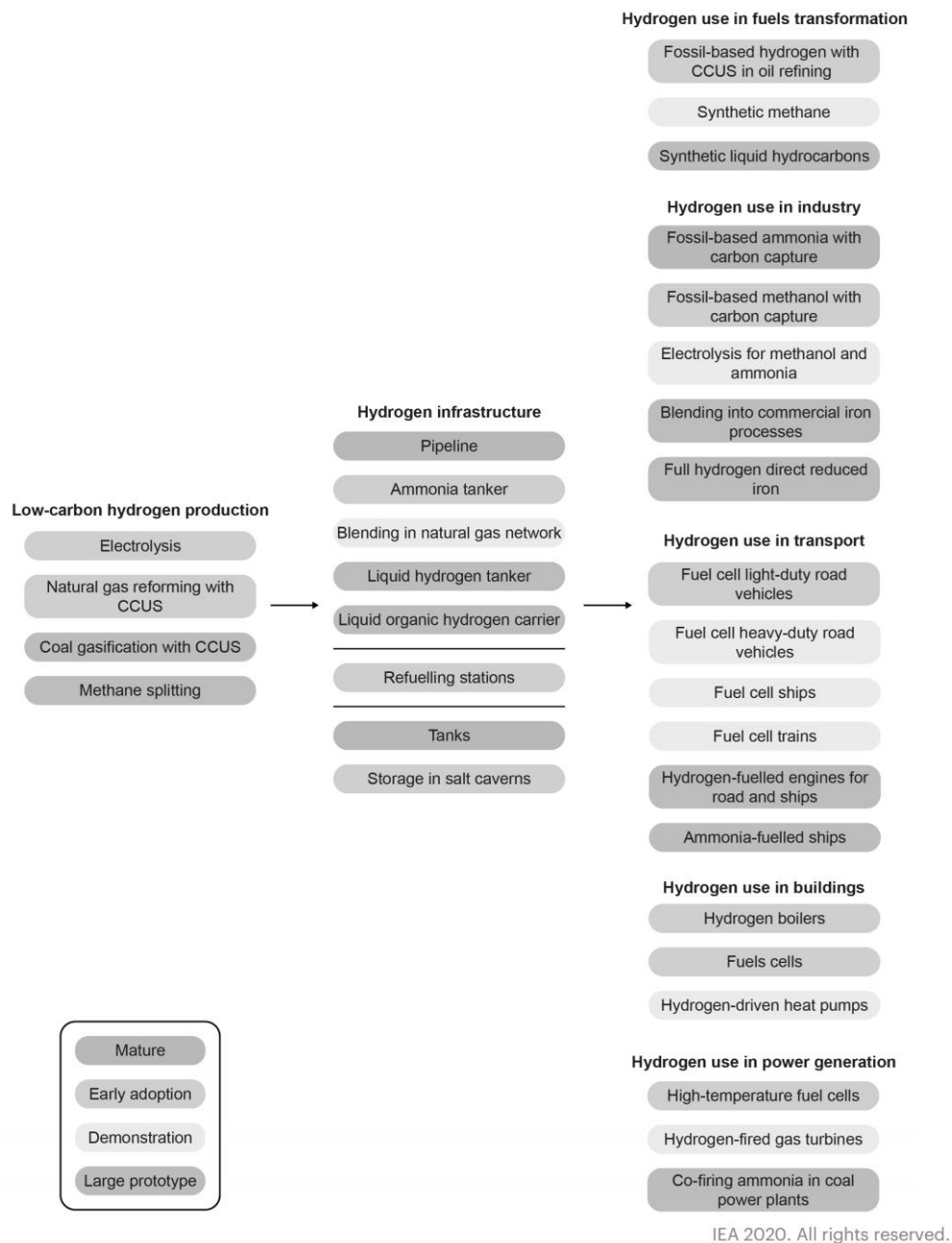


Figure 2. Technology readiness level of technologies along the low-carbon hydrogen production (International Energy Agency, 2021)

2.1. Hydrogen application

From a commercial standpoint, hydrogen is expected to be a future energy carrier but first and foremost it is currently one of the main chemical products used in a variety of industrial processes. Both perspectives must be addressed in order to provide a useful overview of hydrogen uses. The highest requirement for hydrogen is currently driven by a

variety of industrial chemical processes, mainly refining. In 2018, the global demand for hydrogen reached the value of 38,2 Mt a year (International Energy Agency, 2021). Some processes need hydrogen as feedstock (ex. hydrocracking, hydrotreating), while others produce it as a byproduct (in catalytic or thermal cracking). The overall balance is negative, thus hydrogen has to be supplied. Due to two major causes, the refining industry has recently seen an increase in the need for hydrogen: petroleum fuel specifications have become more rigorous and the oils used in refining processes have become heavier (Azzaro-Pantel, 2018).

The second largest sector today in terms of hydrogen need is the fertilizer industry, which uses it for ammonia production. The global demand in 2018 has accounted for 31,5 Mt a year. The other applications of the industrial sector are very low in demand but involve processes like metallurgy, methanol production, and food production, as well as new fuel production.

Mobility applications of hydrogen are another contributor to growing hydrogen demand. Very often it is associated with only passenger cars, however, it covers a wide spectrum of land vehicles (trucks, busses, forklifts), marine vessels and ferries, as well as light aircraft. The maturity of each application varies, but for example, forklift trucks have proven their worth in terms of prices and autonomy, which resulted in the large acceptance of those types of vehicles in warehouses. Companies like Ikea, FedEx, and Coca-Cola have successfully installed them in their facilities (Denhoff, 2016). To decarbonize the constantly growing logistics and transportation market, Maersk (an integrated shipping company) invested in a methanol-powered vessel, which is going to be fueled with e-methanol derived from clean hydrogen and carbon dioxide. The company's mission is to implement the first carbon-neutral cargo ship by 2023. To achieve that they have already secured 10.000 tons of hydrogen base fuel (Maersk, 2021).

Hydrogen can also be applied in stationary applications, where it is used to power fuel cells generating electricity. This mainly refers to energy storage applications where hydrogen plays the role of energy carrier but can also be applied as an electricity source in off-grid locations and microgrids (Lamas, et al., 2015).

Overall, the application of hydrogen use includes:

- Refining industry for fossil fuel processing and petrochemicals,
- Chemical industry for ammonia manufacturing,
- Hydrogenated fats and oil production in food industry,

- Metal production and fabrication,
- Mobility vehicles fuel (fuel cells engines) and component of transportation fuels (methanol engines),
- Stationary application for power generation and energy storage.

2.2. Hydrogen transportation and storage

The storage and transportation of hydrogen are strongly connected. Ships, lorries, trains, and airplanes can transport hydrogen in bulk containers, but it can also be transported continuously through pipelines. Existing infrastructure built for natural gas transport can be used for hydrogen transportation on long and short distances, both as a hydrogen gas itself or as a mixture with natural gas (Witkowski, et al., 2018). Nevertheless, in any of these cases hydrogen transport infrastructure requires a storage system such as pressurized tanks. In ambient conditions, hydrogen occupies a significant space of 11 m³/kg of storage, which is 3,000 times more when compared to natural gas with the same amount of energy. Hence, the biggest challenge in storage is to decrease the volume of the gas through compression, liquefaction, and other methods for utilities in transport and storage applications. Looking at the simplified phase diagram of hydrogen it can be found that its molecule can exist in a variety of configurations depending on temperature and pressure (Figure 3)

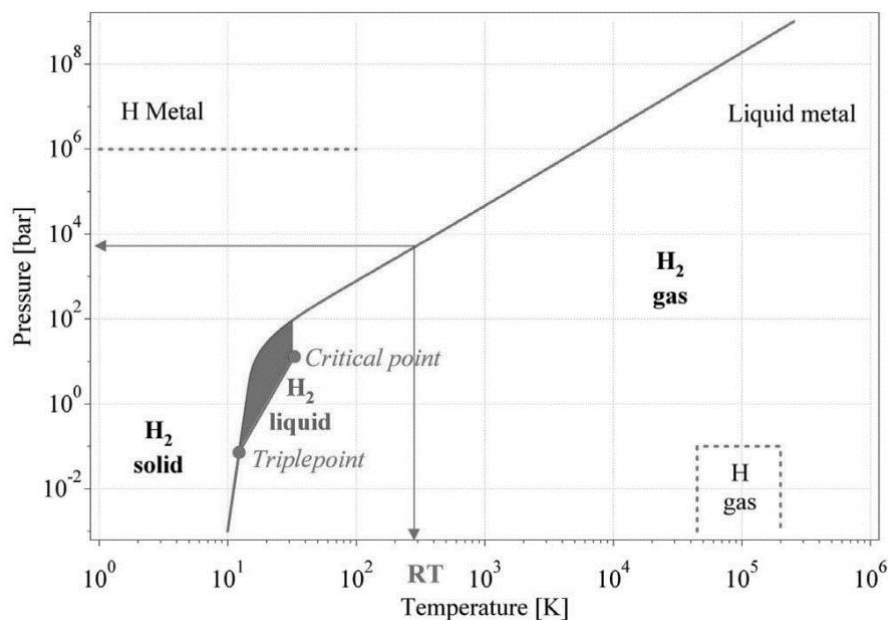


Figure 3. A primitive phase diagram from hydrogen. Adopted from (Züttel, 2003)

At a low temperature of -262 C° hydrogen has a solid form with a density reaching 70.6 kg/m³, whereas, at 0 C° and 1 bar pressure, it's a gas with a density of 0.09 kg/m³

which is maintained in ambient conditions. The liquid form of hydrogen can be accomplished by reaching temperature and pressure parameters corresponding to the small zone between the triple and critical points. The density there is 70.8 kg/m^3 at -273 C° (Züttel, 2003). In superficial high pressures, it is speculated that hydrogen is at a solid metal state. In 2017 Harvard researchers claimed to create metallic hydrogen at a pressure of 495 GPa, which could have been a breakthrough in hydrogen economy evolution, but it was never accepted by the scientific society (Harvard Gazette, 2017).

Considering hydrogen properties there are four main techniques that can be used for storage, which are compressed gas, cryogenic liquid, metal hydride, and carbon adsorption (Calise, et al., 2019). In terms of maturity, the first two methods are commercially developed. The interstitial metal hydride method is at an advanced stage, but it needs further research to compete in the market. Although the carbon adsorption method is not yet a mature process, it is viewed as a viable option if the current research and development objectives are accomplished. For each of those methods, the application varies, as well as the amount of hydrogen that can be stored (Table 4).

Table 4. Hydrogen storage methods summary (Calise, et al., 2019).

	Volumetric storage density [kg/m ³]	T [K]	P [bar]	Description	Advantages	Challenges
Compressed gas	<40	273	800	Compressed hydrogen gas, lightweight, high-pressure cylinder	Allows for rapid fueling. Commercially available.	Tank material strength capabilities and weight Relativity low capacity
Liquid	70.8	21.5	1	Liquid hydrogen, continuous loss of few % per day at RT	Commercially available. Cheaper in storage and transportation.	Liquefaction is both high time and energy consumption process Safety concern over vacuum jacket layer in tank
Physisorption	20	77	100	Physical adsorption by porous materials like carbon with very large specific area, fully reversible	Fully reversible	+ low cost materials thermal management
Interstitial Metal hydrides	150	273	1	Atomic hydrogen occupies interstitial sited fully reversible	Fully reversible, very high capacity	Metals are heavy

Complex hydrides	150	>100	1	Complex compound [BH ₄] ⁻ or [AlH ₄] ⁻ desorption at elevated temperature	High capacity	High operating temperatures for hydrogen release
Chemical hydrides	>150	273	1	Thermal decomposition of chemical hydrides, not directly reversible	Low operating cost considering hydrogen volume	Lack of energy efficient regeneration methods for storage material

Although storage of hydrogen presents more challenges, the transportation from the production facility to end users is also a key element for hydrogen economy deployment. The mode of delivery varies depending on the transportation range, volumes, and conditions. For shorter distances of 150 up to 300 km, hydrogen is transported as gas in high-pressure tanks and tube trailers. In case of longer distances, it can be liquified and transported in insulated, cryogenic tankers.

2.3. Production routes and raw materials

Currently, 96 per cent of world's consumed hydrogen is derived from fossil fuels through hydrocarbon reforming as the primary production mechanism. Other production routes based on renewable resources include water splitting and hydrogen production based on biomass, which can be classified to thermochemical or biological routes. All the methods are presented on Figure 4 and main technologies are described in Table 5.

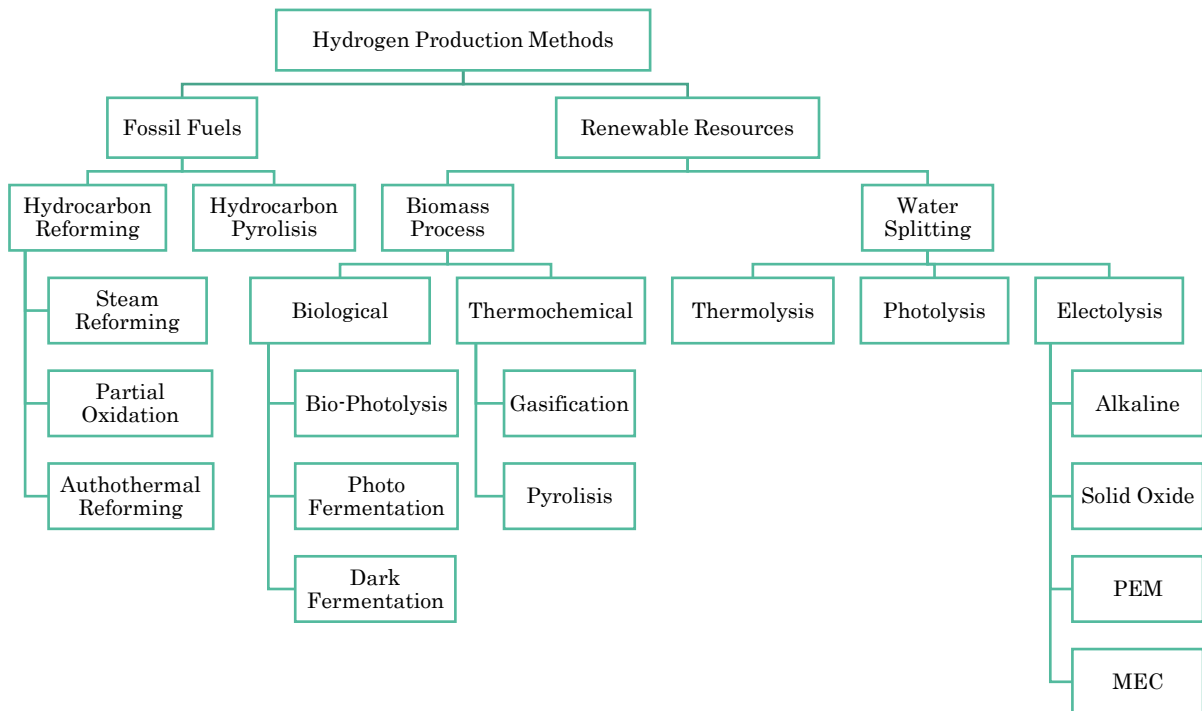


Figure 4. Hydrogen storage methods summary (Calise, et al., 2019).

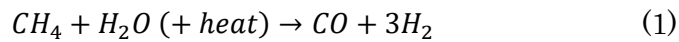
Table 5. Description of hydrogen production methods in terms of advantages and disadvantages, efficiency and cost (Züttel, 2003) (Calise, et al., 2019) (Balat & Kirtay, 2019)

	Hydrogen production method	Advantages	Disadvantages	Operational Efficiency	Total Cost [\$/kg]
Hydrocarbon Reforming	Stream Reforming	Developed technology and existing infrastructure	High CO and CO ₂ production, unstable supply	74-85	2.27
	Partial Oxidation	Established technology	Production of heavy oils and coke	60-75	1.48
	Auto-thermal Reforming	Well established, existing infrastructure	CO ₂ production, Need of using fossil fuels	60-75	1.48
Biological Biomass Process	Bio photolysis	Consumed CO ₂ and produced O ₂ , mild operating conditions	Low yield of H ₂ , sunlight and large reactor is needed, sensitive to O ₂	10-11	2.13
	Photo Fermentation	Recycles wastewater, CO ₂ neutral	Very low yield of H ₂ , sunlight and large reactor is needed, sensitive to O ₂	0.1	2.83
	Dark Fermentation	Simplicity, no light required, no limitation O ₂ , recycles wastewater	Low yield of H ₂ , very large reactor needed, fatty acid elimination	60-80	2.57
Thermochemical Biomass Process	Pyrolysis	A lot of cheap feedstocks available, CO ₂ neutral	Unstable production of H ₂ due to feedstock availability, tar formation	35-50	1.47-2.57
	Gasification	Higher H ₂ production than in pyrolysis, plenty of cheap feedstocks available, CO ₂ neutral		30-40	1.44-2.83
Water Splitting Process	Thermolysis	CO ₂ neutral, sustainable, O ₂ as byproduct, abundant feedstock	Hight capital cost, toxicity, corrosion	20-45	7.98-8.40
	Photolysis		Low efficiency on photocatalytic material	0.06	8-10
	Electrolysis	Established technology, CO ₂ neutral, O ₂ as by product, existing infrastructure	Storage and transportation problems	60-80	5.55-10.30

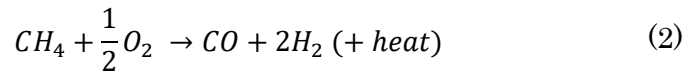
Hydrocarbon reforming

Hydrogen produced from fossil fuels is mainly achieved in steam reforming process, autothermal reforming, or partial oxidation with the use of natural gas. In the steam reforming process (1), hydrogen is produced with carbon monoxide and a small amount of CO₂ in presence of high-temperature steam (700-1000 °C) and catalyst. Autothermal reforming is based on the same reactions, but it uses a portion of natural gas to raise the temperature of the process gas before it reaches the catalyst. In partial oxidation (2), hydrocarbons are reacting with a limited amount of oxygen forming primarily carbon monoxide and hydrogen. Following both processes, water-gas shift reaction (3) and swing adsorption are used to raise the ratio of hydrogen to carbon dioxide and then remove carbon compounds for pure hydrogen fuel. All of them above are mature and efficient technologies nevertheless, they are based on unsustainable resources and have high amounts of CO and CO₂ as byproducts.

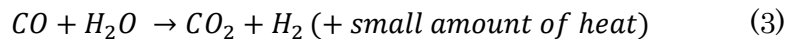
Steam reforming reaction:



Partial oxidation of methane reaction:



Water-gas shift reaction:



Water splitting process

From water splitting methods, electrolysis is the most capable method as it uses water as a reactant and produces only oxygen as a byproduct. In this process, the H₂O molecule is dissociated into pure hydrogen and oxygen under an electrical current. There are three types of electrolysis depending on electrolyte, ionic agents, and process conditions (alkaline, solid oxide, PEM water electrolysis, and MEC microbial electrolysis). As it is a high-energy intensity process, renewable energy must be supplied to achieve sustainable hydrogen production. Currently, in industrial electrolyzes we can observe the efficiency from 52 to 85% depending on the size and type of apparatus (Kraussler, et al., 2018). Electrochemical conversion is still considered far off from feasible for scale-up application, due to its high energy intensity (approximately 45kWh/kg of H₂), which results in a high cost of hydrogen (Jun Chi & Hogmei, 2018). Thermo- and photolysis are based on the same

principle but use either high-temperature or sunlight to decompose water molecules. Both processes need transition metals in form of catalysts to support the chemical reaction (Rand, 2011).

Basic reaction of water electrolysis.



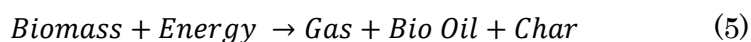
Biological biomass process

Biological hydrogen production methods leverage microbes (bacteria and microalgae) activity which can convert water and organic matter into hydrogen. In the process, microorganisms are breaking water molecules using catalytic properties of two essential enzymes, hydrogenase and nitrogenase. Biological hydrogen routes can be categorized based on the processes included – photolysis, dark-fermentation, photo-fermentation, and CO gas-fermentation. In bio-photolysis, microalgae and cyanobacteria have the ability to absorb solar energy and produce hydrogen from water and carbon dioxide. Photo-fermentation uses purple non-sulfur (PNS) bacteria which utilize solar energy to generate hydrogen from diverse carbon sources. On the other hand, dark fermentation takes advantage of anaerobic bacteria which decompose organic matter such as agricultural wastes and wastewater producing hydrogen. CO gas-fermentation is the bioconversion of carbon monoxide (WGS reaction) by photosynthetic bacteria under anaerobic conditions (Silva, et al., 2018). All of those processes are still at the research and development stage. The main challenges to further deployment of those technologies are related to both possibilities of scaling up the process and improving yields, as well as developing new strains of feedstock bacteria and algae that would use the resources (sunlight, organic matter) more efficiently (Akhlaghi & Najafpour-Darzi, 2020).

Thermochemical biomass process

Thermochemical processes of hydrogen production are the most effective and fast when biomass is used as a resource (Department of Energy, n.d.). While water splitting and biological routes are difficult to scale up and provide limited amounts of hydrogen, gasification and pyrolysis are gaining popularity (Barbuzza, et al., 2019). The main principle in both processes is the conversion of the biomass feedstock into gaseous biofuel or liquid biofuels which can be processed to pure hydrogen, but the conditions and process requirements are different (Balat & Kirtay, 2019).

In the pyrolysis process, the biomass is thermally decomposed (at around 500 °C) in an oxygen-free environment to solid, liquid, and gaseous fractions. When used specifically for hydrogen production pyrolysis should be carried out at a higher temperature of around 700 °C, where tar cracking is taking place improving the yield of H₂ production and overall gas quality. At the same time, produced bio-oil should be processed by steam gasification for H₂-rich gas production. If pyrolysis is running at a temperature lower than 700 °C, a catalyst should be applied to the reactor for tar cracking. There are several pyrolysis technologies that can enrich hydrogen production and based on the recent reviews, fast pyrolysis of plant biomass at above 800 °C is the most efficient technology, where only 10% of solid material is produced and around 60% is converted into syngas (CO and H₂) (Kalinci, et al., 2009).



In comparison with pyrolysis, biomass gasification process requires higher temperature (from 800 °C to 1200 °C) and controlled presence of oxidizing agents, such as steam, air, oxygen, or nitrogen. The amount of oxidizing agent is limited to avoid complete combustion. As a result, mostly gaseous products are obtained which require less post-recovery and upgrading work, therefore gasification is preferred over pyrolysis for hydrogen production. Depending on the oxidizing agent we can distinguish three main gasification types – air gasification, oxygen gasification, and steam gasification (Xu, 2018).

Biomass conversion happened through four primary processes (Figure 5.), (i) drying, (ii) pyrolysis, (iii) partial combustion and (iv) gasification of volatile products (Molino, et al., 2016).

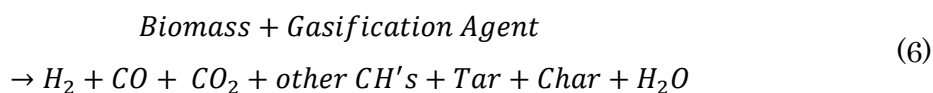


Figure 5. Process steps in gasification.

During those steps, feedstock undergoes a series of physical and chemical changes that result in carbon monoxide CO and hydrogen H₂ mixture (syngas) and accompaniment gases, carbon dioxide CO₂, and nitrogen. In gasification, the quality of produced hydrogen

depends on biomass properties, used catalyst, working parameters, and technology chosen for the process. The gasification process will be described in depth in Chapter 4.

There are different types of gasification and pyrolysis, depending on process conditions and apparatus used, but based on the extensive research made, there are three main routes specifically oriented for hydrogen production, steam gasification, supercritical water gasification, and fast pyrolysis (Table 6). According to gathered data on the efficiency and advantages of the process, steam gasification was chosen for the purpose of this thesis (Ebadi, et al., 2019) (Gai, et al., 2018) (Shahbaz, et al., 2017).

Table 6. Summary for three main hydrogen production technologies using thermochemical processing of biomass

	Average H ₂ production	Advantage	Disadvantage	Challenge
Steam gasification	without catalyst: 4g with catalyst: 7g	Suitable for large scale industrial production, high gasification rate, low ash production	Product gas separation and purification	Decrease tar content, reduce catalyst deactivation, reduce cost.
Supercritical water gasification	without catalyst: 3g with catalyst: 5g	High H ₂ conversion with low tar and coke formation	Recycling of alkaline catalyst, strict operation conditions	Technological development, reduce energy demand.
Fast pyrolysis	without catalyst: 2g with catalyst: 3g	O ₂ free	High energy requirement with low H ₂ yield.	Scale up process, reduce catalyst deactivation

3. Biomass

Biomass is defined as organic matter derived from plant or animals, and it is mostly composed of carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and trace amounts of sulfur (S).

It can be referred to as sustainable and carbon-neutral resource, as plant biomass growth is driven by the photosynthesis process which uses ambient CO₂. It is then released back into the atmosphere through combustion or wood degradation (World Bioenergy Association, 2012)

According to extensive research made on the biomass sources, it can be expected that these resources may be among the primary sources for energy in the future once they are

exploited under proper supervision. Alongside development of the biomass cultivation routes, its cost may be more competitive when compared to fossil fuels, considering the CO₂ penalties which may be soon imposed to fossils. Additional advantage of the biomass resource for hydrogen production is its abundancy all over the world. The current challenge in biomass use for gasification is the cost of the feedstock compared to energy equivalent, and high capital cost. (Parthasarathy & Narayanan, 2014)

3.1. Biomass Sources

Depending on the source, biomass can be divided into two categories – primary and waste biomass. Primary biomass is obtained directly from botanical resources such as plants, wood, and crops. Waste biomass consists of all types of waste with high organic content which includes municipal solid waste, agricultural waste and industrial wastes (sawdust) (Basu, 2010).

Table 7. Sources of biomass (Pfeifer, et al., Science in Thermal and Chemical Biomass Conversion,)

Primary (virgin) biomass	Woody biomass	forest wood, grasses
	Aquatic	algae, water plant,
	Energy crops	cultivated corn, sugarcane
Waste biomass	Agricultural waste	livestock manure, crop residue
	Municipal waste	organic solid waste, sewage landfill gas
	Industrial waste	sawdust, waste oil
	Forestry waste	bark, leaves

Waste biomass is seen as a viable option for heat and power generation and attractive alternative to extensively used fossil fuels. The circular approach of transferring the waste back to a usable product can reduce emissions of GHG and help mitigate climate changes. Based on the characteristics of food waste, it is a feasible feedstock especially for supercritical gasification process, as it contains high amount of organic compounds, such as carbohydrates (cellulose, sugars), proteins and oils, and has high moisture content (Zheng , et al., 2018).

Agricultural waste usually has lower calorific value and higher ash and nitrogen content, nevertheless it is a potential feedstock for thermochemical conversion and fertilizer production. Using crops feedstock can limit the emissions from open field burning as well as improve a socio-economic factor by driving income in rural areas where it is sourced from.

Virgin biomass utilization is highly dependent on various conditions specific to a location where the feedstock is sourced from, sustainable forest and crop management and harvesting. Under properly fulfilled conditions worldwide biomass potential is estimated for 150 EJ in 2035, where 52% of it is sourced from forestry industry (wood fuel, forestry residues, wood industry byproducts) (World Bioenergy Association, 2016).

Based on the research made by A. Sharma et al, among different types of agricultural waste and virgin biomass, the highest hydrogen content (18 vol%) in produced gas was found in pine gasification, and at the same time, it had the highest content of carbon monoxide. Another sample with high hydrogen content was cypress mulch, where the content of H₂ in produced gas reached 16 vol% and had low CO content of only 6 vol%. Those two were also characterized by the higher HHV of 18.5 MJ/kg and 16.8 MJ/kg respectively, closely followed by switch grass whose HHV is 16 MJ/kg. Out of all tested types of biomasses which additionally included corn, hardwood, bagasse, manure and litter, pine was preferred for gasification processes thanks to high both H₂ and CO production. (Sharma, et al., 2017)

3.2. Biomass Properties

The main biomass feedstock properties affecting the performance of a gasification process are type of biomass, particles size and moisture content (Fremaux, et al., 2015).

The composition of biomass is one of the most important pieces of information to assess the compatibility of chosen process technologies. For this purpose, two analytics methodologies are used, the ultimate analysis and the proximate analysis. In the ultimate analysis, basic elements of the feedstock are analyzed. For biomass, the overall equation including ash and moisture content can be expressed as in equation below, where all the elements represent the mass percentage content in feedstock.

$$C + H + O + N + S + Cl + Moisture + Ash = 100\% \quad (7)$$

The proximate analysis is based on estimation of volatile matter, fixed carbon, moisture, and ash composed in biomass. Volatile matter represents the vapor that is released during fuel heating, whereas fixed carbon is a solid carbon content which remains after the pyrolysis process.

$$Fixed\ carbon + Volatile\ matter + Moisture + Ash = 100\% \quad (8)$$

Another important characteristic of biomass feedstock are heating value, ignition temperature and specific heat capacity, which are directly related to thermodynamics of

the gasification process. Specific heat capacity is influenced by moisture content of the biomass, which negatively influences the dynamics of the gasification process. Heating value indicates the maximum heat that can be released during complete combustion under standard conditions.

4. Process description of hydrogen production through biomass gasification

4.1. Biomass pretreatment

Before biomass or organic waste may be used as feedstock for gasification process, pretreatment is usually required for the feed to meet necessary specifications and ensure the efficiency of the process. These specifications may differ depending on type of feedstock, type of the gasifier used as well as final product requirement.

Pretreatment of the biomass before gasification process can include processes such as cutting, crushing, and drying, which are ruled by mechanical properties and moisture content of the fuel. Calorific value and volatile matter have significant impact on the process conditions. Density of fuel is equally important as it plays important role of dictating the residence time in the gasifier. On the other hand, moisture content can influence the heating value and therefore gasification efficiency. Wood biomass can have from 30% to 60% of moisture content. It can undergo a drying process to lower the moisture levels down to 10-15%. With such parameters it is easier to sustain gasification process and the requirement for supplemental fuel is reduced. Furthermore, biomass drying prior the gasification allows for size reduction of gasifier and feeding system which is beneficial from cost perspective (Krishna, et al., 2019).

In research work made by Alamia, for biomass, the energy required to evaporate the moisture entirely and heat up the biomass, which has LHV of 19 MJ/kg and moisture content of 50%, is around 22% of its LHV. However, once biomass is dried to 10% of moisture content before the gasification, the energy need during gasification process can be minimized by 2.5% (Alamia, et al., 2010). As a result, it is desirable from an energy standpoint to connect the drying system with gasification, allowing waste heat at lower temperatures to be utilized. The heat necessary for moisture evaporation can be recovered internally and added with additional drying agents. Integrated system of drying and gasification was explored by Heyne & Simon, in which steam, flue gas and air are employed as drying agents in a 100 MWh gasification plant. It has been demonstrated that steam drying performs better, accounting for almost half of the energy required to

dry the biomass from 50% moisture content to 10%. Nevertheless, there are certain precautions that need to be taken in biomass drying, since there is a threat of explosion and fire, particularly in the case of air drying, where accumulation of volatile compounds may take place (Heyne & Simon, 2009).

4.2. Gasification technology

In general, gasification follows four main steps as mentioned in chapter 2, which are:

- Drying: reduction of the moisture content in biomass under high temperature
- Pyrolysis: separation of the biomass compounds into volatiles and char
- Combustion: by which the heat needed for entire process is provided through oxidation of gasifying medium
- Gasification/Reduction: where syngas production takes place under reduced of air provided (less than theoretical stoichiometric value) through series of chemical reactions presented on the Figure 6 (Basu, 2010).

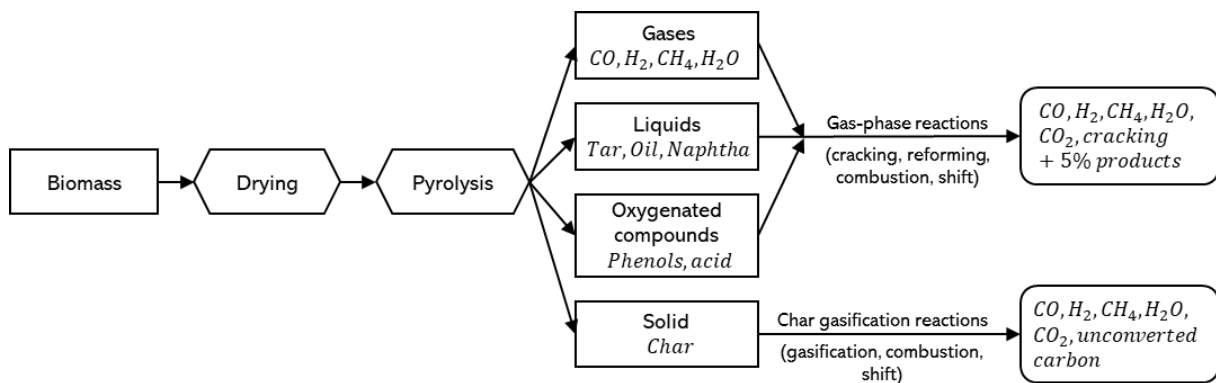


Figure 6. Gasification process path. (Basu, 2010)

Moreover, gasification process is running at a high temperature of up to 1200 °C, which affects the final products of physical and chemical transformation of feedstock. Volatiles and solid residues are created, and final product ratio is highly depended on temperature, pressure, reactor type, and fuel composition. There are different types of gasification reactors, where three main types are fluidized bed reactor, moving bed reactor and entrained flow reactor. Choice of reactor is driven by type of feedstock and required process conditions, as it is directly related to thermodynamic and fluid mechanics governing laws. Depending on the gasifier, four main gasification processes might take place in different positions in the reactor. For the most ubiquitous reactor, downdraft gasifier, position of reaction zones, together with temperature are presented on Figure 7.

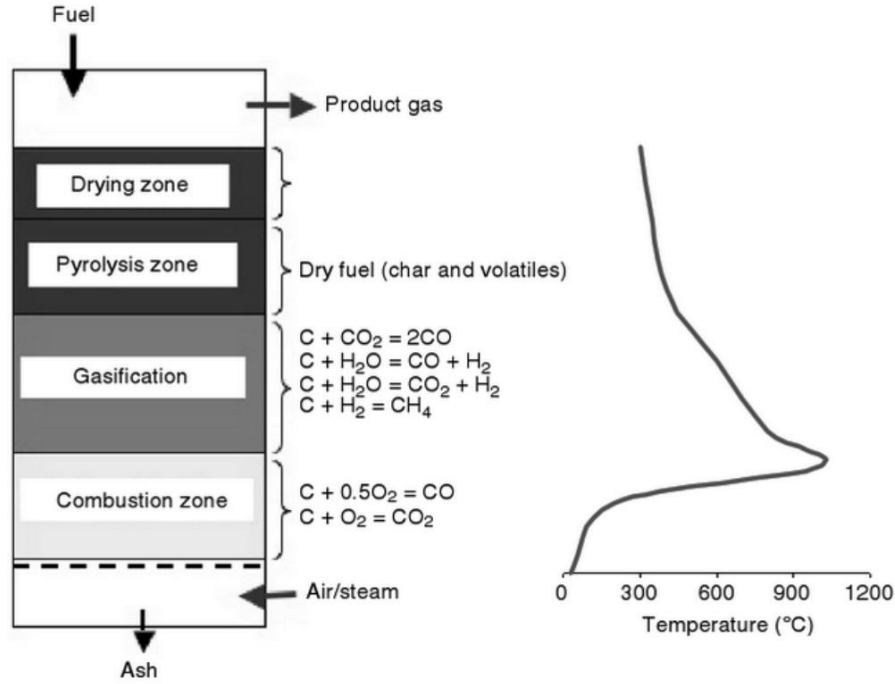


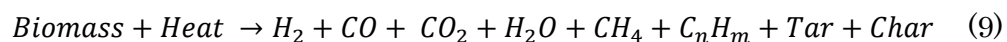
Figure 7. Gasification process sequence and temperature level in moving bed-reactor gasifier. (Basu, 2010)

4.2.1. Drying

The moisture in biomass forms water vapor in the first zone in gasifier at a temperature of 100-250 °C. This conversion is performed thanks to the heat transfer from oxidation/pyrolysis zone to drying zone. The surface moisture from biomass particles evaporates first and it is followed by inherent moisture evaporation. The generated water vapor is employed in reduction reactions, such as water-gas shift reaction to raise the hydrogen yield. (Susastriawan, et al., 2017)

4.2.2. Pyrolysis

Once the moisture evaporates completely inside the gasifier, the pyrolysis process occurs. The feedstock is thermally decomposed in absence of gasifying agent. At a temperature of roughly 400 °C degrees, up to 80 per cent of the total biomass weights is devolatilized, composing mixture of various gaseous compounds (hydrogen, carbon mono- and dioxide, hydrocarbons) together with tar and solid char (Kaushai & Tyagi, 2017). In majority, the reactions taking place in pyrolysis zone are endothermic.

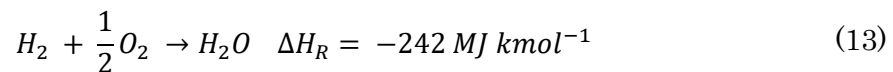
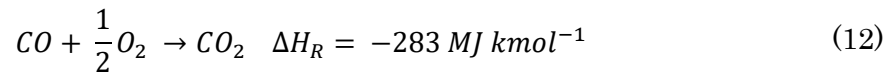
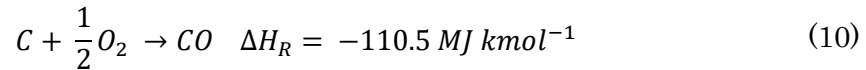


The least favorable process during pyrolysis phase is tar formation. Composition of tar is complex and includes various aromatic hydrocarbon, which can later cause a slugging in the system (Susastriawan, et al., 2017). Exact components of tar and the rate

of its production is affected by factors such as operating temperature and feedstock. Within the temperature range from 400 °C to 700 °C, biomass produces primary tar, which consists of oxygenated organic molecules (acetic acid, methanol etc.) as well as aromatic compounds (benzene, toluene) (Font Palma, 2013).

4.2.3. Oxidation

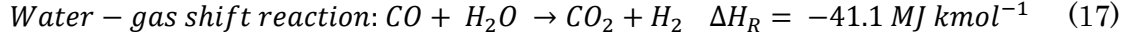
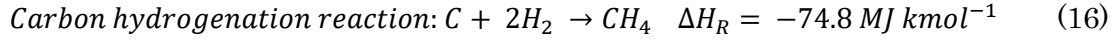
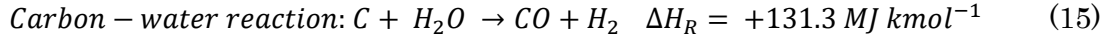
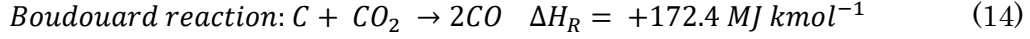
Third zone in gasifier is where the reactions with oxygen are taking place (partial oxidation where oxygen is entered to reactor chamber in amount less than stoichiometric value). Range of temperature is higher compared to pyrolysis and can reach values from 600 °C to 1400 °C. Firstly, at temperature range from 600 to 900 °C partial oxidation occurs. Complete oxidation reactions are taking place at 800 °C to 1400 °C. During oxidation reactions, heat is released in the process together with main products of CO₂ and H₂O. As most of the reactions in oxidation zone are exothermic and following processes (endothermic) derive the heat from this zone. Few of specific to gasification reactions are as follows:



The type of oxidizing agent chosen for gasification influences the main reactions, giving different results of products. The simplest air gasification in autothermal process results in production of N₂ rich gas and therefore is of low heating value. Better result can be achieved by using pure oxygen as medium, where output gas can have heating value of 12-28 MJ/Nm³. In order to support gasification with pure oxygen input, it needs to be generated in efficient manner.

4.2.4. Reduction

The final step in gasification process is reduction, where multiple reactions occur to produce CO and H₂, also known as synthesis gas. Several other unfavorable gases such as methane, ethane and higher hydrocarbons that contribute to tar formation are being reduced in this zone. Desirable temperature should remain around 1000 °C range, under lower pressure. The following reactions occur in reduction zone:



The water-gas shift reaction (17) contributes to increasing hydrogen content in syngas, while the methanation (carbon hydrogenation) reaction contributes to methane production. These reactions are both exothermic, which means lower temperatures are preferred from thermodynamics standpoint. (Susastriawan, et al., 2017) (Sansaniwal, et al., 2017).

4.2.5. Gasification agent

Gasification process requires gaseous medium that will react with solid carbon and hydrocarbons to convert them into low molecular gases (CO, H₂). There are four main gasification agents used: (i) oxygen, (ii) steam, (iii) air, and their mixtures, as well as (iv) carbon dioxide which is also being researched upon (Basu, 2010). The choice of agent is fully based on product gas requirements. Usually, higher values of hydrogen production are reached when using respectively steam, oxygen, or oxygen-enriched air as a gasification agent for wood biomass gasification. Increasing temperature of the process leads to lower hydrogen production rate for all agents, however the drop is relatively flat for steam gasification. Therefore, for high temperatures of over 1100 °C steam is preferred as a gasification agent. Same goes for biomass feeding rate, where hydrogen production rate is slightly affected in steam gasification (2.2% drop for biomass feeding rate from 25 kg/s to 55 kg/s), while in other cases the impact is significant (from 7% to 8%). (Shayan, et al., 2018)

Table 8. Heating value of product gas based on gasification agent. Adapted from (Basu, 2010)

Gasification agent	Heating Value (MJ/Nm ³)
Air	4-7
Oxygen	12-28
Steam	10-18

4.3. Types of gasifiers

There are numerous developed gasifying technologies proven by the industrial application. Each one of them includes a gasifier – a reactor unit, where fuel and gasifying agent are feed into, mixed with additives or a catalyst, and where previously mentioned reactions are taking place. The main purpose of the gasifier is to maintain the product gas

production at the steady state. Along the road of gasification technology development, there are several types of gasifiers, which are different depending on how feedstock and gasifying agent come together in contact. Based on this approach, we can distinguish three main types of gasifiers: fixed bed, fluidized bed, and entrained flow reactors (Figure 8).

4.3.1. Fixed bed technology

Fixed bed technology is the most used and mature gasification technology, thanks to simple design and working principles. The feedstock is usually entering from the top of the gasifier, moves down through the gasifier chamber and lands on a fixed grate. As the fuel moves down in the reactor, fixed bed reactors are alternatively called a moving bed reactors. Construction of fixed bed gasifier is simple, without moving parts, thanks to which it can be built in small sizes and at low-cost. However, mixing and the heat transfer in the reaction chamber are at a low level which yields nonhomogeneous distribution of temperature across the reactor. As a result, during gasification, feedstock is prone to agglomeration which causes drop of efficiency. (Basu, 2010)

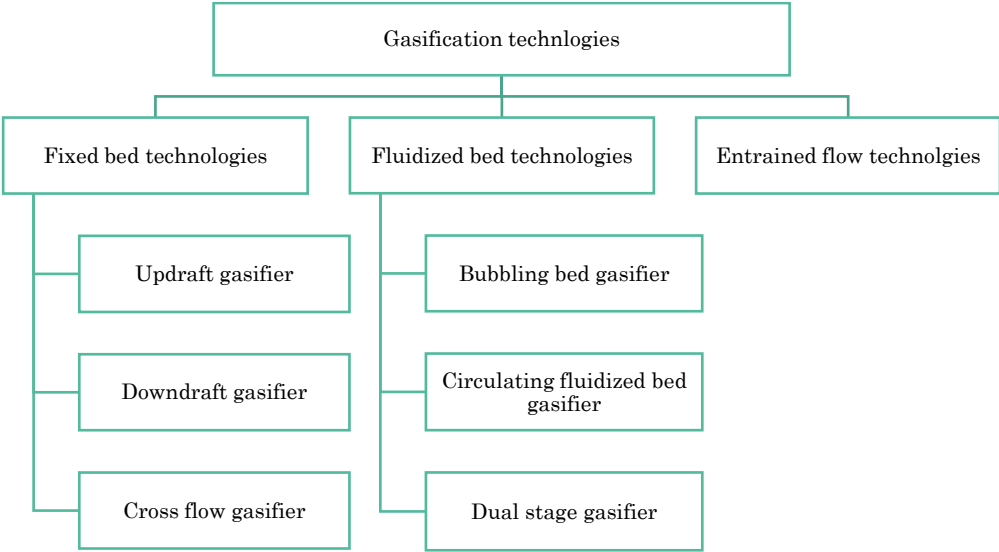


Figure 8. Main gasification technologies. Adapted from (Hossain & Charpentier, n.d.)

In the updraft gasifier (Figure 9.) gasifying agent is fed from the bottom of the reactor, and it flows countercurrent to the biomass. Produced gas leaves the reactor near the top, while ash is discharged down through the grate, which very often uses moving mechanism to support ash removal. This type of gasifier is most suitable for feedstock with high ash (up to 25%) and moisture content (up to 60%) low volatile fuels. In case of highly volatile fuels, updraft gasifier cannot be used due to significant tar generation (from 30 to 150g/nm³). As the flow of the gasifying agent is in the opposite direction to the fuel, the

temperature of the product gas reaches up to 500 °C, which eliminates the need of using costly gas coolers.

In the downdraft gasifier, the gasifying agent enters near the top of the reactor and has co-current flow with feedstock. In this case, the product gas leaves at the bottom of the gasifier through the grate and hot ash bed, therefore its temperature is much higher compared to the updraft gasifier. However, those conditions are promoting cracking and tar reduction.

Cross draft gasifier has inlets for gasifying agent on the side of the reactor. The same goes for product gas, which is leaving the reactor sidewall opposite to the air inlet. Right after air inlet, high oxygen concentration creates a high temperature (above 1500 °C) region where combustion is taking place. Small-scale biomass plants often employ this kind of gasifier. Its comparatively small reaction zone with limited thermal capacity provides faster response time than any other gasifier in this category. It is also quicker in startup time, which allows the gasifier to react faster and with good performance when the load changes. It is not a favorable technology for high ash or tar feedstock, but high moisture fuels can be used if the open top is applied.

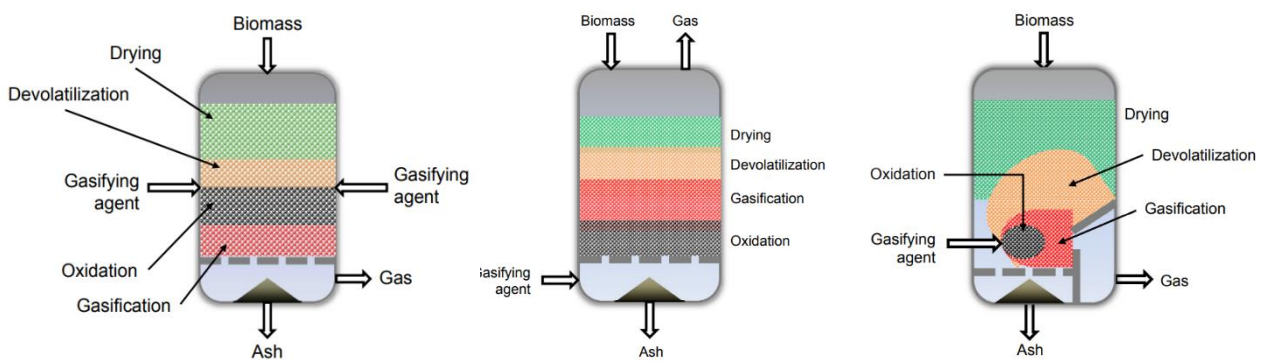


Figure 9. Schematic drafts of fixed bed gasifiers. From left: downdraft, updraft and cross draft gasifier. (Bermudez & Fidalgo, 2016)

4.3.2. Fluidized bed technology

The fluidized bed reactor is significantly better in mixing and ensuring uniform temperature distribution. Instead of simple fixed grate, it has a bed material which consists of granular solids that can be maintained in a semi-suspended state when the gasifying agent is passing through it from the bottom. In consequence, the biomass or coal fed to the gasifier need to be crushed into smaller particles from 0.5 to 6mm diameter, to be able to maintain stable conditions in reactor. The main characteristics of the fluidized bed gasifier

allow it to handle low tar fuel and to not be affected by poor quality of the fuel, therefore it is a preferable type of gasifier to handle biomass. (Basu, 2010)

Winkler bubbling fluidized bed gasifier was the first one to be developed and widely used for biomass application for medium sized gasification units (up to 25MW). Finely grained biomass is fed into the high temperature bed material, and it is fluidized by the gasification agent stream coming from the bottom. The biomass particles react under contact with hot bed material producing gas and ash. Around 70% of the ash is entrained by the product gas and carried out of gasification chamber, the rest 30% falls below the grate underneath bed material. The operating temperature usually is around 860 – 900 °C to avoid ash fusion and agglomeration, resulting in lower carbon conversion and therefore cold gas efficiency compared to other types of gasifiers.

One specific type of fluidized reactor that is preferred for biomass gasification is the circulating fluidized bed gasifier, as it can provide longer gas residence time. In this type of reactor, solids of bed and fuel are distributed along the tall riser, providing longer residence time for gas and particles and therefore higher conversion rate. The feedstock then can be of low-quality and have broad particle size. Fluidization velocity of the bed is higher (3.5-5.5 m/s) compared to bubbling bed (0.5-1.0 m/s). Due to above characteristics, large portion of particles are carried out of the gasifier with product gas. They are captured in cyclones and returned back to the base of the riser. The rate at which particles are returned to reactor and the fluidization velocity are high enough for the parties in the riser to reach unique hydrodynamic conditions called fast-fluidized bed. (Elsevier, 2018)

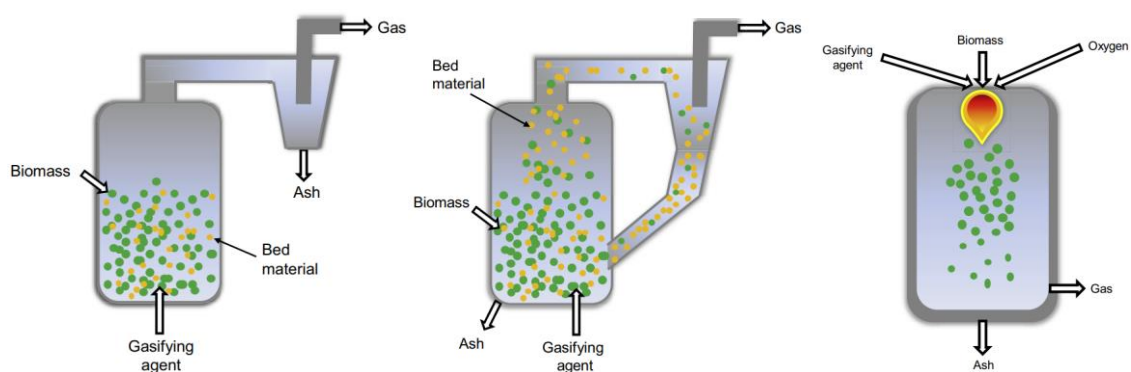


Figure 10. Schematic drafts of fluidized bed gasifiers (from left: bubbling, circulating) and entrained flow gasifier. (Bermudez & Fidalgo, 2016)

4.3.3. Entrained flow technology

In entrained flow gasifiers, fuel particles concurrently react with gasification medium in suspension (entrained) fluid flow mode, which is achieved by high-velocity jet creating

turbulent, recirculation at the entrance. Finely pulverized fuel (preferably below 0.01mm) is heated immediately and starts burning in oxygen rich environment. Next the char undergoes gasification reactions, which are slower than devolatilization. This type of reaction requires larger length to support this conversion. Operating temperature exceeds the conditions of the previous gasifier types, reaching 1200 to 1600 °C, thanks to which higher carbon conversion rate (close to 100%) and tar free syngas is ensured. However, product gas has a higher temperature at the outlet and needs to be significantly cooled before cleaning processes. (Elsevier, 2018)

The entrained flow gasifiers are most widely used for large scale applications, handling feed such as coal, coke and refinery residues, but less suitable for low quality coals and biomass specifically. High content of ash under stable conditions is reducing the gasification efficiency and once melted in the reactor can shorten the life of gasifier. This is specifically applicable to biomass ash, which consists of highly aggressive alkali compounds. Additionally, requirement of pulverized feed is hard to meet with fibrous structure of biomass.

4.4. Syngas technology

The outlet stream out of the gasifier is desirably composed mostly of H₂ and CO, but there are other compounds whose concentration depends on the process conditions, technology used, and type of feedstock. In gasification, syngas impurities can be divided into three groups:

1. Main components: CO₂, N₂, CH₄ – these are normally present in in outlet stream in concentration higher than 2%
2. Minor components: light hydrocarbons (C₂, C₃, C₄) – they are mostly present in quantities of lower than 2%
3. Contaminants: sulfur compounds (H₂S, COS), ammonia NH₄, chlorine Cl, tars and ashes – concentration of those components is highly depended on operating conditions and feedstock used.

All of the contaminants can result in negative effect on gasification process itself, but also downstream technologies. One of the most influential compound is sulfuric acid which has strong corrosive properties, affecting the downstream instalation of syngas upgrading (Basu, 2010). Another contaminant is ammonia. Between 60% to 80% of N₂ contained in biomass is converted to ammonia, which has similar affect to sulfuric acid, and can cause catalyst deactivation. Ammonia contributes as well to NO_x emissions, which are under

strict regulations (Xu, et al., 2010). Subsequent chemical that contributes to apparatus corroding is chlorine. It is produced only if feedstock contains Cl. When combined with ammonia, can form solid agglomerates which result in fouling (Zwart, 2009).

In gasification process, another solid impurities such as tar and ashes are forming. Their formation and removal are one of the main challenges for gasification production route when considering large scale industrial application. The ash and tar particular matter may include complex organic compounds of high molecular weight and volatile metals. Both can deposit in valves, filters and pipes causing fouling. Moreover, for ash specifically, operating temperature needs to be monitored closely as after reaching ash melting point it can cause sintering and slagging (Navarro & Fierro, 2007).

In order to use syngas and achieve pure hydrogen product, product gas from gasification needs to go through number of processes aiming removal of corrosive agents, pollutants and impurities. The removal of all of the impurities is happening in downstream processes, which are described below in process order.

4.4.1. Particulate matter removal

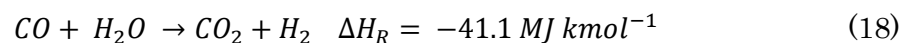
The particulate matter in product gas is composed of ash particles, unreacted carbon, soot, and bed particles (if fluidized bed reactor is used). They are prone to stick on the surface of the heat exchangers, in result causing fouling issues. Currently, in the industrial field there are few main technologies used for particulate matter separation. Those are cyclones, scrubbers, and filters (electrostatic and barrier).

Table 9. Methods for particulate matter removal with operating temperature and efficiency. (Hermann, et al., 2007)

Method	Temperature [°C]	Removal efficiency [%]
Cyclone	20-900	45-70
Sandbed filter	20-900	80-95
Bag filter	150-750	90-99
Scrubber	20-200	40-65
Electrostatic precipitator	40-50	95-99

4.4.2. Water gas shift reaction

In case of gasification process to pure hydrogen production, WGS unit is used to raise the yield of hydrogen in syngas. The principle here is the conversion of carbon monoxide with steam to hydrogen and carbon dioxide.



The equilibrium constant of the reaction is constantly decreasing with temperature. From the thermodynamics point of view, the lower temperature, the higher conversion in WGS reaction (Liu, et al., 2010). For an industrial application, water gas shift unit includes typically one or few reactors. It is mainly correlated to desired products of the process. For syngas production, by-pass high temperature WGS unit is suitable with moderate CO conversion. However, for hydrogen generation, the fuel gas stream can be treated from two to three times at successively decreasing inlet and outlet temperature for high CO conversion.

Additionally, for pure hydrogen production, conversion rate to H₂ can be raised by implementing a catalyst into WGS process. For high temperature step (300 to 500 °C), iron-based alpha-Fe₂O₃ catalyst is mostly used, and for low temperature step (200 to 300 °C) copper-based catalyst as CuO are used. Although better conversion yield of H₂ for the WGS with catalyst is a promising option, it is important to note difficulties that can be met during the process. The high temperature catalyst is sensitive for thermal sintering of iron, which causes deactivation. Secondly, most of the catalysts are paired with promoters as Cr₂O₃, which is a highly toxic oxide. Therefore, catalyst implementation to WGS needs to be done under strict supervision of process parameters, as well as novel catalyst preparation methods. (Lang, et al., 2016)

However, the use of catalyst in WGS allows to process gas with content of sulfur, also known as sour gas. Although the use of catalyst has its disadvantages mentioned above, sour gas shift allows to simplify the syngas processing. Usually, WGS reaction requires partial acid gas removal (AGR) beforehand, COS hydrolysis process afterwards to raise the H₂S yield and another AGR to completely remove the sulfur content. In case of sour gas shift, pretreatment for sulfur is not required and COS hydrolysis reaction takes place in the WGR reactor. After the process, only single AGR is required to clean the sulfur content completely out of gas. It is worth to note here, that sour gas shift is not a feasible for direct application of syngas of a low steam concentration (e.g., After Shell GSP). In this case, usually high amounts of steam are added to the gas before the process, as well as 1st stage reactor can be employed with additional steam input. (Liu, et al., 2015)

4.4.3. Chemical impurities removal

In general, depending on the biomass composition product gas after gasification can contain H₂S, COS and SO_x. They are usually at a much lower concentration compared to fossil fuels feedstock (Higman & van der Burgt, 2008).

If the content of sulfur components is relatively low, any separation methods are not required if the gas is used as fuel. However, for syngas or pure hydrogen production all the sulfur content needs to be removed. The cleaning method is chosen based on specification of end product and amount of gas to be treated. There are three categories of separations methods: chemical, physical, and biological in which several technologies can be distinguished

Chemical methods are preferred over biological and sometimes over physical due to higher removal efficiency. They are also favorable if the partial pressure of H₂S and CO₂ gases is low. In case of high pressure, physical methods perform more efficiently (Hermann, et al., 2007).

The most proven technology based on chemical absorption is the amine scrubbing using monoethanolamine (MEA) or methyldiethanolamine (MDEA). It is a proven and commercially developed technology for H₂S and CO₂ removal from flue gases, and its advantage is very high efficiency (more than 90%). In MDEA process, inlet gas enters bottom of absorber, where H₂S is selectively removed in exothermic reaction. As the moisture content rises, the co-adsorption of CO₂ takes place, which conduces to lower selectivity of H₂S (Hong-Jian, et al., 2002). Therefore, optimal concentration of MDEA for its best efficiency in H₂S removal is around 15% at a temperature of 40 °C. In this case 98.7% of H₂S is removed, with co-adsorption of CO₂ at 9.50% (Zhi, et al., 2010). Cleaned gas is going out from the top of absorption column. The MDEA solvent with absorbed H₂S is directed to heat exchanger for preheating, after which enters from the top of the stripper, where H₂S is desorbed at high temperature. Recycled clean solvent returns back to the absorber column passing through heat exchanger to cool down its temperature (Jung, et al., 2013).

Using amines for absorption processes is in general thought to be energy-intensive due to their degradable nature. Efforts are being made to develop a better, energy and cost-efficient process with solid bed sorbent that would allow H₂S removal at higher temperatures. Certain zeolites and metal oxides including ZnO, Al₂O₃, CaO are being explored.

From physical methods of sulfur compounds removal two most common processes are used: Selexol process and Rectisol. The former is the first choice in the industry due to ambient temperature operating conditions, while the latter is more effective in hydrogen sulfide removal but requires cryogenic temperatures from -25°C to -60°C or lower, which results in higher investment and operation cost (Larson, et al., 2006). Selexol technology

is using a mixture of dimethyl ethers of polyethylene glycols, which act as physical absorber of high selectivity for hydrogen sulfide and carbonyl sulfide. Partial removal of carbon dioxide is an advantage as it ensures cleaner H₂S stream going to sulfur recovery unit (National Energy Technology Laboratory, 2022). For syngas cleanup to hydrogen, two-stage process is usually required with two absorption and regeneration columns. In the first column, H₂S is removed with the lean solvent with little content of CO₂. After leaving the absorber column, rich in H₂S solvent is heated and stripped off in desorber column. Acid gas can be directed to Claus plant for sulfur production, while regenerated solvent goes to CO₂ absorption column. Afterwards, the product gas is free of H₂S and has considerably lower CO₂ content. Regenerate solvent from the second column goes back to CO₂ absorber due to partial content of CO₂.

4.4.4. Hydrogen separation

When it comes to removing the CO₂, CO and hydrocarbons from gas stream, various technologies can be applied. The processes mainly used in the industrial applications are pressure swing adsorption (PSA), absorption on chemical solvents, membrane separation, cryogenic separation and biological methods (Luis, 2016). To achieve pure hydrogen from syngas, CO needs to be removed at a level of at least 99%, which can only be achieved with PSA. Before the PSA, entrained liquids as water and condensed hydrocarbons must be removed as it leads to adsorbent damages

Pressure swing adsorption is based on the principle of physical binding of the gas molecules to adsorbent material. It takes advantage of adsorbing properties of high surface area materials such as activated carbon, zeolites and mesoporous silica. In PSA unit, the process can be divided into two steps: production and regeneration. In the production step inlet gas is gradually introduced to the several adsorber vessels, one at a time. The impurities are absorbed into the surface of the adsorbent bed, separating them from hydrogen. Pressure is then released, causing the ejection of impurities from adsorbent bed. The regeneration step consists of introducing product hydrogen back into adsorber vessels to flush the waste gas out of the adsorber bed to prepare the vessel for the next cycle (Liu, et al., 2010)

The reaction between the inlet gas and the adsorbent is primarily determined by gas composition, its temperature, and its partial pressure. Taking into consideration the main gas components, the strength of adsorption for activated carbon follows below sequence:



According to that, CO₂ is removed in the first instance, followed by CH₄ and CO, and lastly H₂. Apart from activated carbon, silica gels, aluminas and zeolites can be used as adsorbents. The choice of adsorbent is mainly dependent on the operating pressure and temperature, as well as impurities that need to be removed. As an example, activated carbon has a higher efficiency rate when removing H₂ from a mixture of CO₂ and hydrocarbons rather than CO and N₂. (Parra Mendoza & Patel, 2016)

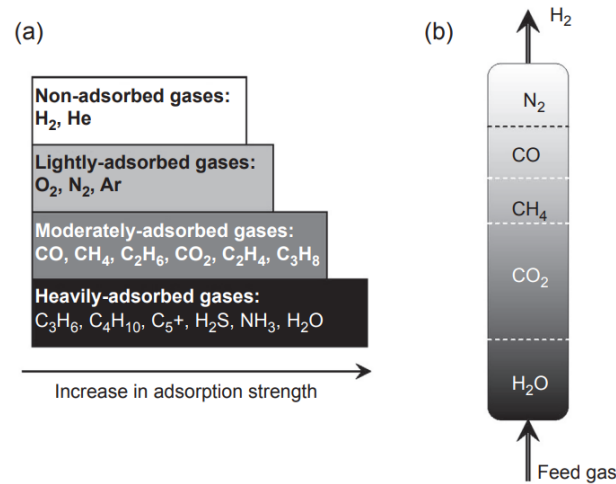


Figure 11. Relative strength of adsorption of main contaminants in the product gas (left) and schematic of one adsorbent bed. Adapted from (Carlos, 2012)

The PSA technology with activated carbon can recover from 60% to over 90% of hydrogen from gas stream where initial content of H₂ was around 50 vol.%. In case of low content of impurities in the gas stream, temperature swing adsorption (TSA) might be cost efficient way for hydrogen separation. (Carlos, 2012).

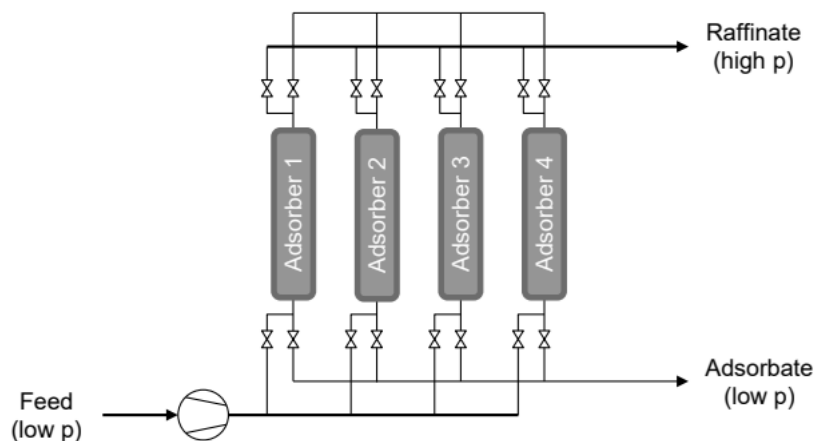


Figure 12. Flowchart of pressure swing adsorption process. Adapted from (International Energy Agency Bioenergy, 2018)

Another way of achieving pure hydrogen gas is by using membrane separation technology. Hydrogen is separated from other gases in the stream by passing through a ceramic, metallic or polymer sequence of membranes. Pressure is the most common driving force for this type of separation system, and only specific method of H₂ penetration through membranes can vary depending on material type and design. In the most studies polymer and silica membranes, micropores of 0.5 nm diameter are selectively separating the chemical molecules by molecular diffusion transport mechanism. They are able to recover from 60 up to 91.71% of hydrogen but have high limitations for operating conditions. (Le, et al., 2016)

5. Design of process model in ChemCAD

Based on the literature review, theoretical production flow chart was drafted as a backbone for the model (Figure 13.). The process simulation is conducted in ChemCAD which is an established chemical processing software with variety of chemical compounds available in build-in data bases. ChemCAD can manage equilibrium calculations and allows to export data for mass and energy balance analysis. Based on those functionalities steady state simulation of gasification and syngas cleaning processes was carried out and served as base for system performance analysis.

The proposed process was built in the ChemCAD software starting from gasification to downstream processes including initial scrubber cleaning, water gas shift station (WGS) and hydrolysis reactor, two stage Selexol process for H₂S and CO₂ removal and pressure swing adsorption (PSA) unit for complete purification of hydrogen. Biomass drying was excluded from the ChemCAD model, nevertheless it is mentioned on the proposed process flow chart as it has a critical influence on the gasification performance and should be considered in case of actual application.

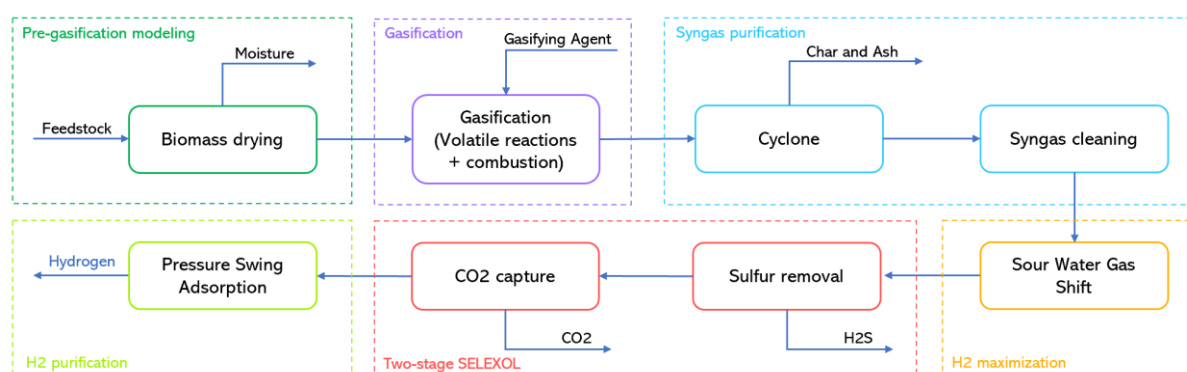


Figure 13. Diagram of proposed system for hydrogen production.

5.1. Gasifying agents' compression

Assumptions: Steam and oxygen as chosen gasification medium; compression process is in steady state. Compression included oxygen only.

Right before the gasification, first part of the model includes gasifying agents' compression unit. The oxygen at a purity of 95%, goes through two compressors with heat exchanger in between supported by water. The nitrogen stream is included in the simulation as it acts as transport gas. Both gases are compressed up to 40 bar, and temperature is 103.2 °C for air and 84.2 °C for nitrogen. Efficiency of the compressors is 85% and pressure drop assumed on each heat exchanger is 0.03 bar. (U.S. Department of Energy, 2011)

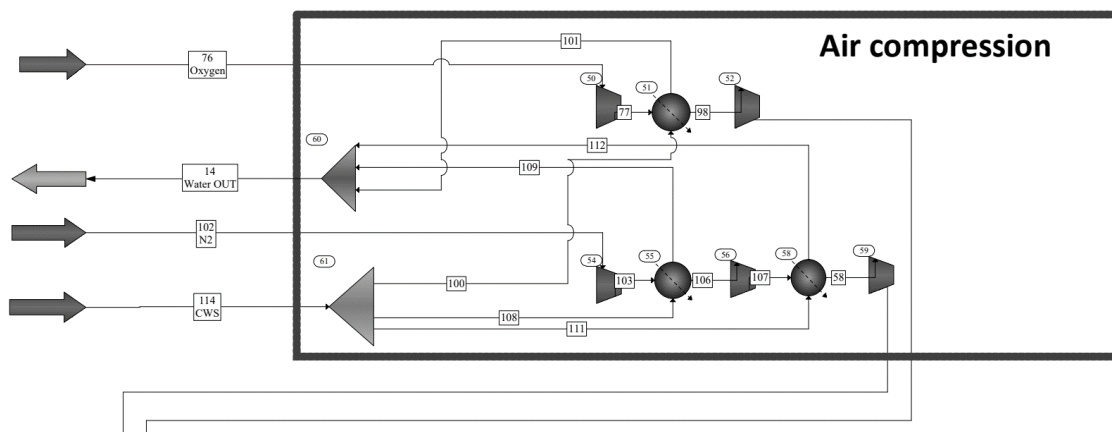


Figure 14. The ChemCAD model of the air and nitrogen compression unit. CWS stands for cooling water stream.

5.2. Biomass gasification

Assumptions: Gasification process is isothermal and in steady state. ChemCAD thermodynamic calculations are based on Soave Redlich Kwong equation. Solid components include carbon, silicon dioxide sulfur and calcium carbonate, other solid components are neglected. Formed tar particles are assumed to be broken down into H₂ and CO by an ideal catalyst. Gas cleaning from a particulate matter is neglected.

The ChemCAD model for biomass gasification is based on the circulating fluidized-bed gasifier, according to SES Gasification Technology (SGT) with oxygen as a gasification agent. The model was developed in Institute of Energy and Fuel Processing Technology Zabrze Poland (IEFPT) and verified using operational data from Yuma Plant (China, Methanol production plant). (Ściążko, et al., 2018) The SES gasifier is designed to manage low rank coals, biomass and municipal solid wastes (MSW) using oxygen, oxygen-rich air or air for the gasification reaction. In case fluidized bed reactor, gasification system should

be equipped with tar reforming which includes thermal cracking to support conversion of higher carbon compounds such as aromatics contained in raw gas. In this study, the tar reforming unit was not included, and contentment of tar in the raw gas is assumed to be zero. (Kaisalo, 2017)

5.2.1. Biomass feed characteristics

As mentioned in Chapter 3, for gasification of a pine biomass presented best results in terms of volumetric production of both H₂ and CO, therefore it was chosen as a biomass for this study. Exact parameters of the feedstock are an average parameter presented for wood stem, branches and needles from the research made on Portuguese Maritime Pine woods. (Viana, et al., 2018). A detailed proximate and ultimate analysis of the sample is presented in below in Table 10 and Table 11 respectively. As the raw wood biomass, the moisture content can vary from 30% up to 45%, it is usually dried to about 10% to 20% based on the technological requirements of gasifiers. In this study, the moisture content in biomass was adjusted to 16.66 % based on values available in research papers and operating requirement of gasifier. (Bermudez & Fidalgo, 2016)

Table 10. Proximate analysis of used biomass feedstock

Proximate Analysis	With Moisture [%]	Dry Basis [%]
Moisture	16.66	0.00
Ash	0.72	0.86
Volatile Matter	68.77	82.52
Fixed Carbon	13.85	16.62
Total	100.00	100.00

Table 11. Ultimate analysis of maritime pine biomass feedstock

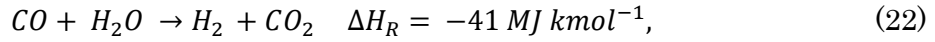
Ultimate Analysis	With Moisture [%]	Dry Basis [%]
Carbon	40.47	48.56
Hydrogen	5.75	6.9
Oxygen	36.62	43.95
Water	16.67	0.00
Sulfur	0.21	0.25
Nitrogen	0.28	0.34
Total	100.00	100.00

The higher and lower heating value (HHV and LHV) of the pine biomass was calculated automatically by the ChemCAD software. HHV and LHV are 21.23 [MJ/kg] and 19.57 [MJ/kg] respectively.

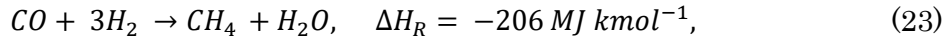
5.2.2. Gasification

Gasification process is complex, and its modeling would require precise reaction kinetics and operational parameters such as local temperature distribution and pressure, feedstock particles sizing and shape and much more. For this work, the modeling strategy intended to simulate potential the experimental data based on verified gasification model from IEFPT.

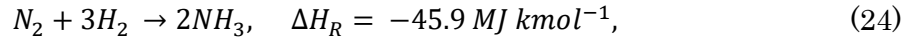
The ChemCAD model (Figure 15) was equipped with series of two following reactors. First one is a Gibbs reactor (equipment no.1), which used the equilibrium model for all possible reactions minimizing the Gibbs free energy on the products to obtain output conditions (pressure, temperature, heat of reaction). Second is a stoichiometric reactor (equipment no.14), in which three additional reactions were added to model conversions of CO and N₂:



$$CO \text{ fractional conversion} = 0.09$$



$$CO \text{ fractional conversion} = 0.11$$



$$N_2 \text{ fractional conversion} = 0.008$$

The operating pressure was 30 bar and operating temperature was at the level of 997 °C and a 95% carbon conversion. Biomass loading rate was defined as 90,000 kg/h. Heavy duty losses of 111.99 MW for gasification reactor were estimated as a sum of heat losses of 1% of chemical enthalpy of the fuel introduced to gasifier (in this case biomass, steam 20) and thermodynamic enthalpy of fuel formation as indicated by Chmielniak et. all. (Chmielniak, et al., 2021). Equation (25) represents described calculation.

$$\Delta_f H^0 = Q_s + \Delta_c H^0 \quad (25)$$

$\Delta_c H^0$ represents thermodynamic enthalpy of combustion and it was calculated according to Equation (26), where C, H, S represents the ratio of carbon, hydrogen, and sulfur in the dry biomass. The Q_s represents the correlation between enthalpy of combustion with the heat of combustion.

$$\Delta_c H^0 = -327.633 * C - 1417.892 * H - 92.768 S_t, \left[\frac{kJ}{kg} \right] \quad (26)$$

Where, $\Delta_c H^0$ – *thermodynamic entaply of combustion*

C – *ratio of carbon in dry biomass,*

H – *ratio of hydrogen in dry biomass,*

S_t – *ratio of sulfur in dry biomass.*

$$Q_s = (-1) * \Delta_c H^0 * f(\theta), \quad (27)$$

where, $f(\theta) = 0.00195 * \ln(\theta) - 0.00305(\theta)^{1.125} + 1.01314$

Oxidating agent chosen for the gasification is steam and oxygen which enters the reactor together with N₂ as a fuel transportation gas. Additionally, the CaCO₃ was introduced to the reactor in ratio of 0.1% of biomass loading rate to promote both gasification and reforming reactions. (Gomez-Vasquez, et al., 2021). In the ChemCAD model, component separator was introduced before the Gibbs reactor which returns 5% of carbon to simulate unreacted carbon composition in the gas after devolatilization. (U.S. Department of Energy, 2011) All input streams (air, nitrogen, steam, calcium carbonate, biomass) reacts to produce the wet gas composition, which values and characteristics are presented in Appendix.

After gasification, ash and all solid components were removed by ideal separator (scrubber in Figure 15.) Hot ash goes though heat exchanger to recycle the heat from quenching process and leaves in form of cooled ash and water. As ChemCAD software estimates only the gas composition based on reaction equilibrium, the product gas leaves reactor at a temperature equal to operating temperature of equilibrium reactor. From there, the product gas was directed to gas cooling which reduces the gas temperature from 997°C to 216°C with total pressure drop of 1 bar. (U.S. Department of Energy, 2011) Hot water vapor from the first heat exchanger was partially recycled as steam going into gasifier.

Following the cooling apparatus, raw gas is treated with scrubber to simulate removal of particulate matter. The water for scrubbing was fed in ratio of 1[m³] of water per 1 [Nm³] of gas, which is within the requirement of 1 – 4 [m³/Nm³].

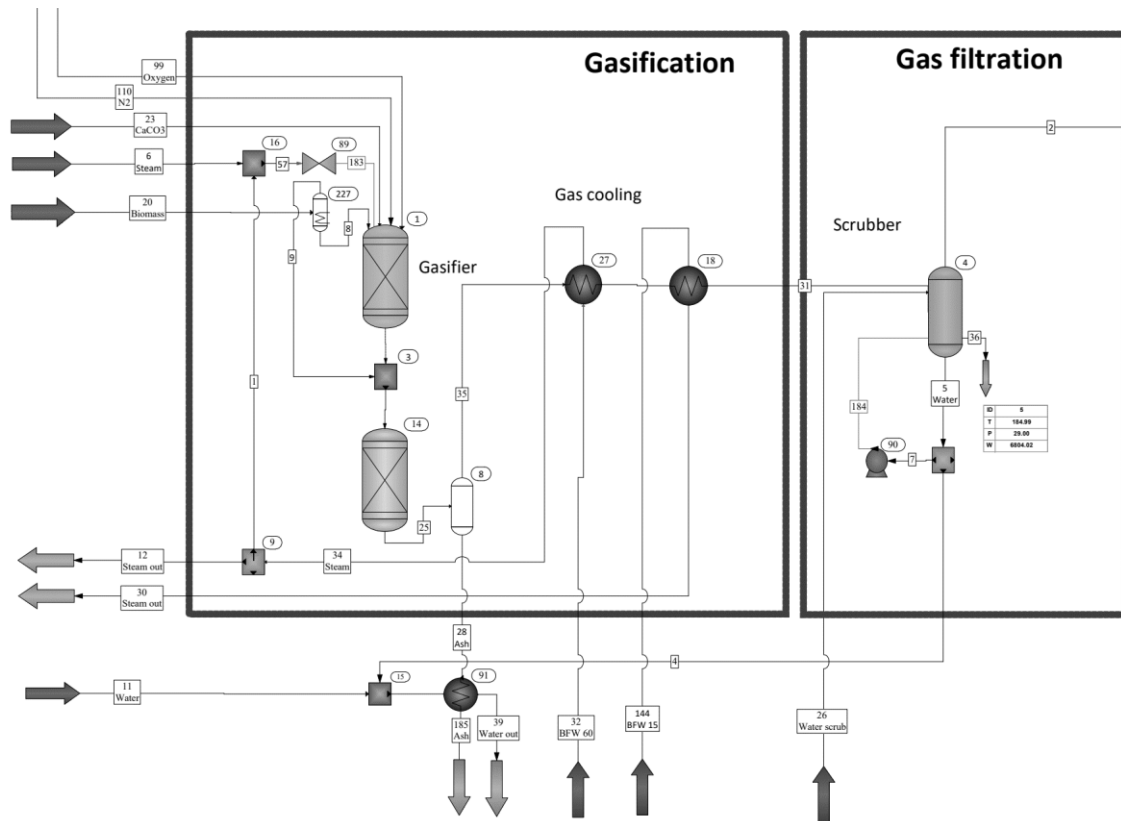


Figure 15. The ChemCAD model of the biomass gasification including ash removal.

5.3. Water-gas shift reaction and hydrolysis reaction

Assumptions: An ideal catalyst is used in both reactors. For high temperature reactor iron-chromium oxide catalyst is used, for low temperature reactor it is copper-zinc oxide aluminum oxide catalyst. Performance parameters were estimated according to quality guidelines (U.S. Department of Energy, June 2019)

To raise the ratio of hydrogen content in the product gas and enable carbon capturing by increasing the carbon dioxide concentration, two water gas shift reactors are used in the model. For prevention of carbon deposition on the catalyst used in the reactor, a steam to carbon monoxide ratio must be maintained above 1.75 to ensure efficient conversion. (U.S. Department of Energy, June 2019) Moreover, high steam content in the product gas supports in shifting the WGS reaction equilibrium to the right side. In the model sour water gas shift is used, meaning that cleaning from acidic sulfur compounds takes place after the WGS reactors. This application is less energy intensive as water gas shift reactors needs inlet temperature of 200 to 400 C, while in case of sweet water gas shift a low temperature processes of sulfur cleaning needs to be applied beforehand.

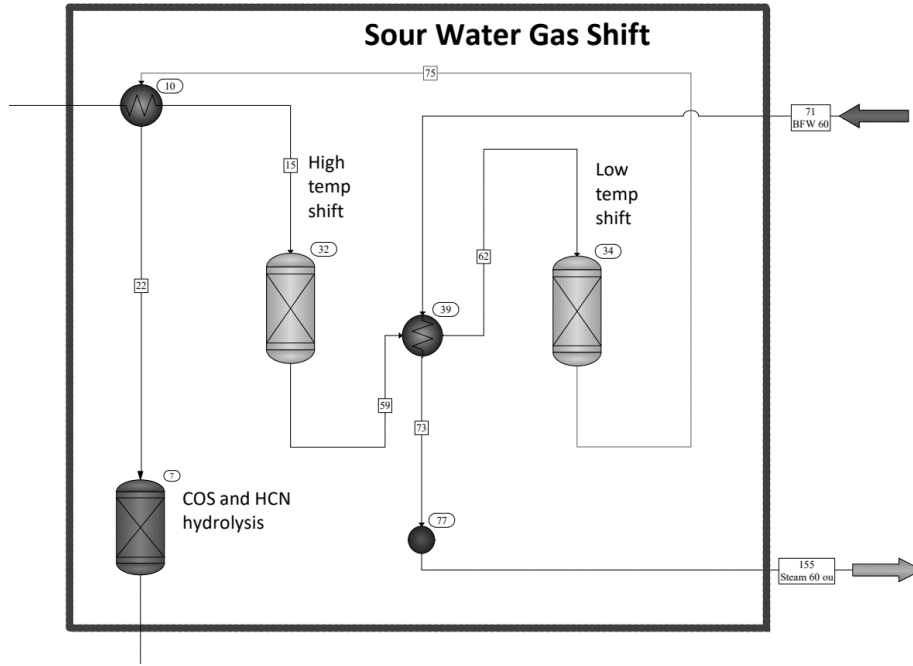


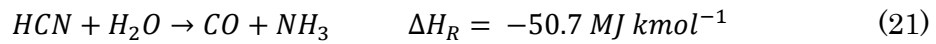
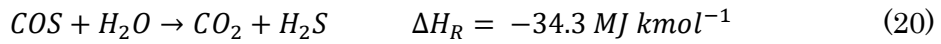
Figure 16. The ChemCAD model of water- gas shift process with high and low temperature reactors.

Table 12. Water-gas shift process parameters for high and low temperature reactors.

Parameter	High temperature reactor	Low temperature reactor
Intel gas temperature	210.5 °C	200 °C
Inlet gas pressure	28.7 bar	27.4 bar
Pressue drop	0.7 bar	0.5 bar
Outlet gas temperatue	336.1 °C	215.8 °C

The parameters of the sour water gas shift process are presented in Table 12. As water gas shift reaction is exothermic, intercooling between reactors needs to be applied at the outlet of the first reactor. In WGS reaction, elevated temperature of reaction is going to be favorable for kinetics properties which are influencing size of reactor and investment cost, however from the thermodynamics point of view it is going to shift the equilibrium of the reaction to CO₂. After the second reactor, hydrogen concentration in the product gas is higher by 56% and the CO conversion is at the level of 97.6%.

In real case applications, when catalyst is used in the sour WGS reactor hydrolysis reactions are supported at the same time which eliminates the need of applying separate hydrolysis reactor, lowering investment cost. (Chiche & Schweitzer, 2017) To simulate that in the ChemCAD model, stream from the low temperature reactor is directed to equilibrium reactor where two main hydrolysis reactions are simulated, namely carbonyl sulfide and hydrogen cyanide hydrolysis according to the reactions below:



The conversion for COS hydrolysis is set at 99.5%, while for HCN it is 95% based on industrial standard. (U.S. Department of Energy, June 2019). After the COS hydrolysis, product gas has a temperature of 186 °C and pressure of 26,5 bar and the hydrogen sulfide concentration has raised up to 0.07 mol% compared with input gas. Next, the product gas goes through series of heat exchanges to lower the gas temperature before the cleaning processes.

5.4. H₂S and partial CO₂ removal with Selexol process

Assumptions: Mercury removal is neglected. Similarly, Claus process for sulfur recovery is not within the project scope. In this study model of Selexol process is simulated with ideal component separator with calibrated performance according to quality guidelines (U.S. Department of Energy, June 2019)

To sweeten the product gas, dual stage Selexol process is applied to remove the H₂S traces and capture CO₂. The fundamental operating principles are described in section 4.4.3. Out of all acid gas removal processes, the Selexol technology is chosen as high pressure of the gas positively impacts the physical absorption, by raising the capacity above the levels of chemical solvents (MEA, MDEA). Nevertheless, the absorption process is highly dependent on the temperature, therefore the lower the temperature, the better absorption capacity. The process gas is significantly cooled down by series of three heat exchanges cooling the gas from 185 to 22 °C. The pressure drop on each heat exchanger is set as 2% of inlet gas pressure, giving on average 0.5 bar pressure from on each heat exchange, which is within the measured range (0.3–0.7 bar) at industrial applications. (U.S. Department of Energy, June 2019)

In the model, dual Selexol process was applied, where the first column selectively removes H₂S together and partially CO₂, while the second column removes remaining CO₂. However, product gas requires compression before entering first absorption column due to pressure drop cause by cooling. According to process quality guidelines the product gas needs to meet requirements of at least 34 bar pressure and 34–35 °C temperature. (U.S. Department of Energy, June 2019). Therefore, a compressor and heat exchanger are applied to meet the specification.

In the first column, significant amount of CO₂ needs to be slip through to ensure high selectivity and removal efficiency for the H₂. Operating parameters and removal efficiencies presented in Table 13.

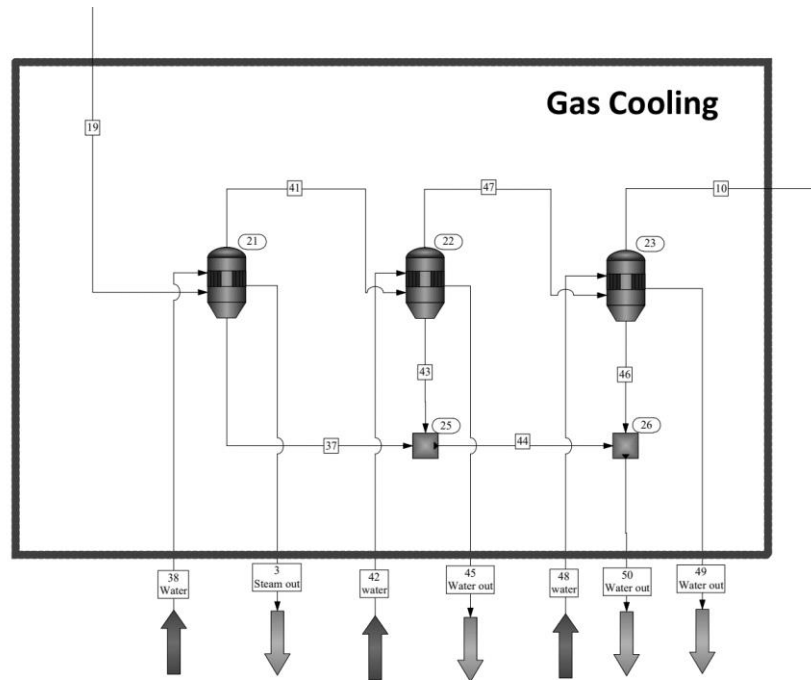


Figure 17. The ChemCAD model for product gas cooling before downstream cleaning processes

Table 13. Dual stage Selexol parameters for first and second absorption columns.

Parameter	First Selexol column	Second Selexol column
Intel gas temperature	39.6 °C	44 °C
Inlet gas pressure	31 bar	30 bar
Pressue drop	1 bar	1 bar
H ₂ S separation efficiency	99.77%	-
CO ₂ separation efficiency	20%	97.5%
H ₂ loss	0.3%	0.3%
Outlet gas temperature	26.7 °C	18 °C

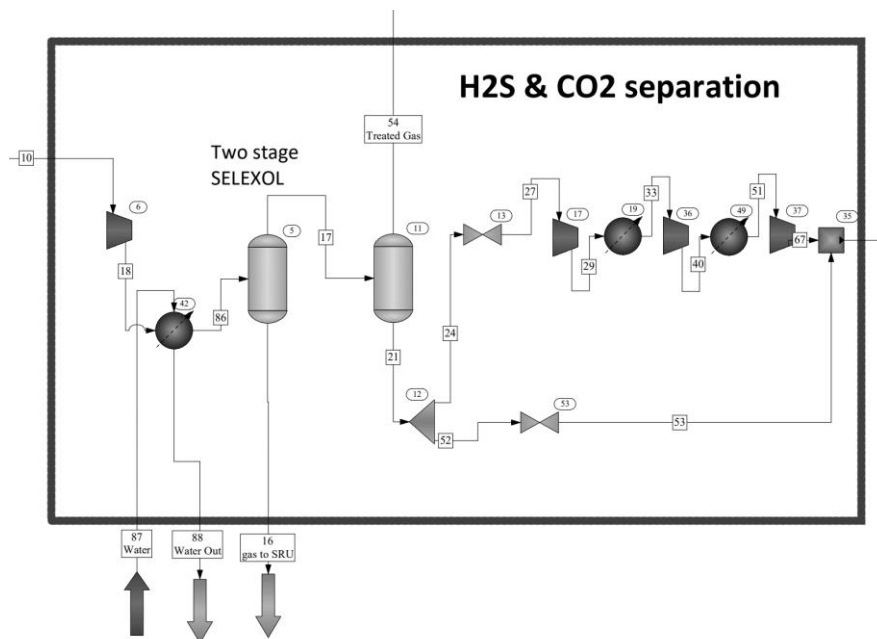


Figure 18. The ChemCAD model for dual stage Selexol process for H₂S and CO₂ removal.

The acid gas from the first absorption column can be directed to the Claus unit to recover pure sulfur from hydrogen sulfide. The CO₂ gas from the second column is received at two pressure levels. The high-pressure stream is at 10 bar. The low-pressure stream is at 1.2 bar and is around 40% of a total CO₂ stream output. It goes through the 3-stage compressor with intercooling to even out the pressure to the level of high-pressure stream. Compression ratio is set at 2.2 bar and efficiency at 86%. The last mile for CO₂ gas stream is multistage compressing up to 135 bar. Process parameters for compression are applied based on industrial measurements. (U.S. Department of Energy, 2011). At a pressure of 135 bar and temperature of 49.4 °C, CO₂ is in the supercritical state, which allows for it to be applied further in enhanced oil recovery (EOR) or sequestered in depleted oil and gas fields or saline aquifers.

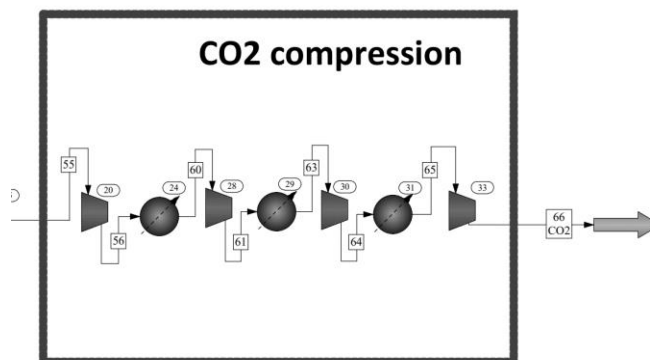


Figure 19. The ChemCAD model for CO₂ compression unit.

5.5. Hydrogen purification with Pressure Swing Adsorption

Assumptions: PSA process is simulated with ideal component separator with calibrated performance according to quality guidelines from NETL. (U.S. Department of Energy, 2013)

Hydrogen of high purity can be used for chemical application, as well as fuel for transportation. Nevertheless, required purity of hydrogen can be as high as 99.5%. In order to achieve high purity hydrogen, all contaminants such as nitrogen, leftover carbon monoxide and carbon dioxide are separated in pressure swing adsorption unit (PSA). After Selexol process, the product gas is at 30 bar and temperature of 18 °C and has 81.8 mol% of H₂ in composition, which according to the requirements, allows for direct application to PSA as it requires at least 60 mol% of H₂.

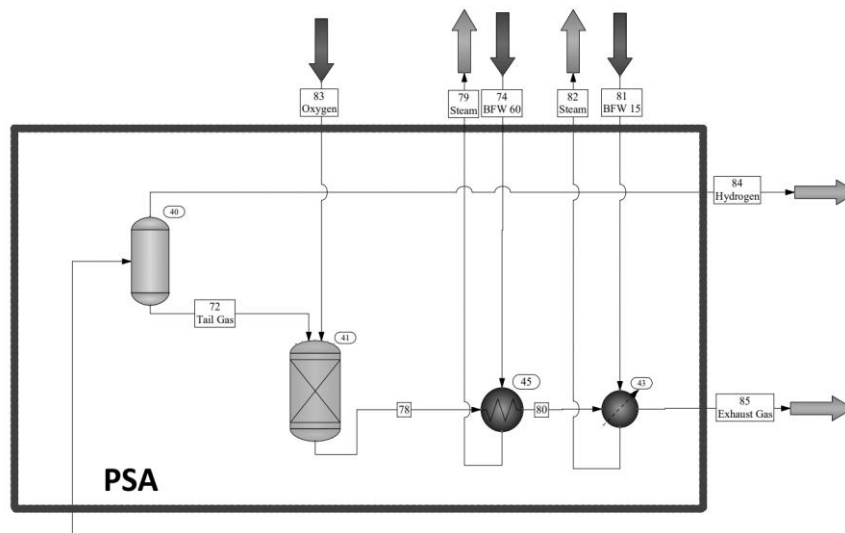


Figure 20. The ChemCAD model for Pressure Swing Adsorption unit.

Parameters of the PSA process were adjusted according to design of experiments (DOE) from U.S. Department of Energy Report. Hydrogen recovery is 95% and pressure drop 2.3 bar based on the research made over PSA specifically for hydrogen purification. (Zhu, et al., 2018) The mass flow of the outlet hydrogen stream of purity 99.99% is 5,9697 kg/h. Depending on the further application of hydrogen, it needs to undergo relevant processing of compression or heating. Detailed condition requirements for hydrogen storage can be found in Chapter 2.2.

The tail gas from PSA unit is at lower pressure due to desorption pressure losses. Due to high mass flow of 17,945 kg/h and high content of methane, tail gas is burned to recover energy. For this purpose, in the ChemCAD model a Gibbs reactor was included to simulate combustion with exhaust gas cooling unit.

5.6. Performance indicators

The complete system, starting from biomass gasification up to hydrogen separation can be evaluated on selected steps with performance indicators to compare the simulation results with industrial standard.

For a comparison of thermodynamics performance various efficiency parameters are going to be evaluated, whose mathematical equations are defined below.

$$CGE = \frac{\Sigma(\dot{m}_p * LHV_p)}{\Sigma(\dot{m}_f * LHV_f)} \quad (22)$$

Equation (22) represents the cold gas efficiency (CGE) of the production process, where the \dot{m}_p stands for mass flow of the raw gas and \dot{m}_f for mass flow of the fuel (biomass).

$$HPE = \frac{\Sigma(\dot{m}_h * LHV_h)}{\Sigma(\dot{m}_f * LHV_f)} \quad (23)$$

Equation (23) represents the hydrogen production efficiency (HPE), which similarly to the CCE is a measure of production rate, where the \dot{m}_h stands for mass flow of the hydrogen and \dot{m}_f for mass flow of the fuel (biomass).

$$CCE = \left(1 - \frac{\dot{M}_r}{\dot{M}_f}\right) \quad (24)$$

Equation (24) represents the carbon conversion efficiency (CCE) which refers for the gasification unit efficiency, where the \dot{M}_r stands for molar flow of the unreacted carbon residue that is contained at the outflow of gasifier and \dot{M}_f is molar flow of the carbon contained in the biomass feedstock.

$$CME = \left(1 - \frac{\dot{m}_{COout}}{\dot{m}_{COin}}\right) \quad (25)$$

Equation (25) represents the carbon monoxide conversion efficiency (CME) which is an performance indicator for water gas shift unit, where the \dot{m}_{COout} stands for mass flow of the carbon monoxide out from low temperature shift reactor and \dot{m}_{COin} for mass flow of the carbon monoxide in the high temperature shift reactor.

6. Results and discussion

To address one of the objectives of this master thesis to find optimal parameters for hydrogen production, four case scenarios of stream to biomass ration (SBR) were simulated in ChemCAD and evaluated – (i) case 1, SBR=0.25; (ii) case 2, SBR =0.45, (iii) case 3, SBR = 0.38, and (iv) case 4, SBR =0.6.

Firstly, the model and simulation output needed to be validated from the thermodynamic point of view. Mass balance for each element as well as energy balance for all input and output streams were performed. As the first scenario, simulation of case 3 was performed, where the SBR is equal to 0.38, which results in 34 ton/h of stream fed into gasifier. In order to maintain the temperature at a level of 997°C, oxygen mass flow rate was adjusted to 34,45 ton/h. Table 14 presents the mass balance for case 3. Each mass flow rate of input and output stream was decomposed into simple elements using their molar weight. Difference for each element is within the acceptable range of 0.5%.

Table 14. Elemental balance for all input and output stream for Case 3.

Element	Total input [kg/h]	Total output [kg/h]	Difference
Oxygen	1,483,464	1,486,797	-0.22%
Hydrogen	179,041	179,459	-0.23%
Carbon	36,062	36,039	0.07%
Nitrogen	106,628	106,628	0.00%
Sulfur	633	633	-0.01%
Silicone	390	390	0.00%
Argon	5565	5565	0.00%
Calcium Carbonate	453	453	0.00%

For the energy balance, both chemical and physical enthalpy was calculated for each input and output stream. The ChemCAD software calculates the enthalpy of formation for each stream according to formula presented in equation (26), which is equal to a sum of enthalpy of formation at standard conditions and physical enthalpy.

$$H_T = \Delta_f H_{298} + \int_{298}^T C_p dt, \quad [MW] \quad (26)$$

Therefore, enthalpy of formation at a standard condition was subtracted from enthalpy given in ChemCAD simulation result to achieve the desired parameter. For all the streams with carbon content the chemical enthalpy was calculated based on the equation (27), where HHV_s stands for higher heating value of stream in kJ/kg and m_s for a mass flow of that stream in kg/h.

$$H_p = \frac{HHV_s * m_s}{(3600 * 1000)}, \quad [MW] \quad (26)$$

Except of the streams enthalpy, calculated earlier heavy-duty losses for gasification reactor were also included in the balance. The total energy balance for Case 3 can be found in Table 16 in Appendix.

Once the model has been verified model in ChemCAD, three other simulations of different stream to biomass ratio (SBR) were made to study the influence of gasification parameters over the hydrogen yield. In order to isolate the influence of SBR ration on the process performance temperature, pressure and biomass loading ration were kept the same. The same rule was applied to further processing units, unless achieved results required system adjustment (temperature of ash cooling etc.) In order to maintain the same temperature at the gasification reactor at a higher steam flow rate, the oxygen flow rate was adjusted accordingly.

In the Case 1, SBR was equal to 0.25 with steam flow of 22.5 ton/h. To maintain the low temperature of gasification, oxygen was fed at a rate of 31.85 ton/h. The Case 2 considered SBR of 0.45 with steam flow of 40,5 ton/h. The Case 3 has a SBR of 0.38, which transfers to 34 ton/h of steam and 34.35 ton/h of oxygen. The Case 4 has the highest SBR of 0.6, with steam flow at 54 ton/h and oxygen flow of 37.72 ton/h. In industrial application, usually SBR between 0.35 and 0,45 is used. (Campoy, et al., 2008)

Table 15. Summary of the parameters and performance indicators for four case scenarios

Parameter	Unit	Case 1	Case 3	Case 2	Case 4
Steam to Biomass Ratio	%	0.25	0.38	0.45	0.60
Steam Flow Rate	kg/h	22,500	34,000	40,500	54,000
Oxygen Flow Rate	kg/h	31,850	34,350	35,500	37,720
Biomass Loading Rate	kg/h	90,000	90,000	90,000	90,000
Gasification Temperature	°C	997	997	996	996
Gasification Pressure	bar	30	30	30	30
Raw Gas Flow Rate	vol. m3/h	25,324	28,136	29,590	32,555
CO ₂	mol %	18.65%	18.19%	17.97%	17.48%
CO	mol %	16.68%	14.56%	13.48%	11.56%
H ₂	mol %	25.40%	25.27%	24.89%	23.72%
CH ₄	mol %	4.56%	3.15%	2.66%	1.96%
CO ₂	kg/h	58,690	63,597	66,126	70,733
CO	kg/h	33,398	32,396	31,575	29,785
H ₂	kg/h	3,661	4,047	4,196	4,398
CH ₄	kg/h	5,233	4,019	3,567	2,899
CGE - Cold Gas Efficiency	%	60.4%	59.2%	58.6%	57.3%
CCE - Carbon Conversion	%	95.0%	95.0%	95.0%	95,0%

CME -CO Conversion Efficiency	%	95.9%	97.6%	98.1%	98.6%
Hydrogen Flow Rate	vol. m3/h	2,478	2,626	2,669	2,705
	kg/h	5,634	5,970	6,067	6,149
HPE - Hydrogen Production Efficiency	%	41.9%	44.4%	45.1%	45.7%

The cold gas efficiency for different cases is ranging from 57.3 up to 60.4 % which is in line with available published research for biomass gasification in fluidized bed reactors. The hydrogen production efficiency can be reached up to 45.7% while implementing SBR of 0.60, which is in between the already documented values from models. (Cohce, et al., 2011)

Additionally, comparison with other hydrogen production technologies was made. From already established processes three technologies can be named: fossil fuel-based methane steam reforming, biogas stream reforming and electrolysis. Natural gas reforming has an efficiency of 79%, with possibility to increase that up to 89% when using additional steam feed. (Simpson & Lutz, 2007). For biogas reforming, considering that the gas is produced through fermentation, the overall efficiency is between 55 to 65%. Electrolyte hydrogen production can reach efficiencies of up to 60% for alkyne electrolysis. To ensure sustainable hydrogen generation, electricity should be supplied from renewable sources. In the light of presented efficiencies, hydrogen production based on gasification has the lowest efficiency of all. However, it also has advantage of continuous production as well as higher potential for a large-scale application compared to previously named technologies.

6.1. Effect of steam to biomass ratio

Based on the four case scenarios, the effect of the steam to biomass ration on the gas composition can be evaluated. Overall, the influence of the SBR within the range of 0.25 to 0.60 on the gas composition is rather weak, which is in line with published experimental observations for fluidized bed reactors. (Shen, et al., 2008) (Rapagna, et al., 2000) By comparing the results in the table, one can notice that mole percentage of each element is declining with higher SBR. That is mainly caused by the higher amount of water vapor that is contained in the raw gas after gasification. Is it worth to note here that the higher SBR, the mass flow rate of carbon monoxide has dropped by 12.1%, however at the same time the hydrogen formation has increased by 16.8% in the raw gas. This can be explained by a shifted equilibrium of water- gas shift reaction to the products already in the gasification reactor. The rising CO₂ mass flow may be a confirmation of the above

conclusion. Higher steam content in the raw gas has a positive influence on the further applied process as well. Higher steam to carbon monoxide ratio ensures increased efficiency of the WGS unit, meaning CO conversion which is increasing comparing the case scenario results.

Looking at the cold gas efficiency of product gas, it can be noted that is falling by almost 3% as a result of lower yield of CO. At the same time hydrogen production efficiency is rising by 3.8%, therefore the influence of the steam to biomass ratio is beneficial for biomass gasification if the desired product is hydrogen rich gas.

Based on the research work made by Shen et al. at around SBR of 0.7 and gasification temperature of 800 to 850 °C hydrogen yield is reaching its maximum. The influence of SBR is not as impactful in case of gasification over 850°, compared to low temperature gasification at temperatures of 650 to 850. (Shen, et al., 2008) Considering this information, can be concluded that increase in production yield of H₂ goes in pair with raising SBR ratio up to a maximum point.



Figure 21. Mass flow rate of hydrogen after each process step based on Case 2.

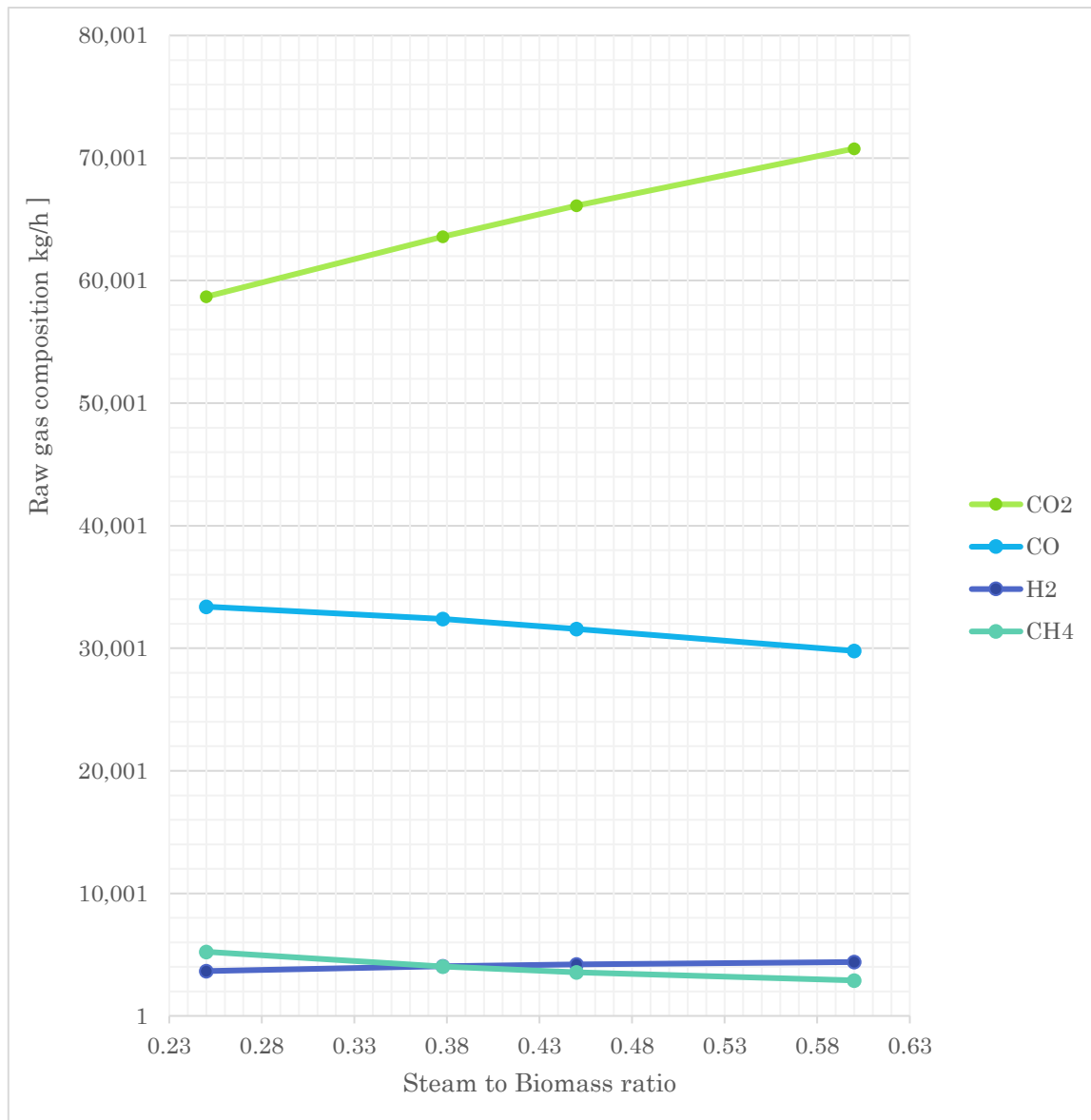


Figure 22. Effect of the SBR on raw gas components in [kg/h]

Overall impact of the SBR on the gas composition is particularly advantageous if system is designed to produce hydrogen. For other applications, such as synthesis gas production or methanation higher steam to biomass ratio is negatively influencing overall process performance as both CO and CH₄ production rates as decreasing. For methane, a SBR change from 0.25 to 0.60 resulted in 80.5% decrease in mass flow, although the total gas flow rate has gone up by 22.2%. The decline rate is also visible on the mole percentage CH₄ content in the gas stream. (Figure 22).

7. Conclusions

The overall picture given by the ChemCAD modeling results indicates that hydrogen production process with integrated biomass gasification system has promising producing

efficiency result using currently deployed technologies. Competitiveness of the technology is ensured by availability of fuel, reliable and stable production as well as the knowledge and expertise that exists in this field thanks to long history of coal gasification. (Zwart, 2009). However, the challenges for further development of such hydrogen production system consist of problem of engineering and chemical nature: tar cracking and tar removal, catalysts sensitivity along the process and hydrogen storage and transportation. Those are the most influencing factors impacting the further deployment of thermochemical hydrogen production processes.

Based on the review of the current technological landscape on hydrogen production, the process model for hydrogen production system was developed in ChemCAD software and simulation of the end-to-end process was conducted. Results of four simulation of the process with different SBR ratio has shown a positive impact on the hydrogen production process. With the higher steam to biomass ratio, the hydrogen production yield is higher as well at the same temperature and pressure in the gasification reactor. The impact of the higher SBR ratio was noticed not only at the gasification process step but also in the WGS unit, where the higher steam content in the inflow gas shifts the reaction equilibrium on the products side. For a large-scale application, it is advised to conduct gasification process at elevated steam to biomass ratio as it has beneficial impact on the total hydrogen production efficiency. However, the positive process results are reachable at the cost of higher steam feed to the gasifier, which can be both energy and cost intensive.

7.1. Future Works

In the following section, future works are presented focusing on what aspects of the topics should be considered for further research.

Firstly, a comprehensive economic analysis of the suggested process is necessary to perform. Investment cost as well as operating cost is one of the most influential factors in the technology assessment. The evaluated model is a large-scale application, and it would only be considered for actual application if final hydrogen production is cost efficient. The estimations over biomass gasification cost are available already and it is the most influential part of production process in terms of energy consumption. However, there are significant operating cost in downstream processing due to catalysts and sorbent usage.

Secondly, the steam to biomass ratio impact on the temperature, but most importantly on the carbon conversion should be studied further. There are several paper articles that are not aligned in terms of impact of the SBR on carbon conversion. (Campoy, et al., 2008)

(Shen, et al., 2008) The goal of further research should be to find correlation and dependencies between those properties. This would support the modeling process bringing reliability of the simulation outcome.

Thirdly, to perform detailed gasification modeling based on the kinetic modeling. The current study was based on industrial data for gasification modeling and performance data available in literature for syngas processing, therefore the model is not responsive and sensitive enough for dynamic parameters change (temperature, pressure, particle distribution etc.). Ideally, for fluidized bed reactor, computational fluid dynamics simulation such as Ansys Fluent should be performed to study deeper possible impacts on the biomass gasification efficiency.

Fourthly, a detailed model for plant design including piping, water supply and wastewater system, logistics of biomass feeding as well as biomass drying unit should be composed and analyzed further. Implementation of the heat recovery system would decrease the amount of additional energy provided to the system. In result it can limit the operating cost.

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Appendix

Table 16. Energy balance for Case 2.

	Stream Number	Name	Mass Flow [kg/m]	Temperature [C]	Pressure [bar]	Chemical Enthalpy [MW]	Physical Enthalpy [MW]	TOTAL
INPUT STREAMS	20	Biomass	90,000	44.0	40.0	530.75	-0.32	530.43
	102	N2	7,920	32.0	4.0		0.01	0.01
	76	Oxygen	34,350	32.0	8.5		0.04	0.04
	23	CaCO3	454	25.0	40.0		0.00	0.00
	26	Water	890	54.6	35.0		0.03	0.03
	144	BFW 15	10,881	100.0	15.0		0.95	0.95
	81	BFW 15	10,187	100.0	15.0		0.89	0.89
	32	BFW 60	91,245	100.0	60.0		8.08	8.08
	71	BFW 60	17,328	100.0	60.0		1.53	1.53
	74	BFW 60	87,174	100.0	60.0		7.71	7.71
	11	Water	4,016	60.7	1.0		0.17	0.17
	114	CWS	78,999	11.0	4.5		-1.28	-1.28
	38	Water	15,737	100.0	4.5		1.37	1.37
	87	Water	90,346	15.6	4.5		-0.98	-0.98
	48	Water	861,826	15.6	4.5		-9.33	-9.33
	42	Water	310,810	50.0	124.0		9.94	9.94
	83	Oxygen	103,867	15.6	1.1		-0.27	-0.27
	TOTAL		1,579,893			530.75	18.55	549.30
OUTPUT STREAMS	84	Hydrogen	5,970	18.0	27.7	235.47	-0.16	235.31
	66	CO2	99,419	49.4	191.7	0.75	-5.57	-4.83
	185	Ash	3,147	98.0	30.0	15.39	0.05	15.44
	16	Gas to SRU	11,545	26.7	31.0	1.66	-0.09	1.57
	85	Exhaust Gas	121,811	120.0	1.0	0.12	10.26	10.39
	12	Steam Out	57,245	285.6	60.0		43.33	43.33
	30	Steam Out	10,881	200.0	15.0		8.13	8.13
	155	Steam Out	17,328	285.6	60.0		13.12	13.12
	3	Steam Out	15,737	157.9	4.5		11.64	11.64
	79	Steam	87,174	285.6	60.0		65.98	65.98
	82	Steam	10,187	208.3	15.0		7.68	7.68
	45	Water Out	310,810	100.0	124.0		27.92	27.92
	49	Water Out	861,826	20.0	4.5		-4.93	-4.93
	88	Water Out	90,346	26.6	4.5		0.18	0.18
	39	Water Out	5,221	232.0	29.0		1.64	1.64
	50	Water Out	33,570	96.9	25.0		2.83	2.83
	14	Water Out	78,999	26.8	4.5		0.18	0.18
	TOTAL		1,579,324			253.38	182.18	435.57
Gasification reactor - Heavy Duty Losses [MW]								111.99
DIFFERENCE								0.3%

Table 17. Energy balance for Case 3.

	Stream Number	Name	Mass Flow [kg/m]	Temperature [C]	Pressure [bar]	Chemical Enthalpy [MW]	Physical Enthalpy [MW]	TOTAL
INPUT STREAMS	20	Biomass	90,000	44.0	40.0	530.75	-0.32	530.43
	102	N2	7,920	32.0	4.0		0.01	0.01
	76	Oxygen	35,500	32.0	8.5		0.04	0.04
	23	CaCO3	454	25.0	40.0		0.00	0.00
	26	Water	890	54.6	35.0		0.03	0.03
	144	BFW 15	10,881	100.0	15.0		0.95	0.95
	81	BFW 15	9,300	100.0	15.0		0.81	0.81
	32	BFW 60	95,879	100.0	60.0		8.49	8.49
	71	BFW 60	17,209	100.0	60.0		1.52	1.52
	74	BFW 60	78,726	100.0	60.0		6.97	6.97
	11	Water	4,016	60.7	1.0		0.17	0.17
	114	CWS	78,999	11.0	4.5		-1.28	-1.28
	38	Water	22,386	100.0	4.5		1.96	1.96
	87	Water	91,106	15.6	4.5		-0.99	-0.99
	48	Water	868,393	15.6	4.5		-9.41	-9.41
	42	Water	313,343	50.0	124.0		10.02	10.02
83	Oxygen	93,765	15.6	1.1		-0.24	-0.24	
TOTAL			1,818,767			530.75	18.74	549.49
OUTPUT STREAMS	84	Hydrogen	6,067	18.0	27.7	239.30	-0.16	239.14
	66	CO2	100,742	49.5	191.7	0.76	-5.65	-4.89
	185	Ash	3,147	98.0	30.0	15.39	0.05	15.44
	16	Gas to SRU	11,696	26.7	31.0	1.67	-0.09	1.58
	85	Exhaust Gas	111,192	120.0	1.0	0.10	9.43	9.53
	12	Steam Out	55,379	285.6	60.0		41.91	41.91
	30	Steam Out	10,881	200.0	15.0		8.13	8.13
	155	Steam Out	17,209	285.6	60.0		13.02	13.02
	3	Steam Out	22,386	157.9	4.5		16.55	16.55
	79	Steam	78,726	285.6	60.0		59.59	59.59
	82	Steam	9,300	208.3	15.0		7.01	7.01
	45	Water Out	313,343	100.0	124.0		28.15	28.15
	49	Water Out	868,393	20.0	4.5		-4.97	-4.97
	88	Water Out	91,106	26.6	4.5		0.18	0.18
	39	Water Out	5,296	232.0	29.0	0.00	1.66	1.66
	50	Water Out	40,893	105.3	25.0		3.84	3.84
14	Water Out	78,999	27.2	4.5		0.21	0.21	
TOTAL			1,824,756			257.22	178.88	436.10
Gasification reactor - Heavy Duty Losses [MW]								111.99
DIFFERENCE								0.3%

Table 18. Energy balance for Case 1.

	Stream Number	Name	Mass Flow [kg/m]	Temperature [C]	Pressure [bar]	Chemical Entalphy [MW]	Physical Entalphy [MW]	TOTAL
INPUT STREAMS	20	Biomass	90,000	44.0	40.0	530.75	-0.32	530.43
	102	N2	7,920	32.0	4.0		0.01	0.01
	76	Oxygen	31,850	32.0	8.5		0.04	0.04
	23	CaCO3	454	25.0	40.0		0.00	0.00
	26	Water	890	54.6	35.0		0.03	0.03
	144	BFW 15	10,881	100.0	15.0		0.95	0.95
	81	BFW 15	12,594	100.0	15.0		1.10	1.10
	32	BFW 60	82,495	100.0	60.0		7.30	7.30
	71	BFW 60	17,264	100.0	60.0		1.53	1.53
	74	BFW 60	110,151	100.0	60.0		9.75	9.75
	11	Water	4,016	60.7	1.0		0.17	0.17
	114	CWS	78,999	11.0	4.5		-1.28	-1.28
	38	Water	4,595	100.0	4.5		0.40	0.40
	87	Water	87,803	15.6	4.5		-0.95	-0.95
	48	Water	839,005	15.6	4.5		-9.09	-9.09
	42	Water	301,708	50.0	124.0		9.64	9.64
	83	Oxygen	131,220	15.6	1.1		-0.34	-0.34
TOTAL			1,811,846			530.75	18.95	549.70
OUTPUT STREAMS	84	Hydrogen	5,634	18.0	27.7	222.23	-0.15	222.08
	66	CO2	95,686	49.4	191.7	0.70	-5.37	-4.66
	185	Ash	3,147	98.0	30.0	15.39	0.05	15.44
	16	Gas to SRU	11,119	26.7	31.0	1.62	-0.09	1.53
	85	Exhaust Gas	150,707	120.0	1.0	0.20	12.47	12.67
	12	Steam Out	59,995	285.6	60.0		45.41	45.41
	30	Steam Out	10,881	200.0	15.0		8.13	8.13
	155	Steam Out	17,264	285.6	60.0		13.07	13.07
	3	Steam Out	4,595	157.9	4.5		3.40	3.40
	79	Steam	110,151	285.6	60.0		83.37	83.37
	82	Steam	12,594	208.3	15.0		9.50	9.50
	45	Water Out	301,708	100.0	124.0		27.11	27.11
	49	Water Out	839,005	20.0	4.5		-4.80	-4.80
	88	Water Out	87,803	26.6	4.5		0.17	0.17
	39	Water Out	5,080	232.0	29.0		1.60	1.60
	50	Water Out	21,204	70.9	25.0		1.14	1.14
	14	Water Out	78,999	26.1	4.5		0.11	0.11
TOTAL			1,815,572			240.13	195.12	435.25
Gasification reactor - Heavy Duty Losses [MW]								111.99
DIFFERENCE								0.4%

Table 19. Energy balance for Case 4.

	Stream Number	Name	Mass Flow [kg/m]	Temperature [C]	Pressure [bar]	Chemical Entalphy [MW]	Physical Entalphy [MW]	TOTAL
INPUT STREAMS	20	Biomass	90,000	44.0	40.0	530.75	-0.32	530.43
	102	N2	7,920	32.0	4.0		0.01	0.01
	76	Oxygen	37,720	32.0	8.5		0.05	0.05
	23	CaCO3	454	25.0	40.0		0.00	0.00
	26	Water	890	54.6	35.0		0.03	0.03
	144	BFW 15	10,881	100.0	15.0		0.95	0.95
	81	BFW 15	7,989	100.0	15.0		0.70	0.70
	32	BFW 60	105,822	100.0	60.0		9.49	9.49
	71	BFW 60	15,961	100.0	60.0		1.41	1.41
	74	BFW 60	66,246	100.0	60.0		5.86	5.86
	11	Water	4,016	50.0	1.0		0.12	0.12
	114	CWS	78,999	11.0	4.5		-1.28	-1.28
	38	Water	37,683	100.0	4.5		3.29	3.29
	87	Water	91,788	15.6	4.5		-0.99	-0.99
	48	Water	874,953	15.6	4.5		-9.47	-9.47
	42	Water	315,586	50.0	124.0		10.45	10.45
	83	Oxygen	78,814	15.6	1.1		-0.21	-0.21
		TOTAL		1,611,268			530.75	20.10
OUTPUT STREAMS	84	Hydrogen	6,149	18.0	27.7	242.56	-0.16	242.40
	66	CO2	102,635	49.4	191.7	0.77	-5.76	-4.99
	185	Ash	3,147	98.0	30.0	15.39	0.05	15.44
	16	Gas to SRU	11,912	26.7	31.0	1.68	-0.10	1.59
	85	Exhaust Gas	95,547	120.0	1.0	0.07	8.18	8.25
	12	Steam Out	51,822	285.6	60.0		39.22	39.22
	30	Steam Out	10,881	200.0	15.0		8.13	8.13
	155	Steam Out	15,961	285.6	60.0		12.08	12.08
	3	Steam Out	37,683	157.9	4.5		27.86	27.86
	79	Steam	66,246	285.6	60.0		50.14	50.14
	82	Steam	7,989	208.3	15.0		6.02	6.02
	45	Water Out	315,586	100.0	124.0		28.35	28.35
	49	Water Out	874,953	20.0	4.5		-5.00	-5.00
	88	Water Out	91,788	26.6	4.5		0.18	0.18
	39	Water Out	5,443	232.0	29.0		1.66	1.66
	50	Water Out	56,614	116.2	25.0		6.04	6.04
14	Water Out	78,999	27.9	4.5		0.27	0.27	
	TOTAL		1,613,965			260.47	177.19	437.66
Gasification reactor - Heavy Duty Losses [MW]								111.99
DIFFERENCE								0.2%