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HYDROGEN PRODUCTION PROCESSES FROM BIOMASS

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Abstract of Final Project

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Abstract

Global warming, climate change and energy security have been gaining more attention worldwide. Hydrogen production from biomass offers an effective solution leaving minimal environmental footprint. This thesis identifies and reviews the most potential bio-hydrogen production pathways, identifies and designs the most promising process, and then conducts a rough feasibility study to check its economic potential for commercial production after simulation (experimental part). Finally, it also tests the viability of the developed process against non-bio-hydrogen process.

Based on literature review, it is concluded that biomass gasification technology is the most promising process for bio-hydrogen production. Simulation results show that 67.5% product efficiency with 99.99% purity and >82% overall efficiency are achieved using forest residues as the biomass feedstock in a plant capacity of 100 MW. The product efficiency of this process might be lower than the product efficiency achieved by hydrogen production from natural gas, which is >80%, but the designed process has low carbon footprint and has higher efficiency compared to other biological and thermochemical processes.

The results from cost analysis show that the production cost of hydrogen based only on its hydrogen production efficiency for the base case accounts to 93 €/MWh. For the same base case, the calculated internal rate of return (IRR) is 7.46%. Sensitivity analysis shows that in order for IRR to increase from ~7.5% to 15%, either the hydrogen selling price should increase from 90 €/MWh to 125 €/MWh while keeping the rest of variables constant. Alternatively, the fixed capital investment (FCI) should decrease from 200M€ to 150M€ and the hydrogen selling price should increase from 90 €/MWh to 99 €/MWh.

To conclude, this study shows that biomass gasification technology is the most promising bio-hydrogen production process and hence should be considered for commercial production.

Keywords hydrogen, production, processes, design, bio-hydrogen, literature review, thermochemical, biological, efficiency, sensitivity analysis

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LIST OF NOMENCLATURE

Symbols

ΔG^0	Standard state Gibbs free energy change (joule)
g_{dwt}	Gram dry weight (kg)
m	Mass (kg)
p	Pressure (bar)
T	Temperature (°C)
x	Moisture content (%)
@	At the rate
%	Percent
<	Less than
>	Greater than
≈	Approximately equal
$	American dollar
€	Euro

Greek letters

ρm	Gravimetric density
ρv	Volumetric density
γ	Relative humidity

Abbreviations

ADP	Adenosine diphosphate
AnSBR	Anaerobic sequencing batch reactor
ATP	Adenosine triphosphate
AR	Air ratio
ATR	Auto-thermal reforming
C	Carbon
C.A.	Currently available

CHP	Combined heat and power
COD	Chemical oxygen demand
CSTR	Continuously stirred tank reactor
Da	Dalton
EDTA	Ethylenediaminetetraacetic acid
ER	Equivalence ratio
FBR	Fluidized bed bioreactor
FCI	Fixed capital investment cost
GHG	Greenhouse gas
H	Hydrogen
HHV	Higher heating value
HRT	Hydraulic retention time
HT	High temperature
IRR	Internal rate of return
LHV	Lower heating value
LNG	Liquefied natural gas
LPG	Liquefied petroleum gas
LT	Low temperature
MOF	Metal-organic framework
MSW	Municipal solid waste
MW	Megawatt
N	Nitrogen
NRTL	Non-random-two-liquid model
O	Oxygen
O&V	Other fixed and variable costs
pH	Percentage of hydrogen
PFOR	Pyruvate ferredoxin oxido-reductase
PNS	Purple no-sulphur

POME	Palm oil mill effluent
POX	Partial oxidation
PS	Photosystem
PSA	Pressure swing adsorption
RT	Room temperature
R&D	Research and development
S	Sulphur
SCW	Supercritical water gasification
SMR	Steam methane reforming
SRK	Soave-Redlich-Kwon
S/B	Steam-to-biomass ratio
TVS	Total volatile solid
U.R.	Under research
vol.	Volume
V	Voltage
wt.	Weight
WGS	Water-gas shift

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Chapter 1

1.1 Introduction

Current worldwide energy consumption is rapidly increasing, leading to a reduction in fossil-fuel reserves (Asif & Muneer, 2007; Dagdougui, 2012). Indeed, the total world energy consumption amounted to 553 × 10^{15} kJ in 2010, which is expected to rise 1.2-fold by 2020 and 1.6-fold by 2035 (USEIA, 2013). The U.S. Energy Information Administration (2013) predicts that the global use of petroleum and other liquid fossil fuels will rise from ~14 × 10^6 m^3/day in 2010 to ~15.5 × 10^6 m^3/day by 2020 and even ~18 × 10^6 m^3/day by 2035. Moreover, energy production processes based on fossil fuels utilization are generating large amounts of greenhouse gas (GHG) emissions responsible for causing climate change and global warming.

Growing concerns over greenhouse gas emissions from the combustion of fossil fuels, as well as the need for a clean high-energy fuel have prompted interest in the production of hydrogen from bio-renewable sources, also known as “bio-hydrogen”. Unlike conventional hydrogen, which is produced from fossil-fuel feed-stocks, such as natural gas, bio-hydrogen is a “carbon neutral” product in the sense that GHGs emitted during its combustion are offset by those isolated during the biomass feedstock growth cycle (Zhang, et al., 2013). Furthermore, bio-hydrogen is regarded as an attractive future energy carrier due to its conversion to energy yielding only pure water (Johnston, et al., 2005; Momirlan & Veziroglu, 2005).

Renewable sources for hydrogen production include biomass, solar, wind and hydropower utilized in water electrolysis, of which only biomass generates hydrogen directly, while the rest of these sources must undergo electrolysis for hydrogen production. Moreover, biomass is often either dumped as such into the environment or used directly for daily energy purposes, though the energy efficiency is far less than that potentially achieved using modern processes. Therefore, utilizing biomass for producing bio-hydrogen has emerged as a promising future technology, since it safeguards the environment and provides a sustainable source for hydrogen. Bio-hydrogen production can make a major contribution to society. Hydrogen recovery from biomass can be sufficient to satisfy the present and future hydrogen demands, as the scope and potential for recovering it is enormous (IEA, 2006). However, in order to meet these demands and future commercialization, it will be necessary to develop technologies enabling new, low-cost, energy-saving hydrogen production methods. Such methods should also be capable of achieving high production rates with acceptable production costs. (Dincer, 2012; Parthsarathy & Narayan, 2014)

Conventional methods of producing hydrogen include coal gasification, water electrolysis (non-renewable electricity source) and hydrogen production from natural gas by steam reforming. However, these methods utilize non-renewable energy sources for producing hydrogen and are considered unsustainable. Therefore, it is necessary to develop sustainable methods or routes for hydrogen production utilizing renewable energy sources

Currently, the available hydrogen production processes from biomass are divided into two general categories: thermochemical and biological processes. Thermochemical processes involve pyrolysis, liquefaction and gasification, whereas biological processes focus on direct bio-photolysis, indirect bio-photolysis, biological water-gas shift reaction, photo-fermentation and dark-fermentation or by a combination of these processes, such as integration of dark- and photo-fermentation (two-stage process), or bio-catalysed electrolysis. Despite the large number of methods that have recently been proposed for production of hydrogen from biomass (Ni, et al., 2006; Manish & Banerjee, 2008), little work has focussed on the commercial production of these new promising technologies.

1.2 Goal, Objectives and Scope

The goal of this thesis is to identify and recommend economical, efficient, simple and sustainable processes for the commercial production of hydrogen from biomass. The thesis will address three main objectives. The first objective is to identify and review those bio-hydrogen production processes having the most potential for future energy production. A second objective is to compare and identify the most promising processes based on several criteria: feasibility, efficiency and maturity. The third objective is to simulate the most promising pathway (experimental part) identified in the literature review and conduct a rough feasibility study to check its economic potential for commercial production and also test its viability against other non-bio-hydrogen reference pathways.

The thesis will however, review only the most commonly presented and promising bio-hydrogen pathways (both thermochemical and biological).

1.3 Structure

The thesis is divided into six chapters. Chapter two describes the basic properties, up-to-date distribution and storage techniques of hydrogen, as well as classifies the raw materials for the production of hydrogen gas. Chapter three summarizes the advanced hydrogen production technologies and pathways from biomass, including both thermochemical and biological methods.

Chapter four compares all the potential hydrogen production processes using different criteria and identifies the most promising process. It also presents the basics of design and specifications of raw materials and products, as well as discusses several technologies for hydrogen production and provides simulation results for the designed process. Chapter five analyses the costs of the designed process, summarizes the sales volume and production cost and presents a sensitivity analysis of the developed process. Finally, chapter six provides discussions and conclusion concerning the chosen and developed technology.

I Theoretical Part

Chapter 2

2.1 Bio-Hydrogen Properties

The previous chapter presented the motivation behind developing a process for producing a high energy content clean fuel namely bio-hydrogen from biomass. This chapter describes different properties of hydrogen, including its uses and applications. Section 2.2 presents different uses and applications of hydrogen. Section 2.3 provides an up-to-date overview of hydrogen storage and distribution technologies. Finally, classification of different biomass that can be used for bio-hydrogen production is discussed in section 2.4.

Hydrogen is the first element in the periodic table, a colourless, odourless gas, which is the most abundant element in the universe. The main isotope consists of one proton and one electron occupying the lowest angular momentum of zero atomic state (i.e., the electron ground state, denoted 1s), relative to the electron being at infinity. Hydrogen is an important energy carrier and has versatile applications in industry and as liquid fuel in rockets. It has been extensively used in the chemical industry for manufacturing ammonia, methanol, petrol, heating oil, fertilizers, vitamins, cosmetics, lubricants and cleaners. (Scragg, 2009)

Hydrogen is a primary feedstock in petroleum industry, fertilizer industry, finds its application in the food industry, cosmetics sector; and plays a prominent role in the electronics industry, metallurgical industry, transport sector, and fuel cell manufacturing. Most hydrogen is produced from fossil fuels and only 4% of world hydrogen production is from other renewable sources. (Deason, et al., 2010; Parthsarathy & Narayan, 2014)

Hydrogen has been put forward as a new energy carrier in a system called “hydrogen economy”, which was first mentioned in the year 1973 by Gregory (1973). According to Gregory (1973), hydrogen would be used as a fuel and to transport and store energy in the way that electricity is used. Hydrogen as an energy carrier has many advantages due to its non-toxicity, high energy content, yielding only water in combustion, and its flexibility to be used both in fuel cells as well as internal combustion engines. Hydrogen has three times higher energy content than petrol and methane but because of its low density (0.0000899 kg/l at 20°C) it has very low energy content per unit volume (Table 1). The properties and a comparison of hydrogen with other fuels are presented in Table 1&Table 2. (Midilli, et al., 2005; Scragg, 2009)

Table 1. Properties of hydrogen as a fuel. Adapted from Midilli, et al. (2005)

Property	Unit	Value
Molecular formula	-	H_2
Molecular weight	g/mole	2.016
Density*	kg/m^3	0.0838
HHV and LHV**	MJ/kg (liquid)	141.9 & 120
HHV and LHV	MJ/m^3 (liquid)	11.89 & 10.05
Boiling point	°C	-252.74
Freezing point	°C	-259.18
Density (liquid)	kg/m^3	70.8
Diffusion coefficient in air	cm^2/s	0.61

*At normal temperature and pressure. **Higher heating value and lower heating value.

Table 2. Comparison of the energy content of liquid and gaseous fuels. (Scragg, 2009)

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

*Liquefied petroleum gas. **Liquefied natural gas.

It is clear from Table 2 that both methane and hydrogen in the gaseous phase have low energy per unit volume but in hydrogen even in liquid state the energy per unit volume is still low. However, there are several disadvantages or complexities in storage and handling, the production, and flammability of hydrogen, which questions the adoption of hydrogen as an energy carrier (Hammerschlag & Mazza, 2005).

2.2 Hydrogen Applications

Hydrogen can be used for various applications covering many industries, including (Scragg, 2009; Mohammed, et al., 2011):

- Petroleum and chemical industries, like fossil fuels processing, ammonia manufacturing and petrochemicals (hydrodealkylation, hydrodesulphurization and hydrocracking).
- Hydrogenation agent to increase the level of saturated fats and oil.
- Hydrodeoxygenation for oxygen removal and saturation of double carbon bonds.
- Hydrotreatment/upgrading of bio-oils to transportation fuels.
- Metal production and fabrication.
- Shielding gas in welding methods such as atomic hydrogen welding.
- Rotor coolant in electrical generators at power stations.
- Filling gas in balloons and airships.
- Energy storage technology.
- Electronic industry.
- Production and processing of silicon.
- Pharmaceuticals.
- Fuel for rocket propulsion.
- Power generation with fuel cells.
- Transportation sector.

2.3 Hydrogen Storage and Distribution

Hydrogen storage and transportation are closely linked together. Hydrogen can be distributed continuously in pipelines or batch wise by ships, trucks, railways or airplanes. All these batch transportation requires a storage system but also pipelines can be used as pressure storage tanks.

Hydrogen as a gas, in ambient conditions, occupies a large volume (11 m^3/kg) for storage. Therefore, the main challenge in hydrogen storage is to reduce the volume of gas in equilibrium with the environment. The hydrogen molecule can be found in various forms depending on the temperature and the pressure shown in the phase diagram (Figure 1). At low temperature of -262°C, hydrogen is a solid with a density of 70.6 kg/m^3 and at higher temperature of 0°C and pressure of 1 bar with a density of 0.09 kg/m^3 hydrogen is a gas. A small area starting at the triple point and ending at the critical point exhibits the liquid hydrogen with a density of 70.8 kg/m^3 at -253°C. And at ambient temperature hydrogen is a gas. (Züttel, 2007; Kauranen, et al., 2012)

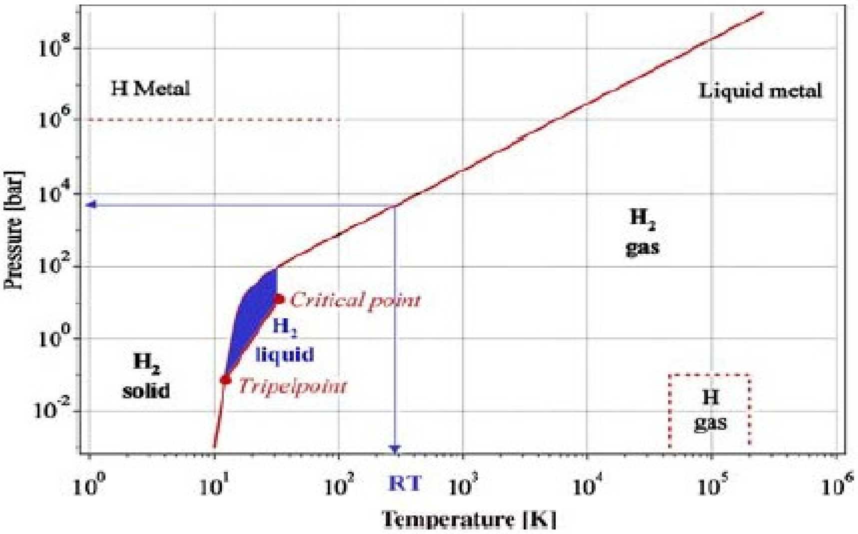


Figure 1. Phase diagram for hydrogen. (Züttel, 2007)

Hydrogen can be stored as pressurized gas, liquefied hydrogen, in metal hydrides, in nanostructured/ porous material, in hydrogen-rich chemical or on the surface of adsorption compounds (Krishna, et al., 2012; Züttel, 2007). At the moment, several kinds of technologies of hydrogen storage are available (Table 3).

The most common as well as the simplest method of hydrogen storage is compression of H_2 gas at high pressure, which is possible at ambient temperature, and the in and out-flow are simple. It is commercially available, and the best known option is the use of C-fibre composite vessels (6–10 wt.% H_2 at 350–700 bar). However, R&D issues include fracture mechanics, safety, need for compression energy, reduction of volume, and is costly. (Riis, et al., 2006; Krishna, et al., 2012)

Table 3. The six basic hydrogen storage methods and phenomena. (Züttel, 2007)

Storage methods	**ρ_m (mass %)**	**ρ_v (kg H_2/m^3)**	**T (°C)**	**p (bar)**	**Phenomena and remarks**
High pressure gas cylinders	13	< 40	RT	800	Compressed gas (molecular H_2) in light weight composite cylinder (tensile strength of material is 2,000 Mpa).
Liquid hydrogen in cryogenic tanks	Size dep.	70.8	-252	1	Liquid hydrogen (molecular H_2), continuous loss of a few % per day of H_2 at RT.
Adsorbed hydrogen	≈2	20	-80	100	Physisorption (molecular H_2) on materials e.g. carbon with a very large specific area, fully reversible.
Absorbed on interstitial sites in a host metal	≈2	150	RT	1	Hydrogen (atomic H) intercalation in host metals, metal hydrides working at RT are fully reversible.
Complex compounds	< 18	150	> 100	1	Complex compounds ($[AlH_4]^-$ or $[BH_4]^-$), desorption at elevated temperature, adsorption at high pressure.
Metals and complexes together with water	< 40	>150	RT	1	Chemical oxidation of metals with water and liberation of hydrogen, not directly reversible?

The gravimetric density ρ_m, the volumetric density ρ_v, the working temperature T and pressure p are listed. RT stands for room temperature (25°C)

Liquid hydrogen is also possible but 25% to 45% of the stored energy is required to liquefy the H_2. In this method, the density of hydrogen storage is very high but hydrogen boils at about -253°C and it is necessary to maintain this low temperature or else the hydrogen will boil away, as well as bulky insulation is needed. This method is also commercially available and cryogenic insulate dewars are mostly utilized, and similar to compressed H_2 gas storage this method is also costly. (Riis, et al., 2006; Krishna, et al., 2012)

The third potential solutions for hydrogen storage are metal hydrides and hydrogen adsorption in metal-organic frameworks (MOFs) and carbon based systems. In metal hydride or solid state hydrogen storage, the powdered metal absorb hydrogen under high pressures (Krishna, et al., 2012). During this process, heat is produced upon insertion and with pressure release and applied heat, the process is reversed. Currently, these methods are in very early development stages with many R&D questions. Some of the R&D issues include, the weight of the absorbing material-mass of a tank would be about 600 kg compared to the 80 kg of a comparable compressed H_2 gas tank, lower desorption kinetics, recharge time and pressure, heat management, life cycle cost, container compatibility and optimisation. (Riis, et al., 2006; Krishna, et al., 2012)

Currently, more popular is carbon absorption, which is the newest field of hydrogen storage. At applied pressure, hydrogen will bond with porous carbon materials such as nanotubes. The more focused ones are micro-porous zeolites, nano-porous MOFs and carbon-based materials, which is still in its developing phase. (Krishna, et al., 2012)

A key element of the overall hydrogen energy infrastructure is the distribution system that delivers hydrogen from its production point to an end-use device. Delivery system requirements necessarily vary with the production method and end-use applications. Hydrogen distribution through high-pressure cylinders and tube trailers has a range of 150–300 kilometres from the production facility. For long-distance distribution, hydrogen is usually transported as a liquid in super-insulated, cryogenic, over-the-load-tankers, railcars and barges. The transported liquid hydrogen is then vaporized for end uses. Hydrogen pipelines in Europe covers 1600 km whereas, 800 km in USA. Further information concerning the distribution of hydrogen can be found in the report presented by (Kauranen, et al., 2012). (Davis, et al., 2002; Kauranen, et al., 2012)

Melaina, et al. (2013) reviewed several key issues concerning blending hydrogen into natural gas pipeline networks that includes, benefits of blending, extent of natural gas pipeline network, impact on end-use systems, safety, leakage and downstream extraction. According to the study, blending hydrogen into natural gas pipeline networks at low concentrations is performed in the USA and some European countries. Relatively low concentrations of hydrogen, 5%–15% by volume, appear to be feasible with very few modifications to existing pipeline systems or end-use appliances. However, the assessed feasibility varies from location to location. Additionally, higher concentrations introduce challenges and requires modifications. They also estimated an extraction cost ranging from \$0.3 - \$1.3 per kg hydrogen for a 10% hydrogen blend, for a station with a pressure drop from 20 to 2 bars, depending upon the capacity and recovery rate. (Melaina, et al., 2013)

2.4 Raw Materials and Their Characteristics

For hydrogen to be renewable, it must be produced from renewable feedstock. In bio-hydrogen production, potential resources in feed-stocks include biomass, such as agricultural waste by-products, lingo-cellulosic products, such as wood and wood waste, waste from food processing and aquatic plants and algae, sewage sludge, agricultural and livestock effluents as well as animal excreta. Based on comprehensive literature studies (IEA, 2006; Mohanty, et al., 2014; Parthsarathy & Narayan, 2014), it can be assumed that if and once these resources are used under appropriate control, they would become one of the major sources of energy in the future.

Of all the renewables, biomass is a promising resource for producing environmentally friendly hydrogen. In fact, considering the CO_2 penalty which may be imposed on fossil fuels, biomass has the potential to become cost competitive with fossil fuels. Biomass is a resource that is abundantly available in many parts of the world. The drawbacks of biomass are seasonal availability (agricultural feedstock), high feedstock and capital costs (Mahishi, 2006). Ni, et al. (2006) categorised a variety of biomass resources that can be used to convert into energy.

The use of any biomass for conversion to hydrogen energy is affected by the values of its physicochemical properties. These values not only determine the conversion process but in general the investment evaluation, as a whole. The understanding of those properties on the different biomass resources is essential before the conversion process can be considered. In general, the biomass properties that are of the greatest importance in energy processes are moisture content, ash content, volatile matter content, heating value, bulk density and alkali metal content (Table 4).

Table 4. Elemental analyses (wt.%, dry basis) and calorific values (HHV) of biomass samples. (Demirbas, 2009)

Biomass source	**C**	**H**	**O**	**N**	**Ash**	**Higher heating value (MJ/kg)**
Olive husk	50	6.2	42.2	1.6	3.6	19
Hazelnut shell	52.9	5.6	42.7	1.4	1.4	19.3
Hazelnut seed coat	51	5.4	42.3	1.3	1.8	19.3
Softwood	52.1	6.1	41	0.2	1.7	20
Hardwood	48.6	6.2	41.1	0.4	2.7	18.8
Wheat straw	45.5	5.1	34.1	1.8	13.5	17
Wood bark	53.1	6.1	40.6	0.2	1.6	20.5
Waste material	48.3	5.7	45.3	0.7	4.5	17.1
Water hyacinth	39.8	5	34.3	1.9	19	14.6
Corncob	49	5.4	44.6	0.4	1	18.4
Corn Stover	45.1	6	43.1	0.9	4.9	17.4
Brown kelp	28.4	4.1	24.3	4.8	38.4	10.8
Tea waste	48.6	5.5	39.5	0.5	1.4	17.1
Bagasse	45.3	5.1	40.2	0.1	9.3	16.9
Spruce wood	51.9	6.1	40.9	0.3	1.5	20.1
Beech wood	49.5	6.2	41.2	0.4	1.4	19.2
Poplar wood	49	6.1	42.8	0.1	1	18.8
Ailanthus wood	49.5	6.2	41	0.3	1.7	19

Chapter 3

3.1 Production Processes

The previous chapter described the basic properties, applications, up-to-date distribution and storage techniques of hydrogen, as well as the classification of raw materials for the production of bio-hydrogen gas. This chapter presents an overview of hydrogen production technologies from biomass. Section 3.2 explains the available thermochemical production processes from biomass: pyrolysis, liquefaction and gasification. Section 3.3 reviews the two different types of biomass technologies used for bio-hydrogen production: biomass gasification and supercritical water gasification. Similarly, Section 3.4 explains the available biological production processes from biomass, including direct- and indirect bio-photolysis, photo-fermentation and dark-fermentation. This section includes cost analysis of hydrogen production methods done by Mahishi (2006). For general understanding, basic description of some conventional methods are also explained in this section. The explained methods are steam methane reforming, partial oxidation, auto-thermal reforming and electrolysis. An overview of available thermochemical and biological technologies are presented in the latter sections.

Four energy paths have been proposed for hydrogen production that can be obtained using renewable energy sources by Dincer (2012): thermal energy, electrical energy, biochemical energy and photonic energy. The electrical and thermal energy can be derived from renewable energies, such as solar, wind, geothermal, tidal, wave, ocean thermal, hydro, biomass, or from nuclear energy, or from recovered energy. The photonic energy is comprised in solar radiation only, which drives the processes like PV-electrolysis, photo-catalysis photo-electro-chemical method and bio-photolysis for producing hydrogen. The biochemical energy is that stored in organic matter (in form of carbohydrates, glucose and sugars) and can be manipulated by certain microorganisms that can extract hydrogen from various substrates or it can be chemically converted to thermal energy. Biochemical energy can be assisted or not by solar radiation to generate energy, depending on the case (viz. bio-photolysis or dark-fermentation). (Dincer, 2012)

This thesis mainly focuses on sustainable methods for hydrogen production from biomass (Figure 2). The main routes for hydrogen production using biomass are bio-chemical/ biological processes and thermo-chemical processes.

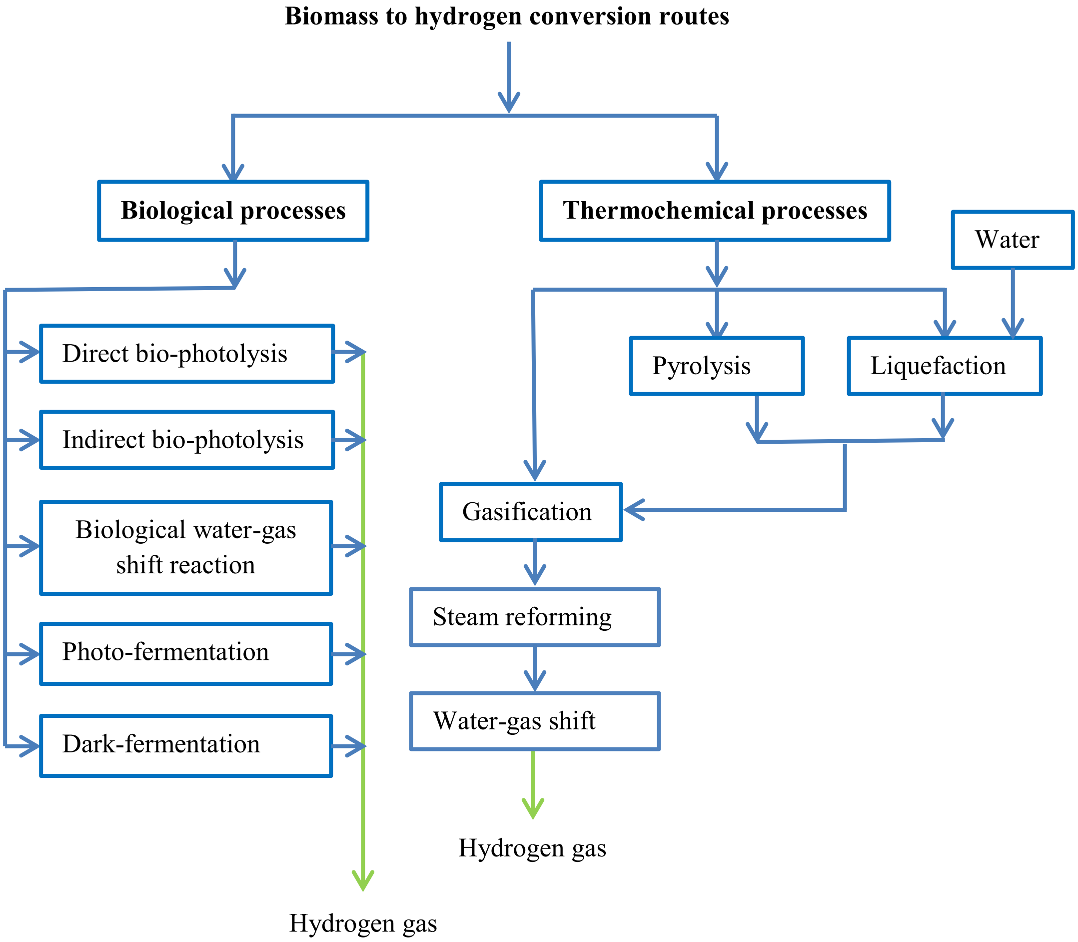


Figure 2. Hydrogen production routes from biomass.

Mahishi (2006) calculated the economics of hydrogen (Table 5). The table lists the status of technology and the average cost of producing hydrogen during the year 2006. Efficiency is defined as the ratio of lower heating values of hydrogen in product gas to total energy supplied to the process (Equation 1).

Equation 1. $\eta = \frac{\mathrm{Product}_{\mathrm{LHV}}}{\mathrm{Feed}_{\mathrm{LHV}}} * 100\%$

Despite the fact that the table shows the average energy efficiency, average hydrogen production cost and production scale; the reports, where the table is taken from, fails to clarify the meaning of this table leaving many questions unanswered. For instance, the feedstock used by all these methods are not mentioned; the sources of steam methane reforming (SMR) are not shown; fluctuations in energy efficiencies of partial oxidation and autothermal reforming is not explained as well as the size of production scale is not clear.

Table 5. Cost analysis of hydrogen production methods. Adapted from Mahishi (2006) & Parthsarathy & Narayan (2014)

Method	**Energy efficiency (%)**	**H_2 production cost ($/ kg in 2006)**	**Production scale**
Steam methane reforming (SMR)	83	0.75 (without CO_2 sequestration)	Proven technology, Economical
Partial oxidation	7–80	1.39 (residual oil)	Large/ available
Auto-thermal reforming	7–74	1.93	Large/ C.A.*
Coal gasification	63	0.92 (without CO_2 sequestration)	Large/ C.A.
Biomass gasification	40–50	1.21–2.42	Mid-size/ C.A.
Biomass pyrolysis	56	1.21–2.19	Mid-size/ C.A.
Electrolysis	25 (including electrical efficiency)	2.56–2.97 (Nuclear source)	Small/ C.A.
Photo-catalytic	10–14 (theoretical)	4.98	U.R.*
Biological	24 (speculative)	5.52	U.R.
Bio-photolysis of water by algae			U.R.
Dark fermentation			U.R.
Photo fermentation			U.R.

C.A.* = Currently available & U.R.* = Under research

Conventional Technologies for Hydrogen Production

Steam Methane Reforming (SMR)

SMR is the most widely used method for hydrogen production. SMR process is characterized by its high efficiency, favourable economics, proven technology, and is ideal for large scale hydrogen production.

Steam methane reforming produces hydrogen in the following three steps:

- Methane is first catalytically reformed at elevated temperature and pressure to produce synthesis gas (synthesis gas or syngas is a mixture of H_2 and CO) as shown in the following reaction (Equation 2):

  Equation 2. $\mathrm{CH_4 + H_2O \leftrightarrow CO + 3H_2}$

- A catalytic water gas shift (WGS) reaction is then carried out to combine CO and H_2O to produce additional hydrogen as shown in the following reaction (Equation 3):

  Equation 3. $\mathrm{CO + H_2O \leftrightarrow CO_2 + H_2}$

- The hydrogen product is then separated by adsorption

Methane is treated with high temperature steam to produce a mixture of H_2, CO, CO_2 and other impurities. The reaction is carried out in a reformer containing tubes filled with nickel catalyst at temperatures between 500–950°C and a pressure of 30 bars. Excess steam promotes the second step in the process, which is the conversion of syngas to the desired end product (hydrogen) via the water-gas shift reaction. The third step of separation is conventionally accomplished by pressure swing adsorption (PSA). PSA is a process used for the production of high purity hydrogen from steam methane reforming off-gas and refinery off-gas. (Mahishi, 2006)

The classical method of producing hydrogen from natural gas is depicted in Figure 3. This method produces hydrogen via catalytic steam reforming of natural gas, which is a mature technology and is the route by which hydrogen is made today. The step by step description of the process can be followed in the report done by Spath & Mann (2001).

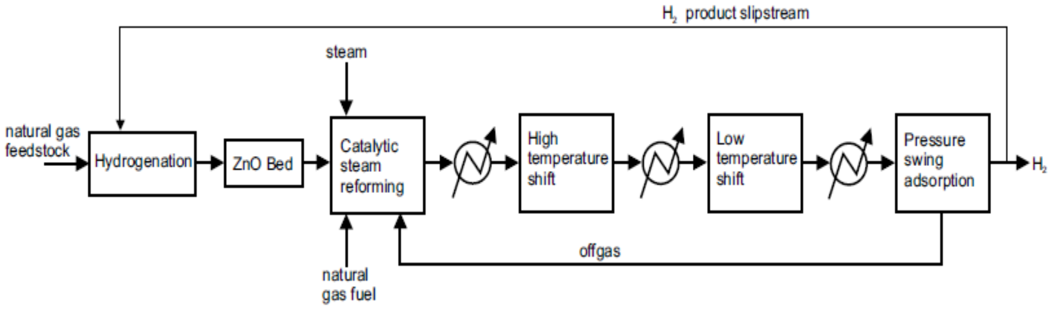


Figure 3. Hydrogen production from natural gas. (Spath & Mann, 2001)

Partial Oxidation or Auto-thermal Reforming of Methane

Partial oxidation (POX) and Auto-thermal Reforming (ATR) are similar alternatives to SMR. The POX process partially oxidizes methane in a one-step reaction, while ATR combines partial oxidation and reforming reaction, catalytically reacting methane with a mixture of steam and oxygen. This differs from the steam methane reforming process which treats methane with steam only. Partial oxidation of methane produces a syngas mixture of CO and H_2 as per the following reaction (Equation 4), which is then followed by WGS reaction (Equation 3):

Equation 4. $CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2$ (Mahishi, 2006)

Electrolysis

Electrolysis uses electricity to dissociate water into diatomic molecules H_2 and O_2. An electric potential is applied across a cell with two electrodes containing a conducting medium, generally an alkaline electrolyte solution such as aqueous solution of potassium hydroxide (KOH). Electrons are absorbed and released at the electrodes, forming hydrogen at the cathode and oxygen at the anode. Under alkaline conditions, this process may be described by the following reactions (Equation 5, Equation 6 and Equation 7):

Equation 5. Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Equation 6. Anode: $2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

Equation 7. Overall: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

The net effect of this process is to produce hydrogen and oxygen by supplying only water and electricity. The theoretical voltage for the decomposition at atmospheric pressure and 25°C is 1.23 volts. At this voltage, reaction rates are very slow. Therefore, in practice higher voltages are applied to increase the reaction rates. However, this results in increased heat losses to the surrounding, decreasing the energy efficiency. The necessary voltage may be lowered by using catalysts or sophisticated electrode surfaces. Increasing temperature and pressure may also increase the efficiency at the cost of additional material needed to resist corrosion or higher pressures. (Mahishi, 2006)

3.2 Thermochemical Processes

This section reviews the available thermochemical processes for the production of hydrogen using biomass. As mentioned in the earlier section, the available thermochemical production processes from biomass involve pyrolysis, liquefaction and gasification.

3.2.1 Pyrolysis

Pyrolysis is the heating of biomass at a temperature of 400–600°C and close to atmospheric pressure in the absence of air to convert biomass into liquid oils, solid charcoal and gaseous components. Pyrolysis is further classified into slow and fast pyrolysis. Slow pyrolysis usually occurs at temperature between 400 and 450°C, with low heating rate of 1–5°C /s and high residence time (4–8 minutes). And fast pyrolysis usually occurs at temperature between 450–950°C, with the high heating rate of about 100–300°C/s and a very short residence time of about 1–5 seconds to produce high quality products.

The products of pyrolysis can be found in all gas, liquid and solid phases (Ni, et al., 2006):

(i) Gaseous products include mixture of (H_2), CH_4, CO, CO_2 and other gases depending on the organic nature of the biomass for pyrolysis.
(ii) Liquid products include tar and oils that remain in liquid form at room temperature.
(iii)Solid products are char, which is almost pure carbon, and inorganic components such as ash and alkali metals from biomass

The typical product mass yield from woody biomass under slow pyrolysis conditions are about 30% liquid product, 35% gas and 35% char. Similarly, the mass yield for fast pyrolysis are about 70% liquid product, 15% gas and 15% char. The gaseous product can be used for providing heat for the pyrolysis reaction or for drying of the biomass.

The organic liquid and solid products can be processed for hydrogen production. The pyrolysis oil can be separated into two fractions based on water solubility.

These fractions can either be used separately or as mixtures for hydrogen production through gasification process. The material flow is illustrated in Figure 4. (Ni, et al., 2006)

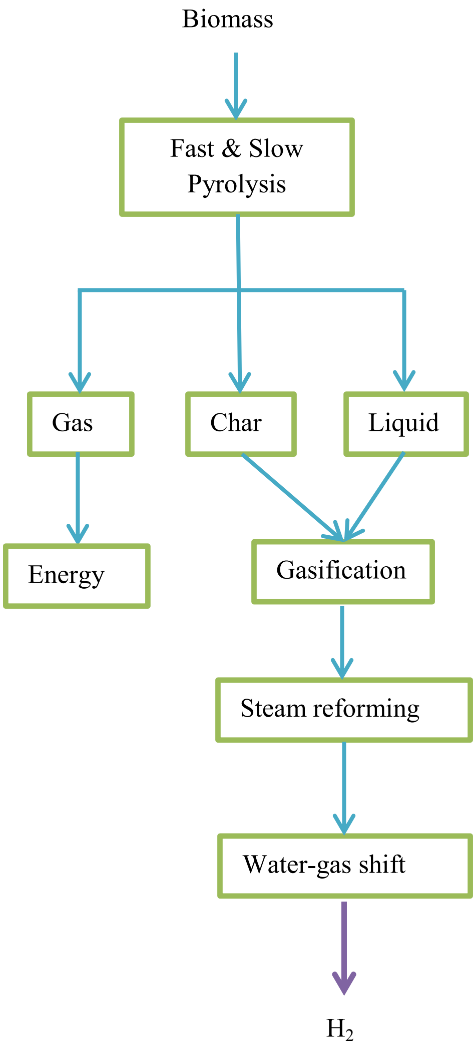


Figure 4. Biomass to hydrogen based on pyrolysis with a co-products strategy. Adapted from Ni, et al. (2006)

3.2.2 Liquefaction

Water present in biomass poses negative effect on pyrolysis, as it requires high heat of vaporization. In general, pyrolytic liquefaction usually liquefies biomass suitably having < 40% of moisture contents. Water contents in tropical grasses can be as high as 80–85% or similarly ~90% for aquatic species. Biomass usually requires pre-processing to suit pyrolysis application, which is energy consuming or/ and costly. One solution to handle high moisture contents in biomass can be hydrothermal liquefaction of biomass. (Akhtar & Amin, 2011)

Liquefaction is a thermal conversion process where biomass is heated to 250–350°C in water at a pressure of 5–20 MPa in the absence of air in order to obtain liquid fuel. Solvent or catalyst can be added depending on the process parameters and or product specifications. The liquid substances are mostly hydrocarbons and are also known as bio-oils. Like pyrolysis oil, liquefied oil can be either separated into two fractions based on water solubility, meaning that the water soluble fraction can be used for hydrogen production, or the mixture itself can be used for hydrogen production through gasification process (Figure 5). (Mohammed, et al., 2011; Akhtar & Amin, 2011)

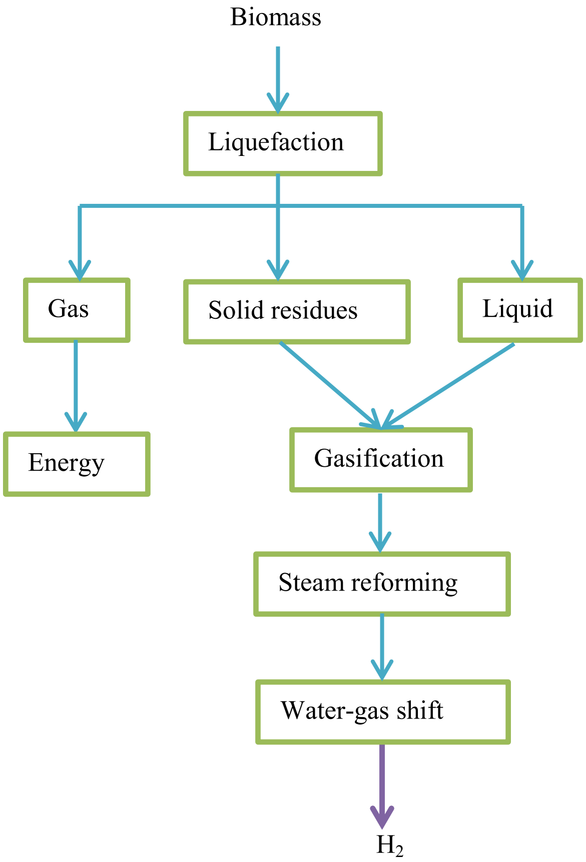


Figure 5. An overview of biomass to hydrogen based on hydrothermal liquefaction.

3.2.3 Gasification

Biomass gasification is a process by which either a solid or liquid carbonaceous material, containing mostly chemically bound carbon, hydrogen, oxygen, and a variety of inorganic and organic components, is reacted with air, oxygen, and/or steam to produce a primary gaseous product containing mostly CO_2, H_2, CO, CH_4, H_2O (g), and light hydrocarbons laced with volatile and condensable organic and inorganic compounds. Biomass can be gasified at high temperatures of above 750°C, during which the biomass particles undergo partial oxidation resulting in gas and charcoal production. Finally, the charcoal is reduced to form CO_2, H_2, CO and CH_4. This conversion process can be expressed as (Equation 8):

Equation 8.

$$\text{Biomass} + \text{heat} + \text{steam} \rightarrow$$
$$\mathrm{H_2} + \mathrm{CO} + \mathrm{CO_2} + \mathrm{CH_4} + \text{light and heavy hydrocarbons} + \text{char.}$$

(Lin, et al., 2002; Ni, et al., 2006)

Figure 6 illustrates the general biomass gasification process. Solid biomass is pre-treated before gasification by drying and grinding whereas, liquid fuel from pyrolysis or liquefaction does not require similar pre-treatment procedures. In gasification stage, the solid/liquid biomass reacts with oxygen in high temperature to form synthesis gas. Gasification consists of drying, structure disintegration, pyrolysis as well as char combustion reaction of biomass feedstock. The gases produced can be steam reformed to produce hydrogen and this process can be further improved by water-gas shift reactions.

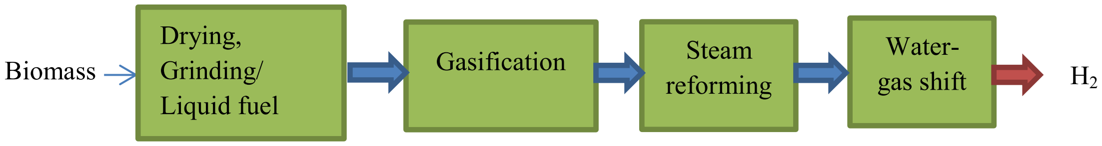


Figure 6. Block diagram of biomass gasification process. (Patronen, 2011)

The gasification process is applicable to biomass having moisture content less than 35% because higher moisture content reduces the thermal efficiency (since heat is used to drive off the water and consequently this energy is not available for the reduction reactions and for converting thermal energy into chemical bound energy in the gas), and it is likely to gasify biomass in supercritical water condition. (Ni, et al., 2006; Patronen, 2011)

There are multiple reactions ongoing in the gasification process. Udomsirichakorn & Salam (2014) explain the mechanistic steps of biomass gasification in their review article. The important reactions of biomass gasification for the production of hydrogen are summarized in Table 6 (Udomsirichakorn & Salam, 2014).

Table 6. Important reactions in biomass gasification. (Mohammed, et al., 2011)

Name of reaction	**Chemical equation**
Pyrolysis	$\text{Biomass} + \text{heat} \leftrightarrow \text{gases}\ (H_2 + CO + CO_2 + H_2O + CH_4)$ $+ \text{light and heavy hydrocarbons} + \text{char}$
Combustion	$2C + O_2 \leftrightarrow 2CO$ $C + O_2 \leftrightarrow CO_2$ $2H_2 + O_2 \leftrightarrow 2H_20$
Boudouard	$C + CO_2 \leftrightarrow 2CO$
Water gas (primary)	$C + H_2O \leftrightarrow CO + H_2$
Water gas (secondary)	$C + 2H_2O \leftrightarrow CO_2 + 2H_2$
Water-gas shift	$CO + H_2O \leftrightarrow CO_2 + H_2$
Methanation	$C + 2H_2 \leftrightarrow CH_4$
Methane reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$
Tars reforming	$\text{Tars} + H_2O \leftrightarrow H_2 + CO_2 + CO + \text{hydrocarbons} + \dots ..$
Hydrocarbon reforming	$\text{Hydrocarbons} + H_2O \leftrightarrow H_2 + CO_2 + CO$

3.3 Thermochemical Technologies for Hydrogen Production from Biomass

This section reviews the two different types of biomass technologies used for bio-hydrogen production: biomass gasification and supercritical water gasification. Hannula (2009) reviewed and presented a selection of ongoing biomass gasification projects and related activities. The report mainly presents the currently used technologies for the production of transportation fuels, and these technologies could also be used for the production of renewable hydrogen.

3.3.1 Hydrogen from Biomass Gasification

During gasification process, solid biomass or liquid fuel from either pyrolysis or liquefaction is thermally decomposed to small quantities of char, liquid oil and high production of product gases under limited presence of oxygen. The product yields and the composition of gases are dependent on several parameters, including biomass types, gasifying agent, tar formation, ash formation, temperature, feedstock, particle size, heating rate, pressure, catalyst and reactor configuration.

All biomasses are mainly composed of cellulose, hemi-cellulose and lignin and their composition differs depending on biomass types. These components play a major role in the decomposition of biomass as larger composition of cellulose and lignin yield more gaseous products. This in turn increases the potential of hydrogen recovery from biomass. Many biomass types have been tried out so far to generate hydrogen, including pine sawdust, cedar wood, waste water sludge, palm oil waste, municipal solid waste and sawdust. (Mohanty, et al., 2014)

3.3.1.1 Factors Influencing Hydrogen Yield in Biomass Gasification

Gasifying agent

In gasification reactions, gasifying agent is one of the issues that has significant influence on quantity and quality of the product gas. Generally, air, oxygen, steam as well as mixtures of these can be utilized as a gasifying agent; choice of which totally depends on the desired product gas composition (Table 7).

Table 7. Comparison between different gasification processes. (Parthsarathy & Narayan, 2014)

	Air gasification	**Oxygen gasification**	**Steam gasification**
Heating value of product gas (MJ/Nm^3)	Low 4–6	High 10–15	High 15–20
Products	CO, H_2, Water, CO_2, HC, Tar, N_2	CO, H_2, HC, CO_2	H_2, CO, CO_2, CH_4, light HC, tar
Average product gas composition	H_2–15%, CO–20%, CH_4–2%, CO_2–15%, N_2–48%, H_2:CO: 0.75	H_2–40%, CO–40%, CO_2–20%, H_2:CO:1	H_2–40%, CO–25%, CH_4–8%, CO_2–25%, N_2–2%, H_2:CO:1
Reactor temperature (°C)	900–1100	1000–1400	700–1200
Cost	Cheap	Costly	Medium

Air-blown gasification of biomass have a feasible application and has been developed actively for industrial purposes. However, this process technology produces low calorific value gases of 4–6 MJ/Nm^3 and an 8–16.5 vol.% H_2 (Ji, et al., 2009; Kim, et al., 2013; Udomsirichakorn & Salam, 2014; Galindo, et al., 2014). A better quality of product gas with medium calorific value (10–15 MJ/Nm^3) can be produced using oxygen as a gasifying agent; but the process requires a pure oxygen supply which leads to simultaneous problem of cost and safety (Ni, et al., 2006; Saxena, et al., 2008; Mohammed, et al., 2011; Udomsirichakorn & Salam, 2014). Biomass steam gasification could produce medium calorific value gases (10–20 MJ/Nm^3) and especially the product gas rich in hydrogen content (30–60 vol.%) (Xiao, et al., 2011; Udomsirichakorn & Salam, 2014; Parthsarathy & Narayan, 2014; Wu, et al., 2014).In the open literature, there are many research works using these kinds of gasifying agents but this study mainly emphasizes the important aspects of the biomass gasification process relevant to hydrogen-enriched gas production.

Kim, et al. (2013) investigated air-blown gasification of woody biomass in a pilot scale bubbling fluidized bed gasifier aimed to produce product gas rich in hydrogen. Air was used as the gasifying agent as well as a fluidizing gas. The feed rates of biomass and air were controlled to change the equivalence ratio (ER) and vary the internal conditions. Changes in the biomass and air feed rates affected the product gas composition and temperature profiles in the gasifier. The concentration of syngas tended to increase as ER went from 0.27 to 0.19. The hydrogen concentration increased from 14.5% to 16.5%, carbon monoxide increased form 13.8% to 16.1% and CH_4 from 4% to 5.3%. The total volume of the product gas decreased as ER was reduced. The concentration and calorific value (above 4.7 MJ/Nm^3) of hydrogen are relatively higher than previous researches and it results from the configuration of the gasifier: longer free board and top fuel feeding.

Galindo, et al. (2014) presented an experimental evaluation of the quality of the product gas in a two-stage, air supply downdraft gasifier, referred to its tar and particle content for different operating conditions utilizing Eucalyptus wood (6 cm cubic shape) as feedstock. A slight increase in the gasifier efficiency was observed when the ER and the air ratio (AR) between the stages were carefully selected. For a total air flow of 20 Nm^3/h and an air ratio between the two stages of 80%, the gasifier produced a fuel gas with low tar and particles content from 54.25 to 102 and 4 mg/Nm^3, respectively compared to a tar and particles content of 418.95 and 146.03 mg/Nm^3 obtained for a total air flow of 20 Nm^3/h and an AR of 0%. The results confirmed that the use of a second stage air supply enables a reduction of 87% in tar yield and of 29.9% in the particle content of the gas. The product gases for this operational condition had a composition of 19.2 vol.% of CO, 1.3

vol.% of CH_4, 17.14 vol.% of H_2, 14.22 vol.% of CO_2 and with an average LHV of 4.74 MJ/Nm^3.

Chang, et al. (2011) experimentally investigated gasification of commercial cellulose and agricultural wastes (bagasse and mushroom), with air and mixture of air and steam in a fluidized bed for hydrogen production. They also investigated the influence of varied steam-to-biomass ratio (S/B). With S/B of 0.0 (i.e., no steam or only-air gasification), reaction temperature of 800°C and ER of 0.27, hydrogen content was found to be 13.5 vol.%. But once S/B increased to 1, hydrogen concentration raised to almost 20 vol.%.

Lv, et al. (2007) experimentally studied air and oxygen/ steam gasification of laboratory scale self-heated downdraft gasifier as the reactor using char as the catalyst for the characteristics of hydrogen production from pine wood (3 cm cubic shape). Air and steam/oxygen were utilized as the gasifying agents. The results indicated that biomass oxygen/steam gasification improves hydrogen yield compared to biomass air gasification depending on the volume of downdraft gasifier, and as well nearly doubles the heating value of fuel gas. For biomass oxygen/steam gasification, the maximum lower heating value of fuel gas reaches 11.11 MJ/Nm^3 and under same operating conditions the maximum hydrogen yield of 45.16 g H_2/ kg biomass is reached. The experimental and comparison results proved that biomass oxygen/steam gasification is more effective than biomass air gasification technique.

Udomsirichakorn & Salam (2014) studied, plotted and compared the effect of using different gasifying agents on hydrogen concentration in the product gas in their review article. The comparison showed that using pure oxygen as a gasifying agent rather than air gasification could produce the product gas with better calorific value, which is due to no dilution effect from nitrogen, and hydrogen content. And in case of partial amount of steam diluted in air or oxygen gasification, the resulting product is relatively richer in hydrogen composition. On the other hand, in the absence of both air and oxygen, pure steam gasification experiment shows higher hydrogen concentration. In the same study, it has been shown that the range of hydrogen content is higher in case of gasifying with pure steam compared to the mixture of steam and oxygen. The reason for higher hydrogen content being the phenomenon of higher hydrogen content resulting from the decomposition of water, in the form of steam, added to the thermochemical conversion of biomass.

Although a direct comparison of hydrogen concentration and yield using different gasifying agents is not possible due to variation of many different operating conditions, still the review results provide a general insight into the influence of different gasifying agents.

Tar formation

Another major issue in biomass gasification is to deal with the tar formation that occurs during the process (Ni, et al., 2006). The undesirable tar may cause the formation of tar aerosols and polymerization to a more complex structure, which is not favourable for hydrogen production through steam reforming. Additionally, tar formation causes catalyst deactivation, operation interruption, and the production of carcinogenic elements. The two tar removal technologies are internal treatment in the gasifier (primary methods) and cleansing the heated gas after gasification (secondary methods). Primary methods that are available to minimize tar formation are proper design of gasifier, proper control and operation and additives/catalysts. Also the operation parameters, such as temperature, gasifying agent and residence time play vital role in formation and decomposition of tar. (Ni, et al., 2006; Pereira, et al., 2012)

Pereira, et al. (2012) studied and compared several experimental papers (Sun, et al., 2009; Meng, et al., 2011; Min, et al., 2011; Michel, et al., 2011) and concluded that the total tar content produced from biomass gasification depends not only on temperature but also on other parameters.

Many chemical substances have been proposed to enhance tar removal, since the removal of tars and the reduction of methane content increase the economic viability of the biomass gasification process. Mohammed, et al. (2011) suggest the use of three categorized groups of catalysts, which includes: (1) naturally occurring catalysts such as dolomite and olivine; (2) alkali metals such as KOH,

K_2CO_3, $KHCO_3$, Na_2CO_3, $CsCO_3$, KCl, $ZnCl_2$ and NaCl; and (3) nickel-based catalysts, which have been evaluated for tar reduction in syngas. The main catalysts for tar reforming are listed in Table 8 (Mohammed, et al., 2011).

Table 8. Main catalysts for tar reforming. (Mohammed, et al., 2011)

Catalyst type	Representative catalysts	Main advantages	Technical challenges
Maturely occurring catalyst	Dolomite Olivine Clay Zeolite	Cheap	Moderate reforming efficiency Easily eroded and broken
Alkali metals and salts	KOH $KHCO_3$ K_2CO_3 $NaCO_3$	1. High reforming efficiency 2. Increased amount of hydrogen in syngas	Increased plugging and deactivation of other metal catalysts at a high temperature
Stable metal with oxide support	NiO/Al_2O_3 $Ni/CeO_2/Al_2O_3$	1. High reforming efficiency 2. Increased amount of hydrogen in syngas	Stable metals are expensive Metals are easily deactivated by coke, poisoned by H_2S and sintered by ash melting Require hot-water-resistant support materials

Nickel-based catalysts are reported to be very effective for two different purposes: (1) in reducing tar; and (2) in decreasing the quantity of nitrogenated compounds such as ammonia. Although this provides satisfactory catalytic activity, nickel-based catalysts are expensive, gets easily deactivated, and are poisonous at high temperature.

According to Pereira, et al. (2012), natural dolomite is the most popular catalyst since it is easily available, inexpensive, disposable, and can significantly reduce the tar content of the syngas. A major problem with using dolomite is its deactivation due to the quick calcination in the gasifier as dolomite is a soft and fragile material that erodes easily, generating a raw gas with a high particulate content. They reviewed several studies and concluded that olivine is mechanically stronger than dolomite. One of their reviewed articles (Corella, et al., 2004) reported that although olivine was shown to be 1.40 times less effective for in-bed tar removal than raw dolomite, it generated four to six times fewer particulates in the gasification gas than dolomite. Their second reviewed article (Michel, et al.,

2011) investigated the gasification of Miscanthus X Giganteus (a perennial warm-season Asian grass) in a fluidized bed reactor with the presence if Ni/olivine based catalysts. The results showed that the addition of NiO to olivine catalyst was efficient for reducing tar. And the third study (Rapagnà, et al., 2011) carried out steam gasification of biomass in a fluidized bed reactor using a 10 wt.% Fe/olivine catalyst and found that the studied catalysts reduced naphthalene and toluene by 48% and 59%, respectively.

Along with dolomite and olivine other effective catalysts include, olive kernel, activated carbon, methyl hexadecanoate and paraxylene, bed-material (olivine) coating, and addition of acetylene and hydrogen flames into the blend of gases containing toluene. (Pereira, et al., 2012)

Ash formation

Another problem of biomass gasification is the ash formation containing large quantities of inorganic elements such as alkali metals (K, Na), alkali earth metals (Ca, Mg), silicon, chlorine, and sulphur, as their main constituents. This ash formation may cause deposition, sintering, slagging, fouling, high temperature corrosion and agglomeration; leading to uneconomical operation or even to a shut-down of the plant. In order to resolve these problems, fractionation (Arvelakis & Koukios, 2002) and leaching (washing) (Jenkins, et al., 1996; Arvelakis, et al., 2001) can be employed to reduce ash formation inside the reactor. Fractionation being effective for ash removal might deteriorate the quality of the remaining ash whereas, leaching can remove inorganic fraction of the biomass as well as improve the quality of the remaining ash, but it is a quite expensive process step since large quantities of biomass need to be handled, resulting in large amount of wastewater, extensive energy consumption in drying and large investments due to the large size of systems.. García-Ibañez, et al. (2004) reported gasification of leached olive oil waste in a circulating fluidized bed reactor for gas production that demonstrated the feasibility of leaching as a pre-treatment technique. (Ni, et al., 2006)

A number of efforts have been made by researchers to test hydrogen production from biomass gasification with various biomass types and at various operating conditions, as listed in Table 9.

Table 9. Investigations on biomass gasification for hydrogen production.

Reactor	Biomass	Gasifying agent	Temperature (°C)	Catalyst	H_2 content (Vol.%)	References
Fluidized bed	Pine, eucalyptus and holm-oak	steam	700–900	Not used	21–45	(Franco, et al., 2003)
Fluidized bed	α- cellulose	Steam and air	750–950	Not used	13.50–18.56	(Chang, et al., 2011)
Fluidized bed	Pine sawdust, wood chip and cereal straw	Steam	650–780	Not used	59 @ 750 °C	(Herguido, et al., 1992)
Fluidized bed	Rice hull	Steam	700–800	Not used	32.8–42.62	(Boateng, et al., 1992)
Fluidized bed	Spruce wood	Air	780	Quartize Olivine	31	(Miccio, et al., 2009)
Updraft gasifier	Rice straw	Air	700–850	Alumina-silicate bed and MgO	6–10	(Calvo, et al., 2012)
Stainless steel cylinder tube	Sawdust	Steam	600,670,710	CaO (sorbent)	54.43	(Acharya, et al., 2010)
Semi-batch type	Waste water sludge	Steam	900	Not used	_	(Nipattummakul, et al., 2010)
Fixed bed	Bagasse	Oxygen and steam	800	Ni-Al_2O_3	51.7	(De Filippis, et al., 2004)
Fixed bed	Municipal solid waste	Steam	900	Calcined dolomite	53.22	(He, et al., 2009)

3.3.2 Hydrogen Production from Gasification in Supercritical Water

Supercritical water gasification (SCW) is another gasification technology for hydrogen production, glucose and cellulose being mainly utilized biomass feedstock in laboratory scale. Under normal conditions, water exists in three states, and when the pressure and temperature of water is subjected to supercritical state (22.1 MPa and 374°C), its gas and liquid phase becomes miscible. At this point water acts as an oxidant and when biomass reacts with supercritical water the oxygen molecules of water are transferred to carbon atoms of biomass. The properties of water displayed beyond critical point (supercritical) plays significant role for chemical reactions. The hot compressed water molecules can participate in various elementary reaction steps as reactant, catalysts as well as medium. The overall reaction can be written as (Equation 9): (Mohammed, et al., 2011; Parthsarathy & Narayan, 2014)

Equation 9. $2C_6H_{12}O_{16} + 7H_2O \rightarrow 15H_2 + 9CO_2 + 2CH_4$

CO formed in intermediate reaction step undergoes water-gas shift reaction and produces CO_2 and hydrogen. The hydrogen atoms of water and biomass is set free and thus, hydrogen is generated.

Mohammed, et al. (2011) reports that reaction temperature (500–700°C) will have a strong effect on yields and gas compositions, whereas pressure above the critical has little effect on the extent of gasification or the composition. Studies have been conducted with and without the use of catalysts and the common catalysts include activated carbon, transition metal and alkali salts.

Alkali metal catalyst is known for its effectiveness in improving the water-gas shift reaction during the reaction process, but also may cause corrosion, plugging or fouling of equipment. Transition metal catalysts (Ni, Pt, and Rh) are supposedly known for improving the reaction by accelerating the steam reforming reaction, methanation reaction and C–O and C–C and so on. Additionally, activated carbon catalyst is also effective during water-gas shift reaction and methanation reaction. It is concluded that these catalysts can effectively increase the activation energy in SCW reaction but on the other hand, dozens of studies have confirmed the instability of most catalysts. (Guo, et al., 2010)

A summary of hydrogen production via gasification in supercritical water researches with different operating conditions, catalysts and reactors is tabulated in Table 10.

Table 10. Gasification in supercritical water of different biomass for the production of hydrogen.

Reactor	Biomass	Pressure (MPa)	Temperature (°C)	Catalyst	H_2 yield	References
Autoclave	Glucose	24.5	400	$Ni/\gamma Al_2O_3$ $Ni/CeO_2–\gamma Al2O_3$	12.7 moles H_2/ kg feed	(Lu, et al., 2010)
Batch micro-reactor	Glucose	15–25	340–380	R-nickel	6 mmol H_2/ g feed	(Azadi, et al., 2009; Azadi, et al., 2009)
Packed bed	Glucose	28	575–725	Ni/activated carbon	2.45 moles H_2/ mole feed	(Lee, 2011)
Tubular	Lignin	37.1	400	$RuCl_3/TiO_2$	_	(Yamaguchi, et al., 2008)
Tubular	Paper sludge black liquor	25	500–650	Alkali salts	24 moles H_2/ kg feed	(Rönnlund, et al., 2011)
High pressure autoclave	Cellulose	24-26	450–500	K_2CO_3 Ca(OH)2	8.2 moles H_2/ kg feed	(Guan, et al., 2007)
Tubular	Cellulose sawdust	27	500	CeO_2, Ru/C $(CeZr)xO_2$	4 g H_2/ 100 g feed	(Hao, et al., 2005)
_	Mixed pig-cow manure	24	390–580	Not used	_	(Yakaboylu, et al., 2013)

3.4 Biological Processes

This section reviews the biological hydrogen production processes, which can be classified into five different mechanisms: (i) direct bio-photolysis, (ii) indirect bio-photolysis, (iii) photo-fermentation, (iv) dark-fermentation and (v) biological water-gas shift reaction.

Direct bio-photolysis, also known as bio-photolysis, is associated with plant-type photosynthesis as it utilizes light energy to split water for hydrogen formation. It occurs among certain green algae under anaerobic conditions. Indirect bio-photolysis typically involves cyanobacteria that utilize carbohydrate energy stored from photosynthesis to generate hydrogen from water. Photo-fermentation is the conversion of organic compounds to bio-hydrogen, occurring among various groups of photosynthetic bacteria via series of biochemical reactions. Dark-fermentation, more generally known as fermentation, is a process occurring in dark conditions in which anaerobic bacteria break down carbohydrates to produce hydrogen, among the other by-products (namely CO_2). Biological water-gas shift reaction involves oxidation of CO to CO_2 by utilizing enzymes rather than metals to catalyse the process. The feeds for biological hydrogen are water for photolysis and biomass for fermentation processes. (Holladay, et al., 2009; Brentner, et al., 2010; Azwar, et al., 2014)

Energy source for these processes could either be light (photo-) or chemical compounds (chemo-). Organisms able to use chemicals as electron donors are called chemotrophs, whereas organisms that uses light as their energy source are called phototrophs. Table 11 presents the different types of trophs based on their reducing equivalent source and carbon source. (Madigan, et al., 2009)

Table 11. Microbiological division of organisms based on energy sources. (Madigan, et al., 2009)

Energy source	Reducing equivalent source	Carbon source	Name
Light ***Photo-***	Organic *-organo-*	Organic *-heterotroph-*	Photo-organoheterotroph
		Carbon dioxide *-autotroph*	Photo-organoautotroph
	Inorganic *-litho-*	Organic *-heterotroph-*	Photo-lithoheterotroph
		Carbon dioxide *-autotroph*	Photo-lithoautotroph
Chemical compounds ***Chemo-***	Organic *-organo-*	Organic *-heterotroph-*	Chemo- organoheterotroph
		Carbon dioxide *-autotroph*	Chemo- organoautotroph
	Inorganic *-litho-*	Organic *-heterotroph-*	Chemo- lithoheterotroph
		Carbon dioxide *-autotroph*	Chemo- lithoautotroph

Table 12 provides a summary of previously explained mechanisms, including organisms, reactions and key enzymes.

Table 12. Overview of bio-hydrogen mechanisms, including organisms, reactions, and key enzymes as well as pros and cons. (Brentner, et al., 2010)

Mechanism	**Organisms**	**Reaction**	**Key enzymes**	**Advantages**	**Disadvantages**
Bio-photolysis	green algae, cyanobacteria	$2H_2O \xrightarrow{\text{light energy}} 2H_2 + O_2$	[FeFe] – hydrogenase	• H_2 produced from sunlight and water • Totally carbon independent pathway	• O_2 sensitivity, bio-reactor design challenges to maximize utilization of sunlight, low H_2 production efficiency
Indirect bio-photolysis	cyanobacteria	$12H_2O + 6CO_2 \xrightarrow{\text{light energy}} C_6H_{12}O_6$ $C_6H_{12}O_6 + 6H_2O \xrightarrow{\text{light energy}} 12H_2 + 6CO_2$ $N_2 + 8H^+ + 8e^- + 16ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16Pi$	[NiFe] – hydrogenase Nitrogenase	• Heterocyst separate H_2 production from O_2-evolution within organisms	• Bio-reactor design challenges to maximize utilization of sunlight
Photo-fermentation	purple non-sulphur bacteria	$N_2 + 8H^+ + 8e^- + 16ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16Pi$ $C_xH_yO_z + (2x - z)H_2O \xrightarrow{\text{light energy}} \left(\frac{y}{2} + 2x - 2\right) H_2 + xCO_2$	Nitrogenase	• Utilizes energy from sunlight to convert small organic acids or waste organic acids or waste organic compounds to H_2 and CO_2 with no by-products	• Bio-reactor design challenges to maximize utilization of sunlight Need for inexpensive photo-bioreactors Large surface area required
Dark-fermentation	anaerobic bacteria	$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2$	Dehydrogenases, (fumarate) reductases, hydrogenases	• High H_2 production, utilizes waste streams, mixed-culture friendly	• Many by-products, intensive biogas separation to retrieve H_2, incomplete substrate utilization/ low yields

All processes are controlled by the hydrogen-producing enzymes, namely hydrogenase and nitrogenase, whose properties are shown in Table 13.

Table 13. Comparative properties of nitrogenase and hydrogenase. (Ni, et al., 2006)

Property	**Nitrogenase**	**Hydrogenase**
Substrate	ATP, H^+ or nitrogen, electrons	H^+, hydrogen
Products	H_2, NH_4^+	ATP, H^+, hydrogen, electrons
Number of proteins	2 (Mo-Fe and Fe)	1
Metal components or sulphur	Mo, Fe	Ni, Fe, S
Optimal temperature	30°C (A. *vinelandii*)	55°C (R. *rubrum*) 70°C (R. *capsulatus*)
Optimal pH	7.1–7.3 (A. *vinelandii*)	6.5–7.5 (R. *sulfidophilus*)
Inhibitors	N_2, NH_4^+, O_2, high N:C ratio of H_2 production	CO, EDTA, O_2, some organic compounds
Stimulators	Light	Absence of organic compounds (R. *rubrum*, R. *capsulatus*)

The major components of nitrogenase are MoFe protein and Fe protein. Nitrogenase has the ability to use magnesium adenosine triphosphate (MgATP) and electrons to reduce a variety of substrates (including protons). This chemical reaction (Equation 10) yields hydrogen production by a nitrogenase based system:

Equation 10. $2e^- + 2H^+ + 4ATP \rightarrow H_2 + 4ADP + 4Pi$

where ADP and Pi refer to adenosine diphosphate and inorganic phosphate, respectively.

A hydrogenase is an enzyme that catalyses the reversible oxidation of molecular hydrogen. The current research on hydrogenase focuses largely on understanding the mechanism of hydrogen production, control of cell metabolism and ultimately increase of the hydrogen production. Hydrogenase plays an important role in bio-photolysis by cyanobacteria and green microalgae. Hydrogenase can be distributed into three classes: iron-only ([FeFe]-hydrogenases), nickel-iron

([NiFe]-hydrogenases), and metal-free hydrogenases. The vast majority of known hydrogenases belong to the first two classes, as they are commonly found in various bacteria and algae except for metal-free hydrogenases, which are found in certain types of methanogens. (Vignais, et al., 2001)

FeFe-hydrogenase is an enzyme that plays a vital role in anaerobic metabolism, which is produced by green algae, and become more efficient catalyst hydrogenases. This enzyme is able to catalyse the reversible oxidation of molecular hydrogen.

NiFe-hydrogenases produced by cyanobacteria consist of the centre of several metals, including Ni-Fe bimetallic active sites, iron-sulphur and Mg^{2+} ions. Ni-Fe active site is located inside the protein molecules and functions as bidirectional hydrogenases that involve a number of lines in the catalytic reaction route , namely route of electron transfer, proton transfer lines and gas-access channels. These hydrogenases are grouped into two subunits, which are large and small hydrogenase. Figure 7A and Figure 7B shows the schematic representation of the FeFe-hydrogenase and NiFe-hydrogenases, respectively. The detailed mechanism steps are explained in the review article done by Azwar, et al. (2014).

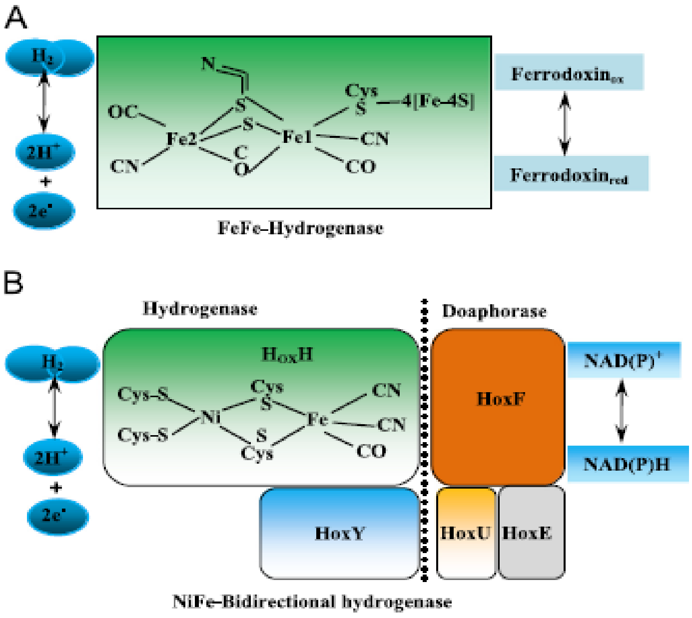


Figure 7. Schematic representation of the FeFe-hydrogenases and NiFe-hydrogenases. (Azwar, et al., 2014)

3.4.1 Fundamentals of Hydrogen Production Processes by Bio-photolysis

As described in the previous section, bio-photolysis is associated with the plant-type photosynthesis process, occurring among cyanobacteria (formerly known as blue-green algae) that use light to split water for hydrogen production under anaerobic conditions. (Akkerman, et al., 2002; Azwar, et al., 2014)

3.4.1.1 Bio-photolysis of water by Cyanobacteria and Green Micro algae

Cyanobacteria and green algae can split water into hydrogen and oxygen molecules in the presence of sunlight. This mechanism of bio-hydrogen production through bio-photolysis, or photoautotrophic process, involves the formation of hydrogen gas from water by utilizing sunlight and carbon dioxide as the sole source for energy, catalyzed by the hydrogenase enzyme. Biophotolysis can occur among various species of bacteria and algae. Examples include photosynthetic bacteria from soil or natural water, certain cyanobacteria (e.g. *Anabaena* species), or eukaryotic algae (e.g. *Chlamydomonas* species Reinhardt). The biological hydrogen gas production through bio-photolysis of water by utilizing such organisms has potential to become environmentally sustainable production process (Azwar, et al., 2014). Figure 8 shows the photosynthetic production of hydrogen under anaerobic conditions using green alga *Chlamydomonas reinhardtii*. (Azwar, et al., 2014)

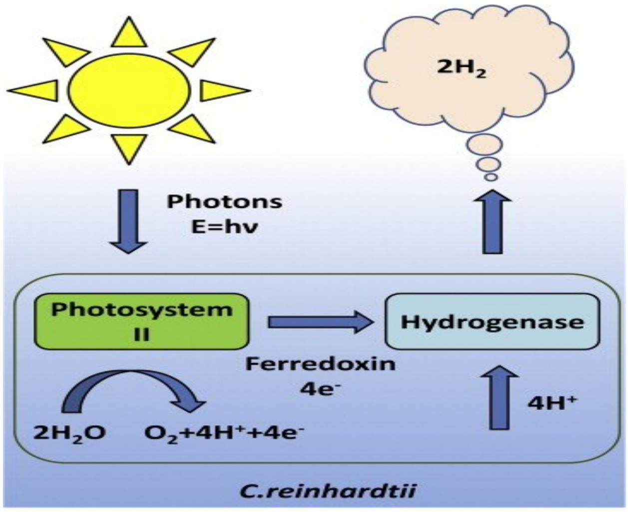


Figure 8. Photosynthetic production of H_2 under anaerobic conditions using green alga *Chlamydomonas reinhardtii*. (Tamburic, et al., 2011)

In the bio-photolysis process, light energy is absorbed by photosystems PSI and PSII of microalgae (Akkerman, et al., 2002). This energy is then transferred through the electron transport chain, in turn reducing the ferredoxin and providing electrons to the hydrogenase enzyme. The process of proton and electron recombination is catalysed by the [Fe]-hydrogenase enzyme to produce H_2 (Figure 8). Hydrogenase activity is inhibited in the presence of molecular oxygen, which implies that the direct bio-photolysis process is self-limiting. In order to maintain a continuous H_2 production process, it is necessary to remove the oxygen as it is being produced. Sulphur deprivation of *C. reinhardtii* diminishes its ability to repair PSII proteins, thus reducing photosynthetic O_2 production below the level of respiratory O_2 consumption, so that overall oxygen is being used up. Algal metabolism is therefore responsible for creating an anaerobic environment that leads to sustained H_2 production. The main barriers to the commercialisation of green algal H_2 production technologies are the low photochemical conversion efficiencies and the prohibitive photo-bioreactor costs. (Akkerman, et al., 2002; Tamburic, et al., 2011; Azwar, et al., 2014)

There are several advantages of bio-photolysis process:

(i) Water being the primary electron donor for the production of H_2 gas.
(ii) Resources are abundantly available, as sunlight and CO_2 are the basic inputs needed to grow the bio-photolysing organisms, and water functions as the substrate.
(iii) If up-scaled, these processes have the potential to be very low-emissive.
(iv) The produced H_2 gas can be used in fuel cell or for other applications.

Several studies have been reported for the hydrogen production through bio-photolysis. Table 14 shows various conditions of optimum and maximum production rate of hydrogen production by green micro algae and cyanobacteria.

Table 14. Comparison of the optimum condition and maximum production rates of hydrogen production by cyanobacteria and green micro algae (laboratory photo-bioreactor). (Azwar, et al., 2014)

Organism	**Bacterial strains**	**Carbon source/ gas for growth**	**Light intensity ($\mu E/m^2/s$)**	**Optimum condition**		**H_2 production rate ($ml/L_{cult}/h$)**	**References**
				pH	**T(°C)**		
Green microalgae	*Chlamydomonas reinhardtii CC-124*	CO_2 (3%); Water (97%); acetate (17 mM)	100	7	28-30	2.2	(Laurinavichene, et al., 2006)
	Platymonas subcordiformis	Air; seawater nutrients	101	8	25	0.05	(Guan, et al., 2004)
	Chlorella sorokiniana Ce	Acetate	120	7.2	30	1.35	(Chader, et al., 2009)
	Chlamydomonas reinhardtii CC –124	Water CO_2	< 200	4–9	20	1.1	(Tamburic, et al., 2011)
Cyanobacteria	*Anabaena variabilis ATCC 29413*	CO_2 (2%); N_2 (25%); Ag (73%)	140	7.5	30	13	(Sveshnikov, et al., 1997)
	Anabaena variabilis ATTC 29413	CO_2 (5%); water (95%)	150	6.9–7.5	30	0.9	(Berberoğlu, et al., 2008)
	Anabaena azollae	CO_2 (2%)	140	_	_	13	(Tsygankov, et al., 1998)
	Chroococcidiopsis thermalis	CO_2 (1%); water (99%)	70	7.5	26	4.03	(Serebryakova, et al., 2000)
	Synechococcus sp. Strain H-1	CO_2 (6%); water (94%)	100	8–8.5	55	0.9	(Asami, et al., 2011)
	Arthrospira sp. PCC 8005	Fe^{2+}; β-mercaptoethanol	40	7	30	5.91	(Raksajit, et al., 2012)

3.4.1.2 Direct Bio-photolysis

Direct bio-photolysis is a biological process (Equation 11) occurring in some microalgae that produces hydrogen directly from water via photosynthetic systems:

$$\text{Equation 11.}\ \ 2H_2O \xrightarrow{\text{solar energy}} 2H_2 + O_2$$

Two photosynthetic systems are responsible for photosynthesis process:

(i) Photosystem II (PSII) splitting water and evolving oxygen
(ii) Photosystem I (PSI) producing reductant for CO_2 reduction, and

In the bio-photolysis process, two photons from water can yield either CO_2 reduction PSI or hydrogen formation with the presence of hydrogenase. In green plants, only CO_2 reduction takes place due to lack of hydrogenase. On the contrary, microalgae, such as green algae and *Cyanobacteria* (blue-green algae), contain hydrogenase, and thus have the ability to produce hydrogen. In this process, the electrons generated when PSII absorbs light energy are transferred to the ferredoxin (Fd) using the solar energy absorbed by PSI. The hydrogenase accepts the electrons from Fd to produce hydrogen as shown in Figure 9. (Ni, et al., 2006)

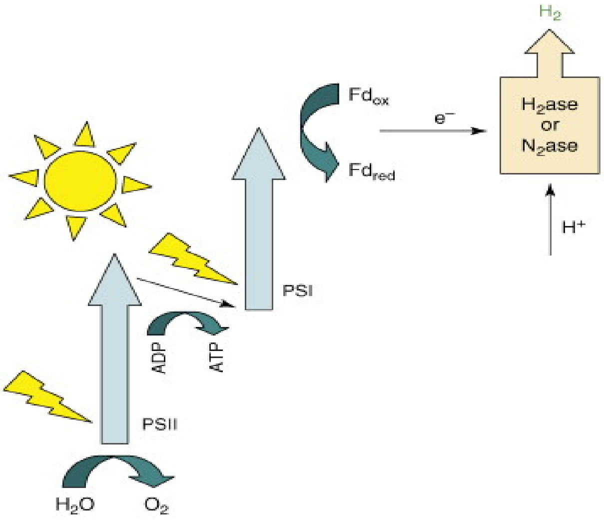


Figure 9. Direct bio-photolysis of green algae or cyanobacteria. (Hallenbeck & Ghosh, 2009)

In other words, during this process, an organism (green alga or cyanobacterium) that carries out plant-like photosynthesis uses captured solar energy to split water (producing water) and reduce ferredoxin, which can in turn reduce a hydrogenase or nitrogenase, both of which are oxygen sensitive, producing H_2. (Hallenbeck & Ghosh, 2009)

Dasgupta, et al. (2010) reviewed that partial inhibition of PSII can generate anaerobic condition for the cell within a photo-bioreactor, which can be achieved by sulphur deprivation, or by selective loss of 32-kDa protein (later identified as the PSII reaction centre protein D1) followed by activation of the reaction centre through rapid inbuilt repair mechanism.

The advantages of this process are abundant substrate (water); simple products (H_2 and CO_2); and the fact that even in low light intensities, green algae in anaerobic conditions are still able to convert almost 22% of light energy by using hydrogen as an electron donor in the process of fixation of CO_2. Hydrogenase sensitivity to oxygen is a big challenge for this method, so it is necessary to maintain the oxygen content at a low level under 0.1%, so that hydrogen production can be sustained. One of the ways to obtain this condition is by the use of green algae *Chlamydomonas reinhardtii* that can deplete oxygen during oxidative respiration. However, due to the significant amount of substrate being respired and consumed during this process, the efficiency is low. Nevertheless, mutants derived from microalgae were reported to have good O_2 tolerance from microalgae, and thus higher hydrogen production (Ni, et al., 2006). (Ni, et al., 2006; Azwar, et al., 2014)

Brentner, et al. (2010) addresses three main issues to improve bio-photolysis system: low photochemical efficiencies, sensitivity of hydrogenases to O_2, and competition for reductant from ferredoxin between hydrogenases and other cellular functions. 10% photochemical efficiency is generally targeted, but current efficiencies (Mussgnug, et al., 2007; Turner, et al., 2008) are far from reaching this target due to limitations in light penetration within photo-bioreactors and the transfer of light energy within cells. Hydrogenase sensitivity to O_2 places strain on the duration of the H_2 production phase. Photo-bioreactor has been used to address the first two issues, and genetic engineering to all three issues. (Brentner, et al., 2010)

3.4.1.3 Indirect Bio-photolysis

Indirect bio-photolysis is a biological process in which hydrogen is produced from water. It occurs among microalgae and cyanobacteria, whose photosynthetic system (Figure 10) is able to convert solar energy into chemical energy in the form of hydrogen through several steps:

(i) Biomass production by photosynthesis
(ii) Biomass concentration,
(iii) Aerobic dark fermentation yielding 4 moles hydrogen per mole glucose in the algae cell, along with 2 moles of acetates, and
(iv) Conversion of 2 moles of acetates into hydrogen

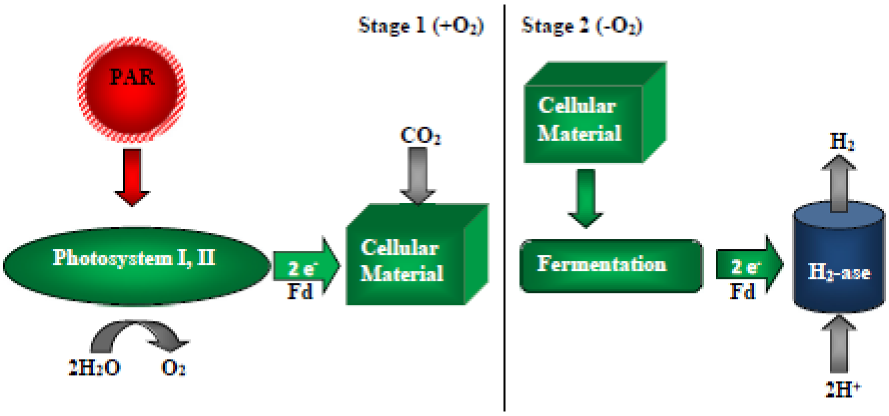


Figure 10. Schematic diagram for indirect bio-photolysis. (Vargas, et al., 2014)

The whole process can be divided or classified into two distinct groups, one of which depends on the light and the other is light independent process. In a typical indirect bio-photolysis, *Cyanobacteria* (Figure 11) are used to produce hydrogen via the following reactions (Equation 12, Equation 13 & Equation 14):

Equation 12. $6H_2O + 6CO_2 + \text{light} \rightarrow C_6H_{12}O_6 + 6O_2$

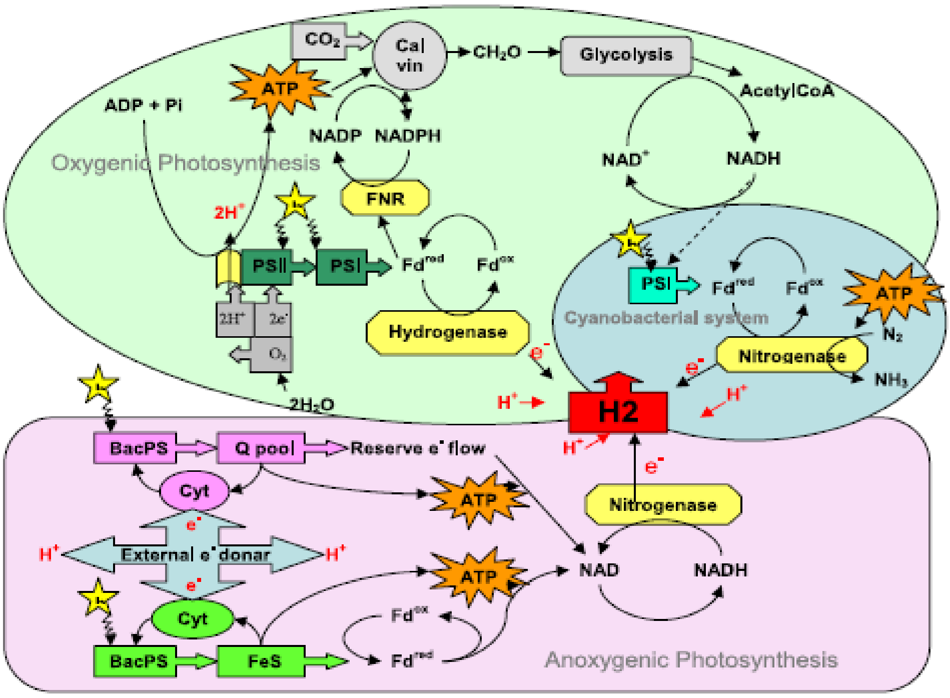
Equation 13. $C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2$

Equation 14. $2CH_3COOH + 4H_2O + \text{light} \rightarrow 8H_2 + 4CO_2$

The overall reaction is (Equation 15):

Equation 15. $12H_2O + \text{light} \rightarrow 12H_2 + 6O_2$

Hydrogen producing cyanobacteria may either be nitrogen fixing or non-nitrogen fixing. Some nitrogen fixing organisms are non-marine *Anabaena* sp., marine cyanobacteria *Calothrix* sp., *Oscillatoria* sp. Non-nitrogen fixing organisms are *Synechococcus* sp., Gloebacter sp. and *Anabaena* sp. All these are found suitable for higher hydrogen evolution compared to other cyanobacteria species. Heterocysts filamentous *Anabaena cylindrica* is a well-known hydrogen producing cyanobacteria yet, *Anabaena variabilis* has received more attention in recent years due to higher hydrogen yield. (Das & Veziroglu, 2008)



🟩Showing the oxygenic hydrogen production in green algae through hydrogenase. 🟦Specially showing how blue-green algae (N_2 fixing) produces hydrogen through nitrogenase, driving electrons from photo-synthetically produced reserve carbon source. O_2 evolution separated from H_2 evolution either by heterocyst or by temporal separation. ◻ Showing the an-oxygenic hydrogen production in photosynthetic bacteria through nitrogenase. 🟪 Purple bacteria. 🟩 Green bacteria.

Figure 11. Light-dependent different electron transport pathways for hydrogen production. (Dasgupta, et al., 2010)

According to Dasgupta, et al. (2010), pyruvate ferredoxin oxido-reductase (PFOR) responsible for decarboxylation (CO_2 evolution) of pyruvate to acetyl-CoA is linked to H_2 production via reduction of ferredoxin in anaerobic dark conditions. In the presence of light, ferredoxin is reduced by NADH produced during catabolism of pyruvate by the pyruvate dehydrogenase (PDH). The N_2-fixing cyanobacteria produce hydrogen mainly by nitrogenase (fixing N_2 to NH_3) instead of bidirectional hydrogenase, however in several non-N_2-fixing cyanobacteria, H_2 evolution is also observed through bidirectional hydrogenase. In filamentous cyanobacteria, such as the genus *Anabaena*, nitrogenase is located in the heterocyst with a functional PSI (no PSII activity). The electrons donated to PSI in the heterocyst come from the reserve carbon transported from the neighbour vegetative cell. However, the hydrogen production is energetically burden due to the biosynthesis and maintenance of the heterocysts and the significant ATP requirement of nitrogenase, which can be seen in the following reaction equations (Equation 16 & Equation 17):

Equation 16. $$\mathrm{N_2 + 8H^+ + Fd(red)(8e^-) + 16ATP \rightarrow\ 2NH_3 + H_2 + Fd(ox) + 16ADP + Pi}$$

Equation 17. $$\mathrm{8H^+ + 8e^- + 16ATP \leftrightarrow 4H_2 + 16ADP + 16Pi}$$

Heterocyst provide spatial separation of O_2 and H_2 evolution, whereas non-heterocystous cyanobacteria can separate O_2 and H_2 production in time (temporal separation). (Dasgupta, et al., 2010)

Extensive research has focused on decreasing hydrogenase O_2-sensitivity, mostly via indirect bio-photolysis, in which H_2 production is spatially or temporally separated from photosynthesis (Turner, et al., 2008). According to Kim & Kim (2011), several experiments exist where green algae and cyanobacteria have been modified to fix N_2 from the atmosphere more efficiently, and to produce enzymes that can catalyse the anaerobic fermentation process.

While indirect bio-photolysis is able to mitigate some of the O_2 sensitivity issues of direct photolysis, they still share many of the same challenges. Designs for efficient photo-bioreactors are needed to make the process cost-effective.

Research and metabolic engineering efforts should be directed at more innovative photo-bioreactors as well as in increasing the efficiency of the hydrogenase enzymes such as [NiFe]-hydrogenase.

3.4.2 Fundamentals of Hydrogen Production Processes by Fermentation

Fermentation is one of the very effective methods of biological hydrogen production processes because it can be operated without the need for light for continuous hydrogen production. Compared to bio-photolysis, fermentation process has a higher stability and efficiency. Furthermore, fermentation process is more appropriate and acceptable in industrial scale because it uses a simple control system in order to minimize the necessary operational costs. One of the major advantages of producing hydrogen via fermentation process is the possibility of using a variety of organic wastes as a substrate. Hence, fermentation has a dual role and benefits: in waste reduction and energy production. Extensive attention from the researchers and scientists has been received for the hydrogen production through fermentation process (Wang & Wan, 2008; Wu, et al., 2009; Elsharnouby, et al., 2013).

In fermentative hydrogen production, potential feedstock resources include biomass, agricultural waste by-products, lingo-cellulosic products such as wood and wood waste, waste from food processing and aquatic plants and algae, sewage sludge, agricultural and livestock effluents as well as animal excreta (Show, et al., 2012). Bio-hydrogen production using carbohydrates as a substrate has received significant attention from the researchers in recent years. The following reactions of hydrogen production by fermentation of glucose show that the most desirable end-products is acetate, with production levels of four hydrogen per mole glucose. Theoretically, 33% of Chemical Oxygen Demand (COD) can be converted to hydrogen from glucose and the rest of the energy is released as acetate. (Azwar, et al., 2014)

Equation 18. $C_6H_{12}O_6 + 12H_2O \rightarrow 6HCO_3^- + 12H_2 + 6H^+ \quad \Delta G^0 = 241\frac{kJ}{mol}$

Equation 19. $C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3COO^- + 2HCO_3^- + 4H_2 + 4H^+$

$$\Delta G^0 = -48\frac{kJ}{mol}$$

Equation 20. $C_6H_{12}O_6 + 2H_2O \rightarrow CH_3CH_2CH_2COO^- + 2HCO_3^- + 2H_2 + 3H^+$

$$\Delta G^0 = -137\frac{KJ}{mol}$$

Equation 21. $C_6H_{12}O_6 + 3H_2O \rightarrow CH_3CH_2OH + CH_3COO^- + 2H_2 + 3H^+$

$$\Delta G^0 = -\frac{97kJ}{mol}$$

The first reaction equation (Equation 18) shows that 12 moles of hydrogen can be produced from one mole of glucose. In all the reactions (Equation 18–Equation 21), Gibbs free energy (ΔG^0 value) at a temperature of 25°C are highlighted (it should be noted that the production of 12 moles of hydrogen in the first reaction is thermodynamically unfavourable).

In contrast to the former reactions, production of propionate decreases the production of hydrogen as shown in the following reaction (Equation 22):

Equation 22. $C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COO^- + 2H_2O + 2H^+$

Undesirable consumption of hydrogen or glucose can be caused by the activity of homoacetogens such as *Clostridium aceticum* (Equation 22 & Equation 23):

Equation 23. $2HCO_3^- + 4H_2 + H^+ \rightarrow CH_3COO^- + 4H_2O$

Equation 24. $C_6H_{12}O_6 \rightarrow 2CH_3CH_2COO^- + 2H^+$

In practice, the fermentation with butyrate as the main product is regarded as the most effective route to produce hydrogen. From the experimental results 2.9 mol of H_2/mol glucose can be produced by Clostridium species. (Azwar, et al., 2014)

3.4.2.1 Photo-fermentation

Photo-fermentation is a process in which organic materials or biomass are converted into hydrogen and carbon dioxide by photosynthetic bacteria under the simultaneous use of solar energy (Figure 12). The process takes place under anoxic or anaerobic conditions by using photosynthetic bacteria and sunlight as energy. The optimal temperature is 30–35°C and pH 7.0. One of the groups of micro-organisms capable of photo-fermentation are purple non-sulphur (PNS) bacteria, which under anaerobic conditions utilizes simple organic acids. Species of such bacteria include *Rhodobacter sphaeroides*, *Rhodopseudomonas palustris*, *Rhodobacter capsulatus* and *Rhodospirillum rubrum*. (Bičáková & Straka, 2012; Azwar, et al., 2014)

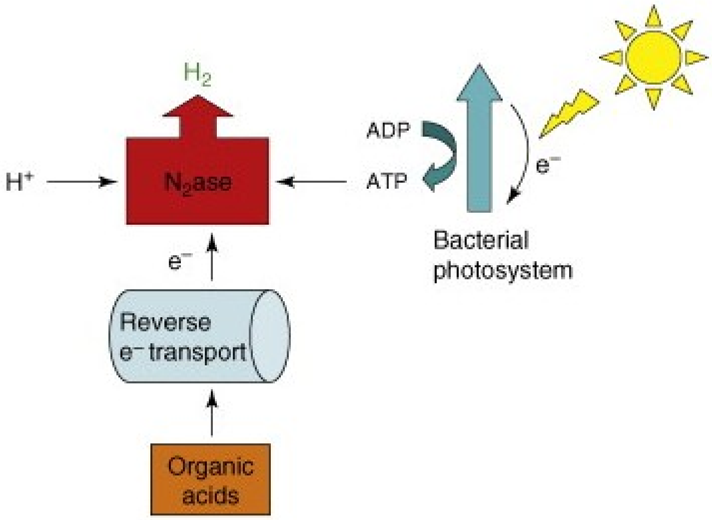


Figure 12.Photo-fermentation. (Hallenbeck & Ghosh, 2009).

In photo-fermentation process, PNS bacteria possesses more advantages than the use of cyanobacteria and algae. These bacteria use nitrogenase enzyme to catalyse nitrogen fixation for the reduction of molecular nitrogen to ammonia. Interestingly, while reducing the nitrogen content, the activation of nitrogenase also leads to the generation of hydrogen. Therefore, cellular stressful induced by the limited availability of nitrogen is required for the hydrogen evolution. Photo-heterotrophs use sunlight as their energy source to oxidize organic compounds and generate the electron potential needed to drive hydrogen production. Azwar, et al., (2014) claim that PNS bacteria can potentially divert 100% of electrons from an organic substrate to hydrogen production by utilizing energy from the sun to drive thermodynamically unfavourable reactions. Thus, waste streams from photo-fermentation contain fewer by-products as the organic compounds are fully reduced to form CO_2 and H_2. (Bičáková & Straka, 2012; Azwar, et al., 2014)

A benefit of these bacteria lies in their flexible metabolic potential. They can be used in a wide range of conditions because they lack the mentioned PSII system, which precludes a reaction with oxygen and also supresses hydrogen production. However, the disadvantages of this process are: (i) use of nitrogenase enzyme with high energy demand, (ii) low solar energy conversion efficiency, and (iii) demand for elaborate anaerobic photo-bioreactors covering large areas. (Ni, et al., 2006; Bičáková & Straka, 2012)

In recent years, some attempts have been made for hydrogen production from industrial and agricultural wastes to effect waste management. As summarized in Table 15, hydrogen can be produced by photo-fermentation of various types of biomass wastes.

Table 15. Example studies on hydrogen production by photo-fermentation.

Reactors	**Bacterial strains**	**Substrate**	**Operating conditions**		**Maximum H_2 yield**	**References**
			pH	**Temp (°C)**		
Batch	*Rhodobacter sphaeroides*	Sodium lactate	8.9	30	2.4 mg/ l	(Zhu, et al., 2007)
Batch	Mixed photosynthetic culture	Acetate and butyrate	6–7	34	3.51 moles H_2/ l h	(Srikanth, et al., 2009)
Batch	*Rhodopseudomonas faecalis* RLD-53	Acetate	7	35	2.61 moles H_2/ mole acetate	(Liu, et al., 2009)
Batch	*Rhodopseudomonas faecalis* RLD-53	Acetate	7	35	3.17 moles H_2/ mole acetate	(Ren, et al., 2009)
Biofilm-based photo-bioreactor	*Rhodopseudomonas palustris* CQK 01	Glucose	7	25	0.2 moles H_2/ mole glucose	(Tian, et al., 2010)
Tubular photo-bioreactor-fed batch	*Rhodobacter capsulatus*	Acetate	≤ 8	10–35	0.6 moles H_2/ fed acetic acid	(Boran, et al., 2010)
Batch	*Rhodobacter sphaeroides* O.U.001	Brewery wastewaters	7–7.2	28 ± 2	2.24 l H_2/ l medium	(Seifert, et al., 2010)
Continuous	*Rhodopseudomonas palustris* WP 3-5	Synthetic wastewater	6.8	28 ± 35	205 ml H_2 l/ d	(Lee, et al., 2011)
Sequencing batch reactor	*Rhodopseudomonas faecalis* RLD-53	Acetate	7	35 ± 1	3.12 moles H_2/ mole acetate	(Xie, et al., 2012)
Cylindrical	*Rhodobacter capsulatus* with cbb3 gene	Acetic and butyric acid	6.8	35	3752.7 ml H_2 l/ l	(Ma, et al., 2012)
Semi-continuous	*Rhodobacter sphaeroides* KD131	Succinate	7.5 ± 0.2	30	3.7 moles H_2/ mole succinate	(Kim & Kim, 2012)
Batch and Continuous	*Rhodopseudomonas faecalis* RLD-53	Acetate	7	35 ± 1	2.64 moles H_2/ mole acetate	(Xie, et al., 2013)
Batch	*Rhodobacter sphaeroides* KD131	Hexose	7	30	8.35 moles H_2/ mole hexose	(Kim & Kim, 2013)

3.4.2.2 Dark-fermentation

Dark fermentation is the fermentative conversion of organic substrate and biomass materials to produce bio-hydrogen which takes place in anaerobic conditions at 30 to 80°C without the presence of light (Figure 13). Unlike bio-photolysis process that produces only H_2, the products of dark-fermentation are mostly H_2 and CO_2 combined with other gases, namely CH_4 and H_2S, depending on the reaction process and the used substrate. Additionally, compared to other biological methods dark-fermentation has several advantages, such as its ability to produce hydrogen continuously without the presence of light, higher hydrogen production rate, process simplicity, lower net energy input and utilization of low-value waste raw materials. (Ni, et al., 2006; Azwar, et al., 2014)

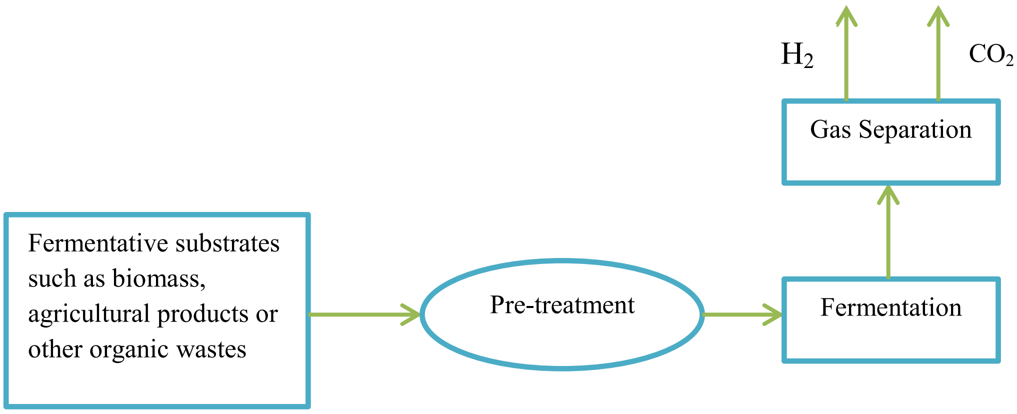


Figure 13. Hydrogen production by dark fermentation.

Dark-fermentation can produce hydrogen from organic compounds as well as from organic wastes by anaerobic microorganisms. With glucose as a model substrate and acetic acid as end product, maximum 4 moles H_2 is produced per mole glucose (Equation 25):

Equation 25. $C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2$

Instead, when the end product is butyrate, only 2 moles H_2 is produced (Equation 26):

Equation 26. $C_6H_{12}O_6 + 2H_2O \rightarrow CH_2CH_2CH_2OOH + 2H_2 + 2CO_2$

However, in practice, the 4 moles H_2 per mole glucose cannot be achieved because the end products normally contain both butyrate and acetate.

The amount of hydrogen production by dark-fermentation depends on several parameters, including the pH value, hydraulic retention time (HRT), gas partial pressure, characteristics of organic food, reactor type, nutrition feed rate, inoculum and temperature. One of the most important parameters on hydrogen production is pH because it is one factor that influences the activities of the hydrogenase enzyme. For the optimal hydrogen production, pH should be maintained between 5 and 6. Partial pressure of H_2 is another important parameter; when hydrogen concentration increase, the metabolic pathways shift to produce more reduced substrates, such as lactate, ethanol, acetone, butanol or alanine, which in turn decrease the hydrogen production. Wang & Wan (2009) summarizes the factors influencing fermentative hydrogen production in their review report. They briefly introduced and discussed the effect of each factor on fermentative hydrogen production and the advance in the research of the effect, followed by some suggestions for the future references.

Several studies have been conducted for the hydrogen production on a batch, anaerobic sequencing batch reactor (AnSBR), fed-batch, fluidized bed bioreactor (FBR), continuously stirred tank reactor (CSTR) and continuous dark fermentation with different types of raw materials (Table 16).

Table 16. Example studies on hydrogen production by dark-fermentation

Reactors	**Bacterial strains**	**Substrate**	**HRT (h)**	**Operating conditions**		**Maximum H_2 yield**	**References**
				pH	**Temp (°C)**		
Batch	POME sludge	Food waste	-	7	55	593 ml H_2/ g carbohydrate	(Nazlina, et al., 2009)
Fed-batch	*Clostridium sp.*	Swine manure	16	5	35	18.7 x 10^{-3}g H_2/ g TVS	(Zhu, et al., 2009)
AnSBR	Seed sludge	Food waste	36	5.3 ± 1	35 ± 1	0.5 moles H_2/ mole hexose added	(Kim, et al., 2010)
Batch	*Clostridium sp.* R1	Carbohydrate	-	6	30	3.5 moles H_2/ mole cellobiose	(Ho, et al., 2010)
Batch	*Bacillus coagulans* IIT-BT S1	Sludge as substrate	12	6	37	37.16 ml H_2/ g COD consumed	(Kotay & Das, 2010)
AnSBR	Seed sludge from a dairy manure	Liquid swine manure	16	5.0	37 ± 1	1.50 moles H_2/ mole glucose	(Wu, et al., 2010)
1. Batch **2. CSTR**	*Clostridium acetobutylicum* and *Citrobacter freundii*	Xylose	-	6.8	45	1. 0.71 moles H_2/ mole xylose 2. 1.97 moles H_2/ mole xylose	(Mäkinen, et al., 2012)
Batch	Bacterial hydrolysis	Grass silage	-	7	37	37.8 ± 5.8 ml H_2/ g silage	(Li, et al., 2012)
Batch	*Clostridium pasteurianum*	Dry Grass	-	7	35	72.21 ml H_2/ g-dry grass	(Cui & Shen, 2012)
Batch	Sewage sludge	Food waste		6.0 ± 1	35 ± 1	2.26 moles-H_2/ mole hexose	(Im, et al., 2012)
Batch	Anaerobic digested sludge	Distillery wastewater		5.5	37	1 l H_2/ l medium	(Wicher, et al., 2013)
Semi-continuous	Seed anaerobic sludge	Glucose		6–8	35	7 mmol H_2/ g_{dwt}-h	(Kan, 2013)

*TVS means total volatile solids *g_{dwt} means gram dry weight

3.4.2.3 Photo-dark fermentation

In fermentation, complete oxidation of 1 mole of glucose yields 12 moles of hydrogen. However, complete oxidation of glucose into hydrogen and carbon dioxide is not possible as the corresponding reaction is not feasible thermodynamically (Equation 27):

Equation 27. $C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2, \qquad \Delta G_0 = +3.2\ \mathrm{kJ}$

With applying external energy i.e., photo-energy in photo-fermentation, theoretically 12 moles of hydrogen per mole of glucose can be produced. However, this process cannot be operated in the absence of light. On the other hand, in the absence of external energy, in the case of dark-fermentation, oxidation of glucose by fermentative bacteria results in producing a maximum 4 moles of hydrogen per mole of glucose consumption with acetate as the sole by-product (Equation 28):

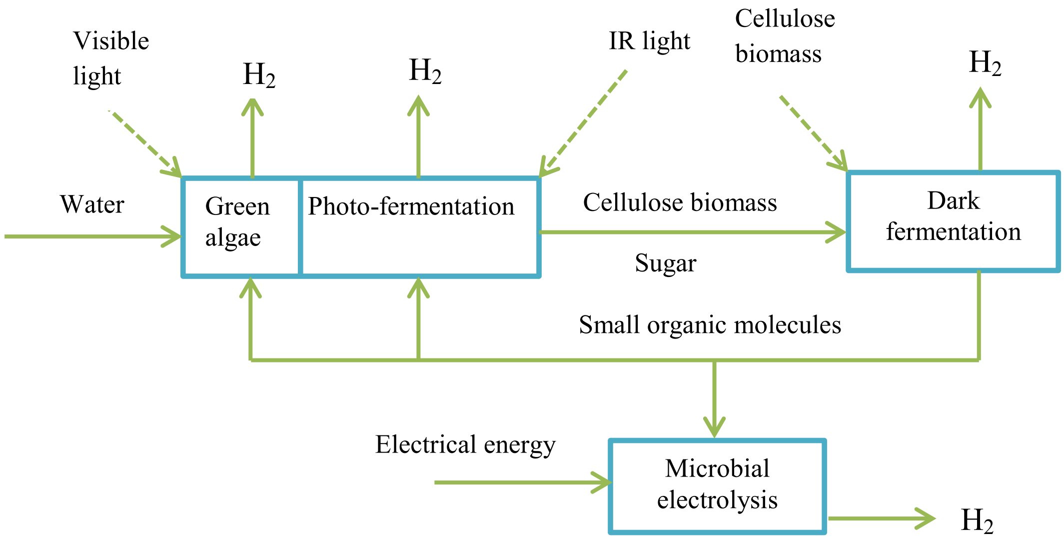
Equation 28. $C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CO_2 + 2CH_3COOH, \ \ \Delta G_0 = -206\mathrm{kJ}$

Acetate produced in the dark-fermentation stage can be oxidized by photosynthetic bacteria to produce more hydrogen (Equation 29):

Equation 29. $CH_3COOH + 2H_2O \xrightarrow{\text{light energy}} 4H_2 + 2CO_2, \ \ \Delta G_0 = +104\mathrm{kJ}$

Therefore, continuous production of hydrogen at maximum yield can be achieved by integrating dark- and photo-fermentation methods. This concept of using a two-stage process is very promising because hydrogen produced by this process is higher than the dark-fermentation alone and photo-fermentation alone. Some of the example studies on hydrogen production by integrating dark- and photo-fermentation are tabulated in Table 17. (Bičáková & Straka, 2012)

Also multi-stage system instead of a two-stage system has been suggested in order to maximize the hydrogen production from the feed (Figure 14).



Illustrative Scenario: Initial raw material (biomass) in the dark-fermentation reactor is subsequently degraded into hydrogen and wastewater. Waste water containing organic acids is further treated with photo-fermentation approach. Firstly, the photo-fermentation process utilizes the infrared rays and then utilizes microbial electrolytic cells, which produce hydrogen from some organic acids while not requiring light. The effluent (wastewater) from the first stage contains ammonia, which inhibits the second stage, so some dilution and neutralization to adjust the pH to 7 is required prior to feeding to the second stage. (Holladay, et al., 2009; Bičáková & Straka, 2012)

Figure 14. A multi-stage integrated system for bio-hydrogen production. Adapted from Holladay, et al. (2009).

Integration of multi-stage methods, however, causes problems connected both with the actual implementation and control of the process and with its operation and maintenance (Holladay, et al., 2009).

Table 17. Example studies on hydrogen production by integrating dark- and photo-fermentation.

Reactors	Microorganism used in dark-fermentation	Microorganism used in photo-fermentation	Carbon source	Operating conditions		Maximum H_2 yield	References
				pH	Temp (°C)		
Batch	*Clostridium butyricum*	*Rhodopseudomonas faecalis* RLD-53	Glucose	7	35	122.4 ml H_2/ vessel	(Xie, et al., 2010)
Fed-batch	Anaerobic sludge	*Rhodopseudomonas sphaeroides*-NRRL	Wheat starch	7.5	35	201 ml H_2 g/ l starch	(Ozmihci & Kargi, 2010)
Batch	*Clostridium butyricum*	*Rhodopseudomonas palutris*	Cassava starch	7 ± 0.02	30 ± 0.5	2.91 to 6.07 moles H_2/ mole hexose	(Cheng, et al., 2011a)
Batch	*Rhodobacter capsulatus* hup$^-$ YO3	*Rhodobacter capsulatus* DSM 1710	Molasses	6.4	35	0.50 mmol H_2/ l_c h	(Avcioglu, et al., 2011)
Batch	*Clostridium butyricum*	*Rhodopseudomonas palutris*	Rice straw	6.5 ± 0.1	35	463 ml/ g TVS	(Cheng, et al., 2011b)
Continuous	Anaerobic sludge	*Rhodobacter sphaeroides* (NRRL-B 1727)	Ground waste wheat	7	30 ± 1	3.4 moles H_2/ mole glucose	(Sagnak & Kargi, 2011)
Fed-batch	*Rhodobacter capsulatus* YO3	*Caldicellulosiruptor saccharolyticus*	Sugar beet thick juice	6.5	≤ 40	1.12 mmol H_2/ l_c h	(Özkan, et al., 2012)
Batch	*Clostridium butyricum*	*Arthrospira platensis*	Zeolite	6.5 ± 0.05	35	96.6 to 337 ml H_2/ g DW	(Cheng, et al., 2012)
Batch	Bacteria (HPB), PSB, and MPB	Bacteria (HPB), PSB, and MPB	*Chlorella pyrenoidosa* raw biomass	8.0 ± 0.1	35 ± 1	198.3 ml/ g TVS	(Xia, et al., 2013)

3.4.3 Biological Water-Gas Shift Reaction

Some photoheterotrophic bacteria, such as *Rhodospirillum rubrum* can survive without the need of light by using CO as the sole carbon source to generate ATP by coupling the oxidation of CO to the reduction of H^+ to H_2 (Equation 30):

Equation 30. $CO + H_2O \leftrightarrow CO_2 + H_2$

In equilibrium, the dominating products are CO_2 and H_2, and therefore this process is favourable for hydrogen production. The organisms that are able to perform this process include photoheterotrophic bacteria such as *Rhodospirillum rubrum* and *Rubrivivax gelatinosus*, and gram-positive bacteria such as *Carboxydothermus hydrogenoformans*. Under anaerobic conditions, carbon monoxide induces the synthesis of several proteins, including CO dehydrogenase, Fe–S protein and CO-tolerant hydrogenase. The electrons released from CO through its oxidation are converted through the Fe–S protein to hydrogenase for hydrogen production. The process takes place at low temperature and pressures, during which the transformation to CO_2 and H_2 is significantly assisted thermodynamically. The speed of transformation is high compared to other biological process but requires a source of CO and darkness. (Ni, et al., 2006; Bičáková & Straka, 2012)

Although the biological water-gas shift reaction is currently at the stage of laboratory development, promising microorganisms working in the environment of CO have been discovered, provided that light is available and the partial pressure of CO is optimized (Younesi, et al., 2008).

Jung, et al. (2002) tested an alternative bacterium (*Citrobacter* sp.Y19) for hydrogen production and found its maximum activity of hydrogen production to be 27 mmol/ g cells per hour and is three times higher than that provided by *R. rubrum*.

Saxena, et al. (2009) reported that 1 kg of cells can produce 1 kg of hydrogen per day in a bubble column or trickling bed bioreactor. It was also reported that hydrogen synthesis rate by bio-water gas shift reaction was 96 mmole H_2/ l h as compared to 20–50 mmole H_2/ l h by dark anaerobic fermentation process. They also estimated that the processing cost of hydrogen production by bio-water gas shift process would be \$3.4/kg as compared to other biological processing cost around \$12–20/kg.

II Design Part

Chapter 4

4.1 Selection of the Process

The previous chapter presented an overview of hydrogen production technologies from biomass. This chapter compares all the potential hydrogen production processes using different criteria and identifies the most promising process. Section 4.2 presents the basics of design and specifications of raw materials and products. Section 4.3 discusses several gasification technologies for hydrogen production and provides simulation results for the designed process.

Many possible thermochemical and biological methods for the production of hydrogen from biomass have been described in the literature part. In this chapter, these production methods are compared with each other in order to identify and recommend the most promising method for further study purposes. Several criteria (cost, maturity, environmental impacts, yield and quality of the product, availability and source of raw materials, and references) are applied for the identification purposes.

Table 18 shows the comparison table of different process alternatives for hydrogen production from biomass. This table is developed based on the literature review. Both, thermochemical and biological processes are compared in the table. Red colour represents that the particular criteria of that process is either comparatively more favourable or higher and green colour represents less favourable or lower.

Table 18. Comparison table of different process alternatives for hydrogen production from biomass.

Process alternatives Criteria↓	Gasification	Bio-photolysis	Indirect	Fermentation	Dark-Fermentation	Integrated Fermentation
Cost analysis	Green	Red	Red	Red	Red	NA*
Maturity	Green	Red	Red	Red	Red	Red
Environmental impact	Green	Green	Green	Green	Green	Green
Product yield	Green	Red	Red	Red	Red	Green
Product quality	Green	Green	Green	Green	Green	Green
Raw materials	Green	Green	Green	Green	Green	NA
References	Green	Green	Green	Green	Green	Red

*Not available

Pyrolysis and liquefaction methods are not taken under consideration for the comparison purposes because they are considered as an additional stage in gasification process, which makes the overall process more complex and costly.

Direct and indirect bio-photolysis, fermentation and integrated fermentation are not selected for the design part because of several reasons. The reasons include high cost and immature technologies with few or no upgrade scale approaches, unknown/lower product conversion rate(s), multiple by-products, and the need for sunlight.

Dark-fermentation could be an option if considered to be an stand-alone technology, as it does not require sunlight, for the production mechanism but it too lacks the maturity; product efficiency is unknown; is very selective with the feed materials, and no demonstration or commercial scale results has been presented.

Supercritical water gasification is a promising option to produce hydrogen from high moisture content biomass but also have some drawbacks. This technology is still under development and involves a lot of research to make it proven. (Parthsarathy & Narayan, 2014)

Nevertheless, gasification identifies itself the best process alternative compared to rest of the methods. It is a mature and known technology. It is a simple process, which makes it easy to handle. The product yield is high with almost no side products. And, the technological and economic analysis of this process can be done relatively easily.

A number of efforts have been made by researchers to test hydrogen production from biomass gasification with various biomass types and at various operating conditions. It is possible to achieve hydrogen production about 60 vol.% using a fluidized bed gasifier along with suitable catalysts. Such high efficiency makes biomass gasification an attractive hydrogen production alternative. In addition, an estimated cost comparison of hydrogen production by biomass gasification and natural gas steam reforming done by Ni, et al. (2006) shows that hydrogen production by biomass gasification is a competitive alternative. Hence, based on the comparison table analysis, gasification technology is selected for further study.

4.2 Basics of Design

4.2.1 Definition of Selected Process

This section presents the definition of the process in terms of capacity, location and technology.

The overall plant capacity is 100 MW and is located in Finland, where there is a vast quantity of available biomass. The plant operates in a continuous mode (i.e., 7500 h/a) with consideration of 51 days per year of overall plant shut down for maintenance purposes.

The specific geographical location of the plant is not stated; however, it is known that the plant will be integrated to a Combined Heat and Power plant (CHP). The idea is to utilize existing resources and logistics, and also feed the produced heat to the district heating net.

As mentioned in the earlier section, gasification technology is considered for the design part. In the gasification stage, dual fluidized bed is used to convert the solid biomass feed into productive syngas. Catalytic reformer is utilized in the steam reforming stage. ZnO-bed, wet scrubber and Pressure Swing Adsorption (PSA) are utilized for gas-cleaning. High Temperature (HT) and Low Temperature (LT) water-gas shifts are carried out in between the gas-cleaning stages for higher product yield.

4.2.2 Specification of Raw Materials and Products

This section describes the quality and properties of raw materials as well as the products. The feedstock is Finnish forest residues.

Table 19 shows the required proximate and ultimate analyses of the feedstock.

Table 19. Proximate and ultimate analyses of the feedstock.

Raw materials	**Forest residues**
LHV	19.3 MJ/kg
Moisture content (%), wet basis*	37.5
Moisture content (%), dry basis**	60
Elemental analysis, (%) dry basis	
C	51.3
H	6.1
N	0.4
O	40.85
S	0.02
Cl	0
Ash content (%)	1.33
Proximate analysis, wt. % dry basis	
Fixed carbon	20.6
Volatile matter	76.8
Ash	2.6

*Wet basis moisture content is described by the percentage equivalent of the ration of the weight of water to the total weight of the material.

**Dry basis moisture content is described by the percentage equivalent of the ratio of the weight of water to the weight of the dry matter.

4.3 Process definition

4.3.1 General information and process design

Several process alternatives using gasification technology exist for the production of hydrogen gas. Main process parameters, namely feedstock type, plant size, product purity, pressure, use of catalyst(s) and temperature, play important roles in choice of process alternatives.

Figure 15 shows an overall process scheme developed by Mckeough & Kurkela (2007) for hydrogen production from biomass. The method in question is the so-called classical method based on maximal conversion of CO to H_2 via the shift reaction.

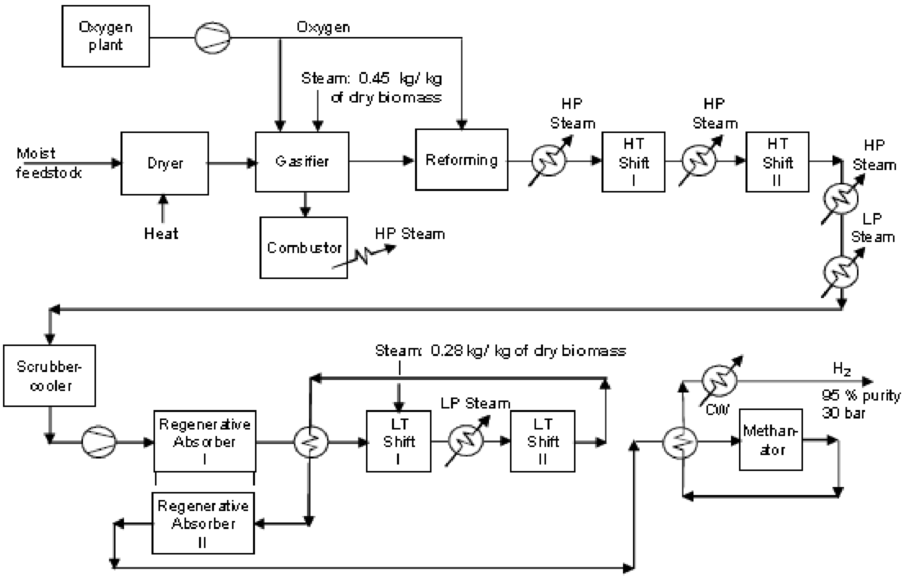


Figure 15. Process scheme for production of Hydrogen. (Mckeough & Kurkela, 2007)

Mann & Steward (2012) developed two different process alternatives (current and future) for producing hydrogen using farmed woody biomass. The systems examined are based on the Battelle/FERCO indirectly-heated biomass gasifier, conventional catalytic steam reforming, water gas shift, and pressure swing adsorption purification. The indirectly-heated biomass gasifier uses hot sand, circulating between the char combustor and the gasifier, to provide the heat necessary for gasification. Steam is used as the fluidizing gas; no oxygen (as pure oxygen or air) is fed to the gasifier. The biomass feedstock is assumed to be a woody biomass, represented as hybrid poplar. The overall process flow diagram for the systems can be seen in the analysis done by Mann & Steward (2012).

WGS–water-gas shift reaction

WGS is a historical and industrially important reaction used for reducing carbon monoxide in a hydrogen rich stream. This project focuses on producing bio-hydrogen from forest residues. The gasified forest residues are first steam reformed and then the formed synthesis gas is passed through multi-stage, fixed-bed reactor containing shift catalysts to convert CO and water into additional H_2 and CO_2 according to the following reaction as the water-gas shift reaction (Equation 31):

Equation 31. $\mathrm{CO} + \mathrm{H_2O} \leftrightarrow \mathrm{H_2} + \mathrm{CO_2}$

Reaction thermodynamic equilibrium favours high conversion of CO and steam to hydrogen and carbon dioxide at low temperatures. Therefore water-gas shift reaction is commonly conducted at low temperature in the presence of catalysts that enhance the reaction rate. Depending up on the catalysts used and the temperature, WGS reaction consists of a high temperature shift (HTS) followed by a low temperature shift (LTS) with intersystem cooling. (Benny, 2010)

The first step involves a high temperature step operating at 310-450°C, which reduces CO content to 2–3%. The iron oxide/ chromium catalysts developed by German researchers still forms the basis for the HTS catalyst today, which has hardly changed since its initial development. The second stage uses a low temperature WGS catalyst based on $Cu/ZnO/Al2O_3$ that operates at 200-250°C. (Benny, 2010)

Pressure swing adsorption

Pressure swing adsorption (PSA) processes are used for the production of high purity hydrogen from steam methane reforming off-gas and refinery off-gas. Since hydrogen is adsorbed much less than almost any other components, PSA has a clear advantage over almost all other possible approaches. PSA is based on the capacity of certain materials, activated carbon and zeolites, to adsorb and desorb particular gases as the gas pressure is raised and lowered. PSA can be used to separate a single gas from a mixture of gases. A typical PSA system involves a cyclic process where a number of connected vessels containing adsorbent material undergo successive pressurization and depressurization steps in order to produce a continuous stream of purified product gas. (Xebec, 2014)

The operation of a simplified PSA process for separating hydrogen from a feedstock gas containing impurities, such as carbon dioxide, carbon monoxide or water is illustrated in Figure 16. The overall process is divided into two steps: production step and regeneration step.

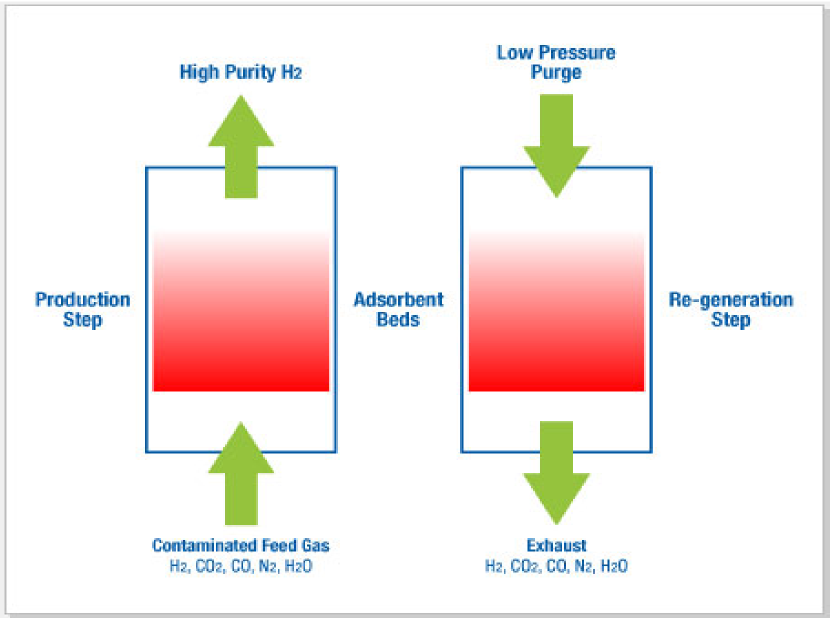


Figure 16. Pressure swing adsorption process for hydrogen gas purification. (Xebec, 2014)

In the production step, the contaminated feedstock gas is first pumped into a cylinder, containing beads of adsorbent material, at high pressure. The impurities in the feed gas, such as CO_2, are adsorbed onto the internal surfaces of the adsorbent beads, leaving hydrogen in the vessel, most of which is removed as purified hydrogen product. Pressure in the cylinder is reduced, releasing the impurities from the adsorbent material. (Xebec, 2014)

In the regeneration step, a small amount of product hydrogen is used to flush the waste gas through and exhaust port, preparing the vessel for another production cycle. (Xebec, 2014)

Zinc oxide

Adsorption of H_2S onto zinc oxide has been commercially used as an effective method for removing trace quantities of sulphur from gas to achieve a purity of less than 0.1 ppm. Therefore, it is the standard method of desulphurization upstream of syngas steam reformers. The adsorption takes place via the reaction of hydrogen sulphide with zinc oxide to form zinc sulphide. In situ regeneration is not possible, and this limits the amount of sulphur that the process can accept in the inlet gas. Hence, for this reason utilization of ZnO bed is not suitable for bigger plants with higher sulphur content. Operating in its optimum temperature range of 350–450°C, ZnO has a pick-up capacity of around 20% weight. That means, if the total sulphur intake is about 33 tonnes/year of a 15350 t/y bio-hydrogen plant, it requires replacement of about 165 t/y zinc oxide. (Higman & Burgt, 2008)

Figure 17 shows an overall process scheme for the production of hydrogen using forest residues with the plant capacity of 100 MW (LHV). The method in question is based on conversion of CO to H_2 via the shift reaction. The system examined is based on band conveyer dryer (belt dryer), indirectly-heated dual fluidized bed biomass gasifier, conventional catalytic steam reforming, ZnO-bed, water gas shift, wet scrubber and pressure swing adsorption purification.

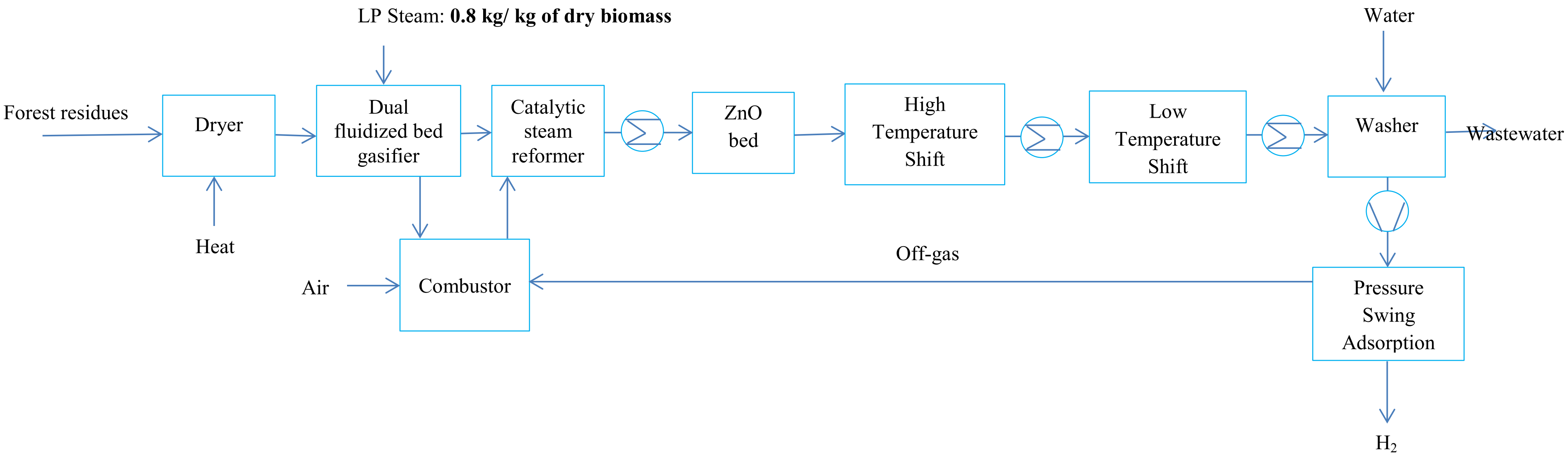


Figure 17. Process block diagram

The process was simulated using ASPEN Plus V8.6 software. The thermodynamic sets selected for each stage are specified in Table 20.

Table 20. Thermodynamics used in ASPEN Plus simulation

Stage	Thermodynamics
Gasification & Reformer	SRK*
Sulphur removal	SRK
High Temperature Shift	SRK
Low Temperature Shift	SRK
Ammonia wash	NRTL**
Pressure Swing Adsorption	SRK

* Soave-Redlich-Kwon model. ** Non-random-two-liquid model.

Soave-Redlich-Kwon (SRK) thermodynamic model was chosen for most of the process because unlike other models, it has an option to calculate enthalpy of water and composition independent fugacity coefficients as well as it favours the water-hydrocarbon system. Non-random-two-liquid model (NRTL) was chosen in the ammonia wash stage, also known as wet scrubber.

Table 21 presents the types and amount of materials required by the overall process. Forest residues are used as the feedstock material, air for drying as well as combusting purposes and fresh water for washing. Detailed calculations can be followed in (APPENDIX 1).

Table 21. Materials required by the process.

Materials required	Unit	Amount
Forest residues	t/a	242.7
Air for drying	m^3/h	846153.7
Air needed for combustion	kmoles/h	1388
Gasifying steam	kg/h	16237
Fresh water		
For washing	kg/h	150000
In start-up	kg/h	26727
Makeup stream	kg/h	16273

4.3.3 Process Description and Simulation

This section describes each stage of the process in detail. The PFD is presented as an attached file due to size and format limitations of this report (APPENDIX 2 and APPENDIX 3).

The as-received forest residues is dried from 37.5 wt.% (wet basis) moisture down to 13 wt.% employing a band conveyer dryer or belt dryer AA-101. The dryer uses air, i.e., heated by the heat generated by the process, as the drying medium. Conveyers and hoppers are used to feed the forest residues to DC-301. DC-301 has two stages: gasification stage and reforming stage. Forest residues are fed to the low-pressure (3 bars) indirectly-heated dual fluidized bed gasifier, which uses low pressure steam as its gasifying agent. Heat for the endothermic gasification reactions can be supplied by circulating hot olivine or dolomite, which is used as a sand for various applications between the gasifier and a char combustor vessel. The product/synthesis gas from the gasifier is sent to the catalytic steam reformer. Reforming and water-gas shift are the main reactions in the catalytic steam reformer. Block DC-301 was simulated as a Gibbs reactor with a steam to dry biomass ratio of 0.8 kg.

The char formed in the gasifier is burned in the combustor, DC-302, to reheat the sand. The combustion medium is air. The amount of air added to the combustor is equal to the number of moles of char (1.1 mole oxygen/mole char). Particulate removal is performed through cyclone separators. Ash and any sand particles that are separated are landfilled.

For sulphur removal, the steam reformed synthesis gas is passed through the Zinc Oxide bed (ZnO-bed) DC-401. The ZnO-bed was simulated as a separator. The sulphur removed gas is then sent through high temperature shift (HTS) DC-303 and low temperature shift (LTS) DC-304 reactors in order to convert the majority of the CO into CO_2 and H_2 through the water-gas shift reaction. The HTS and LTS were modelled as equilibrium reactors with approach temperature of 35°F and 20°F, respectively (Mann & Steward, 2012).

For ammonia removal, a wet scrubber column DA-201 is used that utilizes fresh water as the wash medium. The ammonia free gas stream is compressed up to 30 bar pressure using a multistage compressor GB-201.

For purification, a pressure swing adsorption unit DC-402 is used to separate the hydrogen from the other component in the compressed gas stream, mainly CO2, and unreacted CO, CH_4, and other hydrocarbons. The hydrogen purity achieved from a PSA unit can be greater than 99.99+%. Based on Mann & Steward (2012) analysis, the shifted gas stream must contain at least 70 mol% hydrogen before it can be purified in the PSA unit. Purification of streams more cilute than this decreases the product purity and recovery of hydrogen. For this design, the concentration of hydrogen in the compressed stream prior to PSA is between 67 and 69.5%. Therefore, part of the PSA hydrogen product stream is recycled back into the PSA feed. For a 70 mol% hydrogen PSA feed, a hydrogen recovery rate of 85% is typical with a product purity of 99.99 vol%.

4.3.4 Energy Integration and Optimization

In this section, the energy considerations are taken into account, aiming to provide a feasible energy integration system. The energy integration has been mainly based in the integration between different process streams. Energy integration is a technique for designing a process to minimize energy consumption and maximize heat recovery by calculating attainable energy targets for a given process and identifying ways to achieve it.

The utilities balance is presented in Figure 18 and the overall heat integration flow diagram is presented as an attached file (APPENDIX 4).The heat required by the process is provided by the heat produced by combustor DC-302, reformer DC-301, HTS reactor DC-303 and LTS reactor DC-304. The extra electricity/power (3 MW) generated by the system is utilized for running the compressor; the additional 2 MW electricity can be bought from the power plant.

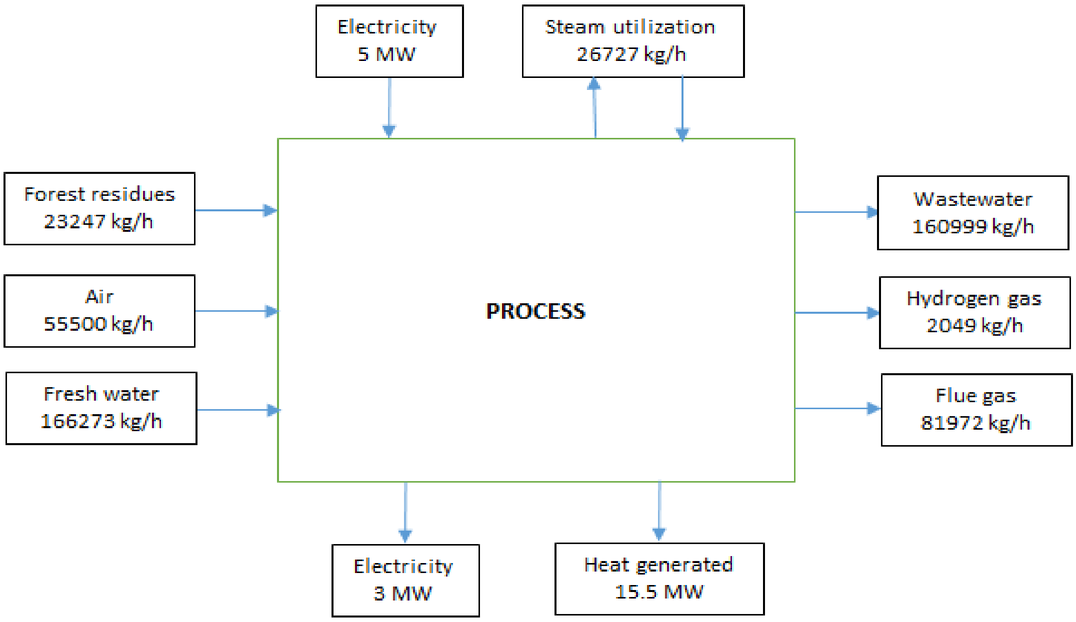


Figure 18. Process overall inlets and outlets

Heat produced by combustor, reformer, HTS and LTS generates 43000 kg/h of high pressure (HP) steam (522°C and 80 bars). Part of this HP steam is sent through a small steam turbine to generate 3 MW of electricity and 16273 kg/h of

LP steam (450°C & 3 bars) needed in the gasifier; and rest of the HP steam provides heat enough to heat the dryer and preheat the air required by the combustor.

Figure 19 shows the overall energy balance of the designed process. The total energy input to the process is 100 MW raw materials and 2 MW electricity. And the overall output equals to 68.7 MW of desired product (LHV), i.e., hydrogen gas, 15.5 MW heat energy that can be used for district heating purposes, and 17.8 MW of heat loss.

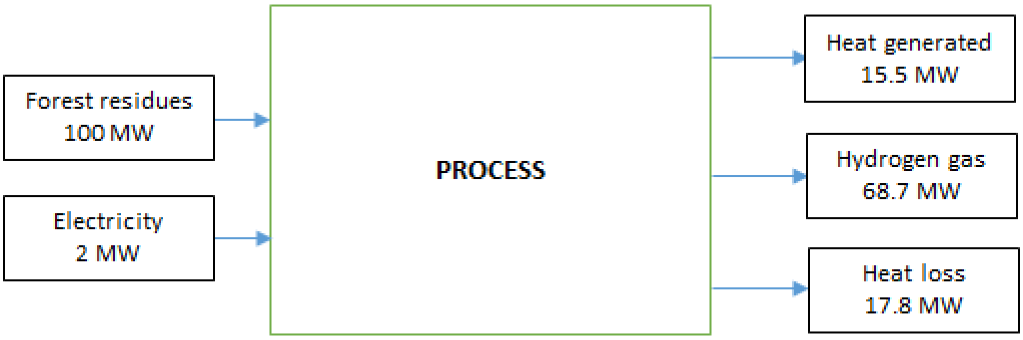


Figure 19. Overall energy balance of the process

Chapter 5

5.1 Cost Analysis

The previous chapter compared all the potential hydrogen production processes using different criteria, identified the most promising process and also defined and simulated it. This chapter analyses the costs of the designed process. Section 5.2 explains the key bases of economic evaluation for the process. Section 5.3 summarizes the sales volume and production cost. Section 5.4 presents a sensitivity analysis of the developed project.

This chapter mainly focuses on capital investment cost, operating cost and production costs estimations. A base case is selected and sensitivity analysis of the process is made. The calculations are shown in € and M€ (Million euros).

Fixed capital investment includes both costs, inside and outside battery limit (ISBL and OSBL). ISBL cost includes equipment costing, piping, instrumentation and other engineering items. OSBL cost is some percentage of ISBL cost that include storage and handling, utilities and services.

Operating cost is comprised of variable operating cost and fixed operating cost. Variable operating cost includes the raw material cost, utility costs (catalysts, water etc.) and waste disposal costs. Fixed operating cost includes salaries and expenses, rent, R&D costs and marketing.

5.2 Capital Cost and Operating Cost

Due to the scope of this thesis and time constraint, dimensioning and sizing of the process was not done; which makes it difficult, if not impossible, to calculate the costs of equipment, instrumentation and other engineering items; leading to the lack of sensible and precise estimate for capital investment cost. Similarly, due to lack of specific data the operating cost of the process is assumed to be some percentage of the investment cost.

Estimations for the fixed capital investment and operating costs are made based on discussions with industry experts, research experts and economic evaluations of this process as well as several similar studies done by VTT (Mckeough & Kurkela, 2007; Mann & Steward, 2012; Hannula & Kurkela, 2013). Key bases of the economic evaluations are given in Table 22. The estimated fixed capital investment (FCI) of this process is 200 M€ for the base case. Apart from ISBL and OSBL costs, FCI cost this plant also include costs related to heat integration system, such as heat exchangers and small turbine.

The fixed capital investment is levelised over the period of 15 years using capital charge factor/annuity factor of 0.103, which corresponds with 6% return on investment. The operating and maintenance costs are valued at 6% of the capital investment, even though all the above mentioned articles valued it to be at 4%. The extra two percent is actually added to take into account the uncertainties related to the limited amount of information available regarding the operation cost, such as catalyst lifetime and price for the designed process. The cost of electricity and heat used by the process are accounted in the operating cost. 20 €/MWh is used for the cost of biomass.

Table 22. Key bases of economic evaluations.

Plant capacity	**100 MW od feed (LHV)**
Annual operating time	7500 h/a
Capital charges factor	0.103 (6%, 15 a)
Ops. and maintenance	6% of investment/a
Feedstock price	20 €/MWh (LHV)

5.3 Production Cost

This section summarizes the sales volume and production cost of the product in Table 23. The selected process produces 2.049 t/h of the desired product, hydrogen gas; which is 68.3 MWh based on its LHV, 120 MJ/kg. Then, the total production/sales volume throughout the year becomes 512 GWh/a hydrogen. The selling price of hydrogen, product gas, is valued at 90 €/MWh, accounting the hydrogen sales revenue to 46.1 M€/a. Process also generates heat that can be sold for district heating purposes. The selling price of DH is valued at 35 €/MWh. Hence, the total sales revenue, including both hydrogen and DH accounts to 50.2 M€/a.

Table 23. Sales revenue and production cost.

Sales Revenue and Production Cost

Hydrogen production (t/h): 2.049
Hydrogen production (MWh): 68.3
Operating time (h/a): 7500

No.	Item	Total	Unit
1	Hydrogen sales volume	512	GWh/a
2	Hydrogen selling price	90	€/MWh
3	Hydrogen sales revenue (1x2)	46.1	M€/a
4	District heat delivery	116.3	GWh/a
5	District heat price	35	€/MWh
6	District heat sales (4x5)	4.1	M€/a
7	Total sales revenue (3+6)	50.2	M€/a
8	Fixed capital investment	200	M€
9	Annual capital charges (6%, 15 a)	20.6	M€/a
10	Biomass feedstock cost	15	M€/a
11	O&V cost (6% of FCI)	9	M€/a
12	Operating cost (10 + 11)	27	M€/a
13	Production cost (9+12)	47.6	M€/a
14	Production cost (13/1)	~93	€/MWh
15	Production cost	~3100	€/t

Apart from hydrogen production, the process also generates heat that can be sold for DH network. For sales revenue calculation, the extra DH produced is not taken into account. The annual capital charges are calculated from FCI using 0.103 annuity factor, which corresponds with 6% interest and 15 years lifetime.

The total annual production cost of the process is the sum of operating cost (item 12) and the annual capital charges (item 9). Hence, the production cost of hydrogen based only on its production efficiency is 93 €/MWh. It is worth mentioning that for base case the production cost is higher than the hydrogen sales revenue, based only on hydrogen production efficiency. Hence, the actual profit is generated by the sales of side product, DH. The calculated internal rate of return (IRR) of the process is 7.46% (APPENDIX 5), which is just a little bit higher than expected 6%. Hydrogen selling price is the most important parameter for generating profit so, any increase on the selling price, at least higher selling price than the production cost, would improve the profitability of the plant.

5.4 Sensitivity Analysis

Sensitivity analysis is a technique used to determine how different values of an independent variable will impact a particular dependent variable under a given set of assumptions in a base case. For the base case of this project, the estimated cost for FCI, operating cost, selling price for hydrogen and selling price for DH are assumed to be 200 M€, 27 M€/a, 35 €/MWh and 90 €/MWh, respectively. For sensitivity analysis, the total sales revenue is used instead of hydrogen sales revenue. Using these data, the calculated internal rate of return (IRR) for the process is 7.46%.

A sensitivity analysis is made with hydrogen selling price, capital investment cost and operating cost as variables for measuring the economic potential of the plant. Note that total operating cost is the sum of raw material cost and other fixed and variable costs (O&V). For sensitivity analysis, the changes in operating cost means the changes in O&V, leaving the raw material price fixed for all the cases. Table 24 shows different case values for the economic variables of the plant.

Table 24. Different case values for the economic variables of the plant.

Variables	low	base case	high
H_2 selling price (%)	-50	0	50
H_2 selling price (€/MWh)	45	90	135
IRR (%)	-30,73	7,46	22,95
FCI (%)	-25	0	25
FCI (M€)	150	200	250
IRR (%)	12,67	7,46	3,56
O&V (%)	-33	0	50
1O&V (M€/a)	8	12	18
IRR (%)	9,37	7,46	4,19

For the analysis, the change of ±50% is taken for hydrogen selling price; ±25% for fixed capital investment cost; and -33 to +50 for operating cost from the base case. These changes are taken based on similar studies done by other research team (Mckeough & Kurkela, 2007; Hannula & Kurkela, 2013; Hannula & Arpiainen, 2014) and discussions with industry experts.

Figure 20 shows that any increase in hydrogen selling price, with no increase in FCI and operating cost, results in increasing IRR. However, a little decrease in hydrogen selling price, with no change in FCI and operating cost, results in negative IRR. Similarly, any increase in FCI and/or operating cost, with no change in hydrogen selling price, results in decreasing IRR; and decrease in FCI and/or operating cost, with no change in hydrogen selling price, results in increasing IRR. Hydrogen selling price has most effect on the IRR/profitability.

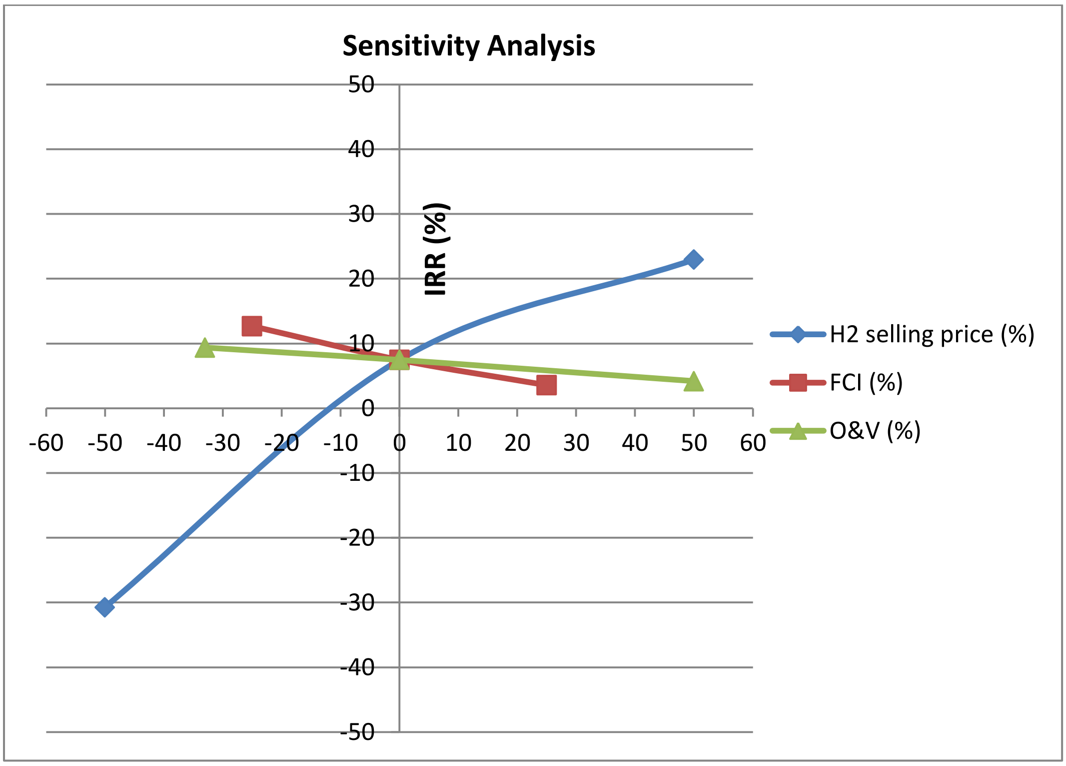


Figure 20. Sensitivity analysis of IRR to the change in selling price, FCI and operating cost for selected plant.

The only likely changes to have positive effect on IRR of the project are increasing hydrogen selling price and decreasing FCI and operating costs. In order for IRR to increase from ~7.5% to 15%, either the hydrogen selling price should be increased from 90 €/MWh to 125 €/MWh keeping the rest of variables constant, or then decreasing the FCI from 200M€ to 150M€ and increasing the hydrogen selling price to 99 €/MWh.

Figure 20 shows changes in IRR based on change in only one variable out of three at a time. It would be more informative to review further the costs associated to hydrogen selling price, FCI and operating cost, by changing all the variables and exploring all the possibilities for checking the economic potential of the project. This process of detailed analysis requires a lot of time as well as expertise. This could be a one field to look into for further studies for future references. The primary issue limiting further analysis is the fact that all the data for analysis purposes of this project are assumptions/estimations. A detailed analysis with actual data would considerably improve the general understanding of the process in terms of economics. However, since it is based on assumptions and estimations, and simulation results, more thorough analysis together with a technology provider would be useful. More reliable analysis of the actual equipment, there sizes and prices.

Chapter 6

6.1 Conclusions

This thesis identifies and reviews the most potential bio-hydrogen production pathways, identifies and designs the most promising process, and then conducts a rough feasibility study to check its economic potential for commercial production after simulation (experimental part). Finally, it also tests the viability of the developed process against non-bio-hydrogen process.

Based on the literature review, a comparison table was developed in the design part, where all the production methods were compared with each other in order to identify and recommend the most promising method for further study purposes. After the result of the comparison, biomass gasification was identified as the best process alternative compared to the other methods, and hence selected for the further study. Though biomass gasification process steps require special attention (tar removal, ash formation); compared to other processes it still is a simple, mature and known technology. Using biomass gasification technology, it is possible to achieve comparatively high product yield, which makes it a competitive alternative (Ni, et al., 2006).

A biomass gasification process was developed for the simulation based on given specifications (plant size, feedstock and other parameters), some referred articles (Spath & Mann, 2001; Mckeough & Kurkela, 2007; Mann & Steward, 2012), and discussions with research experts and industry experts from all around the globe. The developed method in question is based on conversion of CO to H_2 via the shift reaction. The system examined is based on band conveyer dryer (belt dryer), indirectly-heated dual fluidized bed biomass gasifier, conventional catalytic steam reforming, ZnO-bed, water gas shift, wet scrubber and pressure swing adsorption (PSA) purification. In the design part, process stage alternatives were not examined in detail due to the scope of this thesis and time constraint. This increased the complexity in selecting right/appropriate process alternatives, since specific details and specifications concerning different available process alternatives are required for comparing and choosing purposes. Nevertheless, it is rather likely that gasification would have been chosen as the most promising alternative even if more precise analysis had been done

The process designed for the simulation follows the same production principle as the earlier studied ones (Spath & Mann, 2001; Mckeough & Kurkela, 2007; Mann & Steward, 2012), but substitutes some of the stages and parameters, in order to achieve higher product efficiency. The process is specifically designed for plant capacity of less than 150 MW. Some of the purification stages must be reconsidered or even substituted with suitable technologies for plants with higher capacities. Unlike other studied processes (Spath & Mann, 2001; Mckeough & Kurkela, 2007; Mann & Steward, 2012), this process utilizes indirectly-heated gasifier for gasification, steam as the gasifying agent with high S/B ratio and high temperature catalytic reformer that inhibits tar formation, making the process one of its kind.

The process scheme was simulated using a chemical process optimization software ASPEN plus v8.6. To improve the accuracy of the results, the calculations for the drying of biomass was done separately in Microsoft excel. Simulation results show that 67.5% hydrogen product efficiency (LHV) with 99.99% purity and >82% overall efficiency are achieved using forest residues as the biomass feedstock in a 100 MW plant. The product efficiency of this process (67.5%) is lower than the product efficiency achieved by hydrogen production from natural gas (Spath & Mann, 2001), which is >80%. However, compared to the efficiencies (41–57%) of other similar process studies (Hannula, 2009; Mann & Steward, 2012), the designed process has very low carbon footprint and has higher efficiency. The difference in product efficiency depends on the ratio between syngas to hydrogen conversion rate and production of heat and energy. Maximal conversion of syngas produces higher product efficiency but then the energy required by the process is needed to be bought.

A base case was assumed for the cost analysis. For the base case, the estimated cost for FCI, operating cost (based on FCI) and hydrogen selling price were assumed to be 200 M€, 27 M€/a and 90 €/MWh, respectively. For the base case, the production cost of hydrogen based only on the production efficiency was 93

€/MWh, and the IRR was 7.46%. According to research and industry experts, the IRR for bioprocesses is usually negative, which is a good indicator for the designed process, since it is positive.

Sensitivity analysis shows that in order for IRR to increase from ~7.5% to 15%, either the hydrogen selling price should increase from 90 €/MWh to 125 €/MWh while keeping the rest of variables constant. Alternatively, the FCI should decrease from 200M€ to 150M€ and the hydrogen selling price should increase from 90 €/MWh to 99 €/MWh.

The primary difficulties in this study were related to designing and developing the overall production process, and in acquiring/assuming the costs for the cost analysis and sensitivity analysis. Further studies are thus recommended for the selection of the most appropriate process alternative stage as well as parameters for the process. Sizing and dimensioning of the process equipment and definite ISBL and OSBL costs must be done for precise cost analysis. Additionally, sensitivity analysis using actual calculated values for all the applicable parameters should be made for achieving more accurate results and improve understanding of the process.

For future purposes, further studies with different biomass feedstock should be conducted. Also, pilot-scale testing of similar process using the same parameters can be very useful for comparison purposes and result optimization. Once this technology proves to be ready for commercial production, it still requires development in public incentives and policies.

To conclude, this study shows that biomass gasification technology is the most promising bio-hydrogen production process till present but still requires more research and development as well as testing. Laboratory and pilot scale tests need to confirm the efficiency of the developed process before considering it for commercial production, as well as more thorough sizing and economic analysis are required. Also the IRR of the plant should be higher and the hydrogen selling price should be fixed/guaranteed before the plant is realistic to invest.

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Appendices

APPENDIX 1

Amount of forest residues used (t/ a)

Plant capacity (MW) = 100
Lower heating value of forest residues (MJ/kg) = 19.30 (bone dry)
Moisture content, wet basis (%) = 37.5
Latent heat of vaporisation of water (MJ/kg) = 2.5
Lower heating value of wet forest residues (MJ/kg) =

$$\frac{(m_{bone\ dry\ biomass} * LHV_{forest\ residues} - m_{moisture\ content} * LHV_{water}}{m_{total}}$$

= 11.125 (37.5%, wet basis)

Amount of forest residues needed (t/ a) =

$$\frac{Plant\ capacity}{Forest\ residues_{LHV}} = 32.37 \text{ t/h} = 242.7 \text{ kt/ a}$$

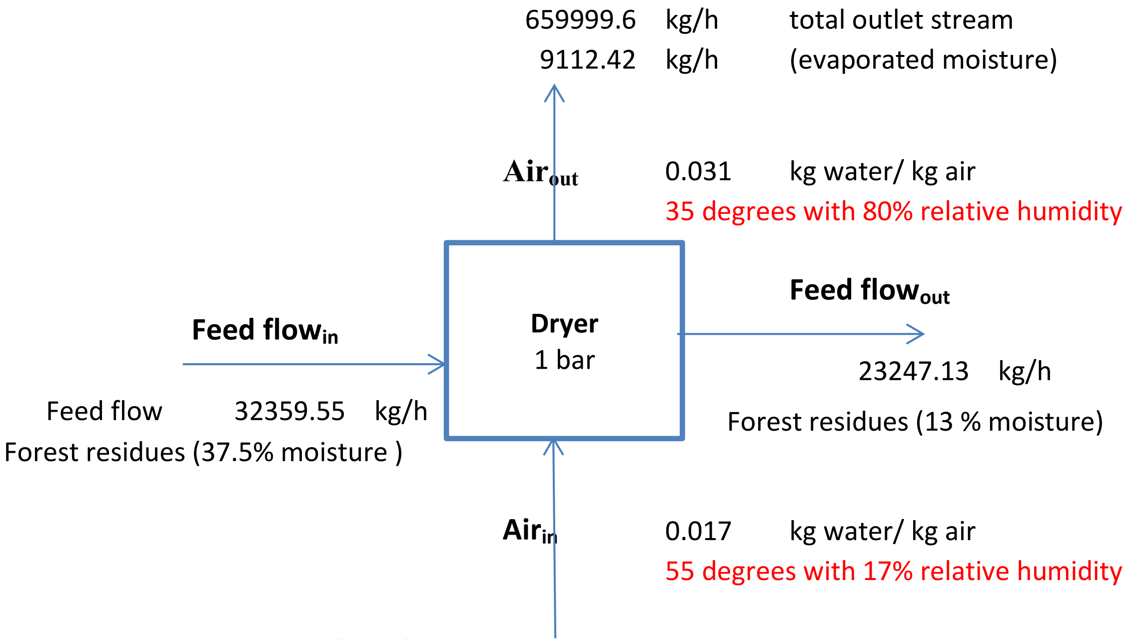
Amount of air needed for drying

Ambient air at room temperature (25°C) with 80% relative humidity (0.017 kg water/ kg air) is heated up to 55°C resulting to 17% relative humidity (0.017 kg water/ kg air) using hot water as the heating media.

IN

Air_{inlet} (°C) = 55
Relative humidity (γ, %) = 80
$Moisture\ content_{in}$ (x, kg water/ kg air) = 0.017 (using i, x-diagram)

$Feed\ flow_{in}$ (kg/h) = 32359.55 (37.5%, wet basis)



Moisture removed from feed =	0.014	kg moisture
Air needed	650887.1	kg air/h
air density	1.3	kg/m^3
	846153.3	m^3 air

OUT

Air$_{out}$ (°C) = 35

Relative humidity (γ, %) = 80

Moisture content$_{out}$ (x, kg water/ kg air) = 0.031 (using i, x-diagram)

Feed flow$_{out}$ (kg/h) = 23247.13 (13%, wet basis)

Evaporated moisture (kg/h) = Feed flow$_{in}$ - Feed flow$_{out}$ = 9112.42

Moisture removed from feed (kg water/ kg air) =

Moisture content$_{out}$ – Moisture content$_{in}$ = 0.014

Therefore, air needed (kg air/h) = Evaporated moisture * Moisture removed from feed = 650887.4 = 846153.7 m^3 air/h

Moles of air needed for combustion

Air: nitrogen (0.79) + oxygen (0.21) =1

Air required for combustion is equal to the number of moles of char = 1.1 mole oxygen/ mole char

From simulation results:

Char (kmoles/h) = 265

Therefore, required oxygen (moles) = 1.1 * 265 = 291.5

Finally, air needed (kmoles/h) = 291.5/0.21 = 1388

Amount of steam required

Steam (kg/h) = 0.8kg steam/ kg dry feed = bone dry feed weight * 0.8 = 16237

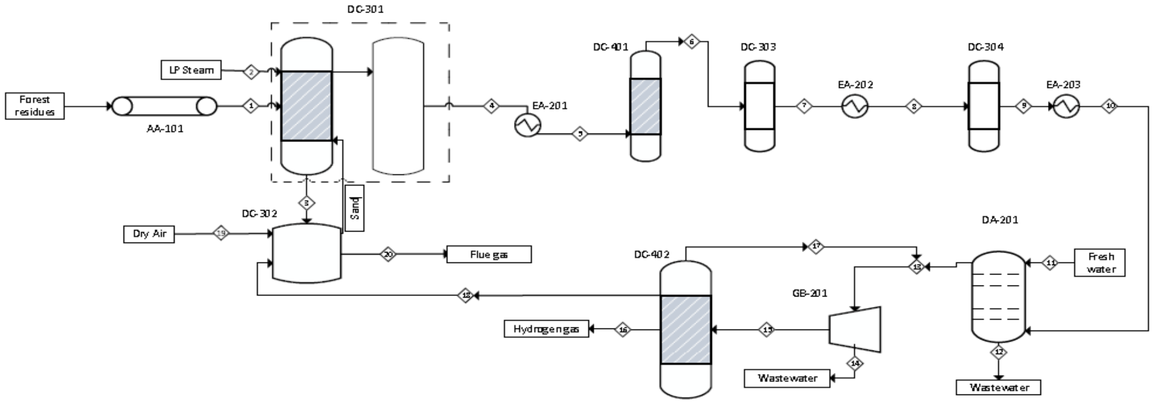
Amount of fresh water needed

For washing (kg/h) = 150000

In start-up (kg/h) = 26727

Makeup (kg/h) = 16273

APPENDIX 2



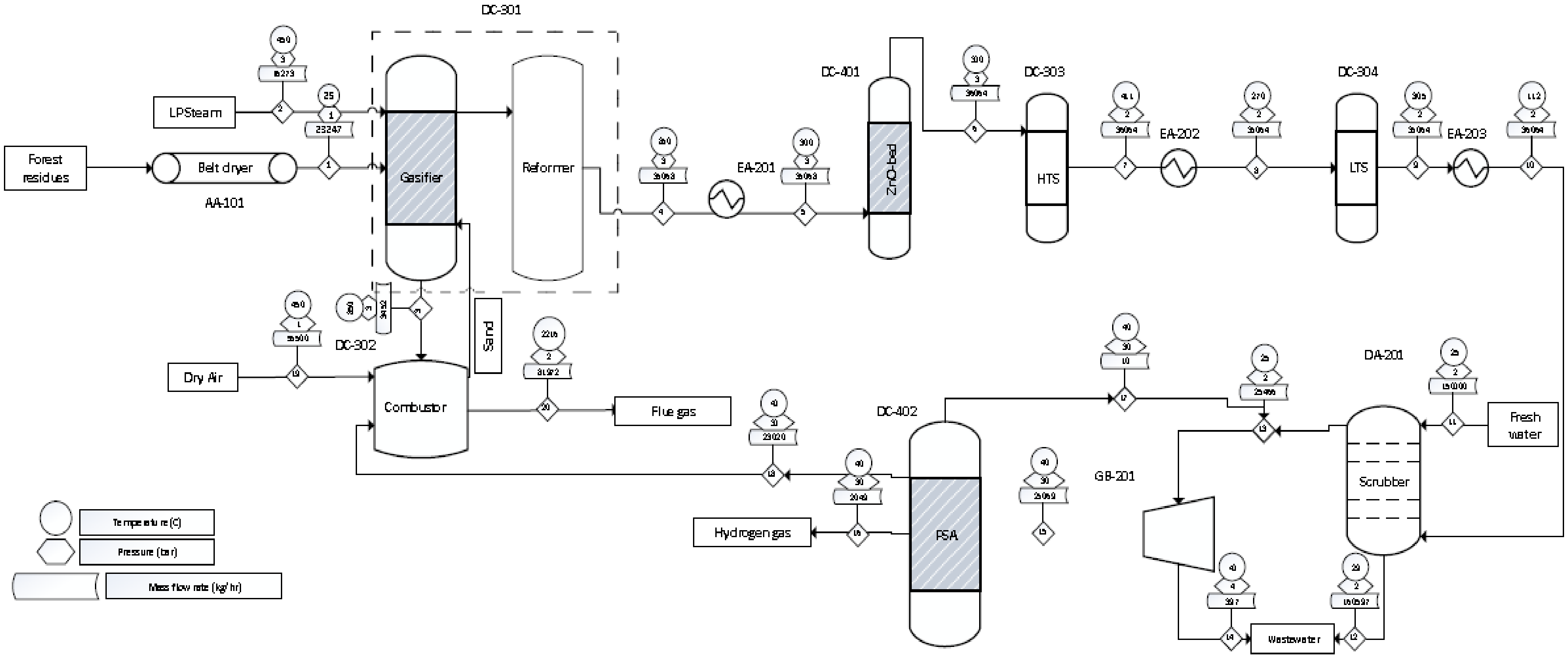
Title	**Process Flow Diagram (PFD)**
Project	**Indirect steam gasification of forest residues for producing hydrogen gas**
Institution	Aalto University, Chemical Technology School
Course	Master's Thesis
Author	S.Shah
Supervisors	J. Koskinen, G. Sarwar
Client	Fortum Oyj

Aalto University
School of Chemical Technology

Stream	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Mass Fraction										
CARBON	0.446312	0	0.922074	0	0	0	0	0	0	0
HYDROGEN	0.05307	0	0	0.052666	0.0526659	0.052672	0.065387	0.065387	0.069392	0.069392
NITROGEN	0.00348	0	0	0.002237	0.0022366	0.002237	0.002237	0.002237	0.002237	0.002237
SULPHUR	0.000174	0	0	2.84E-13	2.84E-13	0	0	0	0	0
OXYGEN	0.355397	0	0	0	0	0	0	0	0	0
H2S	0	0	0	0.000119	0.0001192	0	0	0	0	0
NO2	0	0	0	0	0	0	0	0	0	0
HCN	0	0	0	3.96E-08	3.96E-08	3.96E-08	3.96E-08	3.96E-08	3.96E-08	3.96E-08
H2O	0.129995	1	0	0.368872	0.3688719	0.368916	0.255286	0.255286	0.219494	0.219494
CO2	0	0	0	0.306418	0.3064178	0.306454	0.584044	0.584044	0.67148	0.67148
CO	0	0	0	0.269219	0.2692188	0.269251	0.092577	0.092577	0.036928	0.036928
CH4	0	0	0	0.000462	0.000462	0.000462	0.000462	0.000462	0.000462	0.000462
CAO	0.011571	0	0.077926	0	0	0	0	0	0	0
N2O	0	0	0	0	0	0	0	0	0	0
NH3	0	0	0	7.71E-06	7.71E-06	7.71E-06	7.71E-06	7.71E-06	7.71E-06	7.71E-06
NO	0	0	0	2.12E-14	2.12E-14	2.12E-14	2.12E-14	2.12E-14	2.12E-14	2.12E-14
Total Flow kmol/s	0.530439	0.250914	0.074944	0.634072	0.634072	0.634037	0.634037	0.634037	0.634037	0.634037
Total Flow kg/hr	23247	16273	3451.907	36068.09	36068.09	36063.79	36063.79	36063.79	36063.79	36063.79
Total Flow cum/s	7.193091	5.013211	0.044708	19.7477	10.0698	10.06924	14.43874	11.45337	15.2563	10.14173
Temperature C	25	450	850	850	300	300	411.3324	270	305.548	112
Pressure bar	1	3	3	3	3	3	2.5	2.5	2	2
Vapor Frac	0.547636	1	0.017779	1	1	1	1	1	1	1
Liquid Frac	0.452364	0	0.982221	0	0	0	0	0	0	0
Solid Frac	0	0	0	0	0	0	0	0	0	0
Enthalpy J/kmol	-3333900	-2.3E+08	1.31E+08	-1.1E+08	-129430000	-1.3E+08	-1.3E+08	-1.3E+08	-1.3E+08	-1.4E+08
Enthalpy J/kg	-273860	-1.3E+07	10238700	-6948300	-8191400	-8192300	-8192000	-8503800	-8503700	-8920700
Enthalpy Watt	-1768400	-5.7E+07	9817510	-7E+07	-82069000	-8.2E+07	-8.2E+07	-8.5E+07	-8.5E+07	-8.9E+07

Stream	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Mass Fraction										
CARBON	0	0	0	0	0	0	0	0	0	0
HYDROGEN	0	1.01E-05	0.098205	3.57E-07	0.099762	1	1	0.019634	0	0
NITROGEN	0	4.59E-06	0.003139	2.87E-09	0.003189	0	0	0.003472	0.767083	0.520337
SULPHUR	0	0	0	0	0	0	0	0	0	0
OXYGEN	0	0	0	0	0	0	0	0	0.232917	0.000511
H2S	0	0	0	0	0	0	0	0	0	0
NO2	0	0	0	0	0	0	0	0	0	0
HCN	0	8.89E-09	2.45E-19	0	2.49E-19	0	0	0	0	0
H2O	1	0.980006	0.02079	0.99958	0.00527	0	0	0.005739	0	0.051333
CO2	0	0.019894	0.825448	0.00042	0.83853	0	0	0.913165	0	0.424537
CO	0	8.16E-05	0.05178	4.92E-08	0.052601	0	0	0.057282	0	0
CH4	0	2.50E-06	0.000639	4.67E-09	0.000649	0	0	0.000706	0	0
CAO	0	0	0	0	0	0	0	0	0	0.003282
N2O	0	0	0	0	0	0	0	0	0	0
NH3	0	1.73E-06	7.30E-20	0	7.42E-20	0	0	0	0	0
NO	0	2.25E-17	2.99E-14	0	3.04E-14	0	0	3.31E-14	0	9.29E-15
Total Flow kmol/s	2.312851	2.447279	0.49961	0.006128	0.493482	0.282334	0.001389	0.211148	0.534366	0.709168
Total Flow kg/hr	150000	160597	25466.46	397.5073	25068.95	2048.945	10.0794	23020	55500	81971.91
Total Flow cum/s	0.04192	0.044904	6.205952	0.000117	0.428759	0.248739	0.001224	0.173286	32.14162	73.4027
Temperature C	25	29.40474	25.64984	40.1212	40	39.98757	39.98757	39.98757	450	2216.045
Pressure bar	2	2	2	3.935979	30	30	30	30	1	2
Vapor Frac	0	0	1	7.07E-06	0.998137	1	1	0.992911	1	1
Liquid Frac	1	1	0	0.999993	0.001863	0	0	0.007089	0	0
Solid Frac	0	0	0	0	0	0	0	0	0	0
Enthalpy J/kmol	-2.9E+08	-2.9E+08	-1.1E+08	-2.9E+08	-1.1E+08	460323	460320	-2.6E+08	12779700	-5.3E+07
Enthalpy J/kg	-1.6E+07	-1.6E+07	-7865600	-1.6E+07	-7758900	228348	228347	-8482300	442964	-1651000
Enthalpy Watt	-6.6E+08	-7E+08	-5.6E+07	-1762100	-5.4E+07	129965	639.3333	-5.4E+07	6829020	-3.8E+07

APPENDIX 3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Belt dryer
AA-101
Gasifier
Reformer
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Combustor
Flue gas
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ZnO-bed
DC-303
HTS
EA-202
DC-304
LTS
EA-203
DC-402
PSA
Hydrogen gas
GB-201
DA-201
Scrubber
Fresh water
Wastewater
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23247
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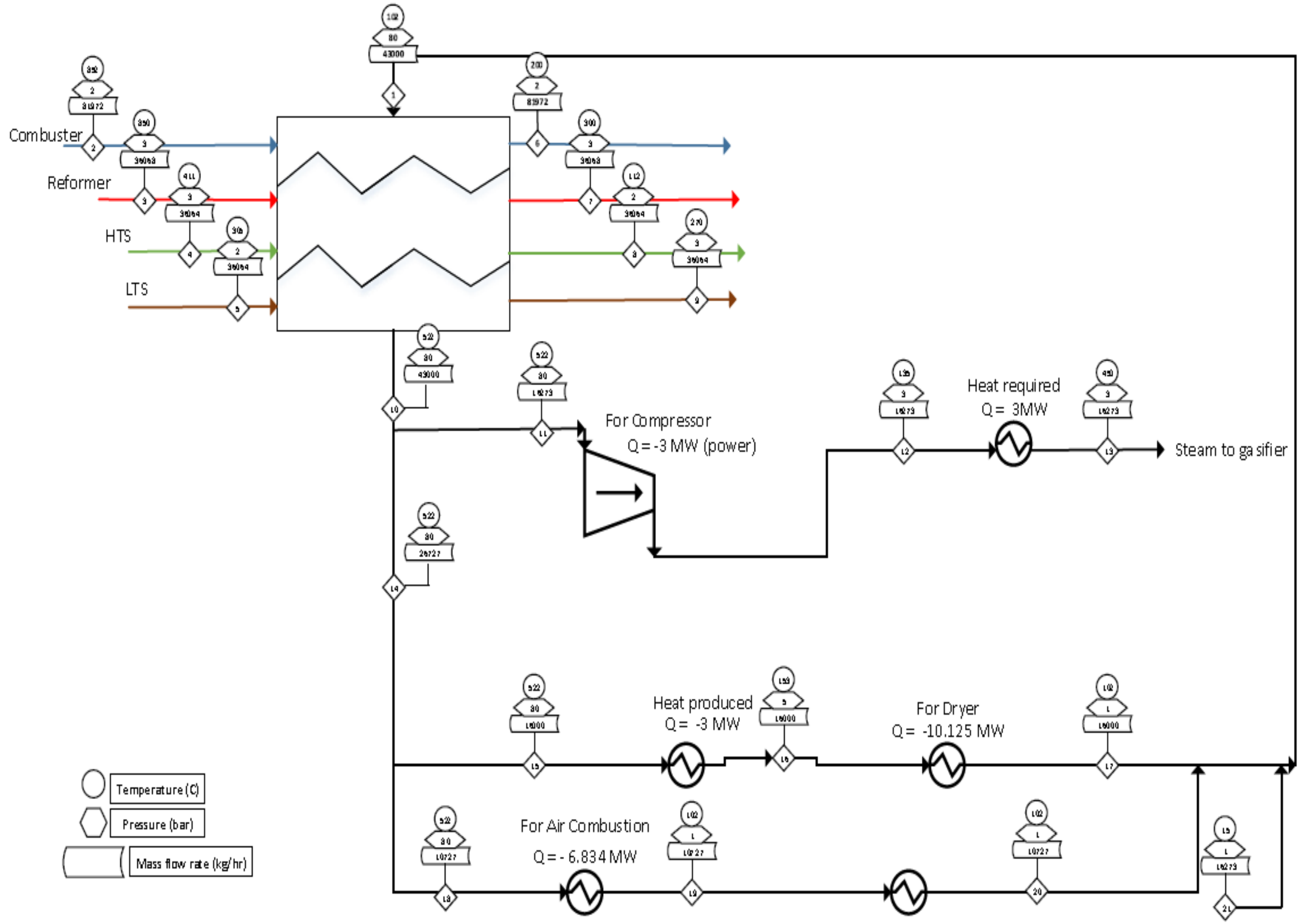
30
Temperature (C)
Pressure (bar)
Mass flow rate (kg/hr)

APPENDIX 4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Reformer
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36064
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102
80
43000
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200
2
81972
6
300
3
36068
7
112
2
36064
8
270
3
36064
9
522
30
43000
10
522
30
16273
11
For Compressor
Q = -3 MW (power)
522
30
26727
14
135
3
16273
12
Heat required
Q = 3MW
450
3
16273
13
Steam to gasifier
522
30
16000
15
Heat produced
Q = -3 MW
153
5
16000
16
For Dryer
Q = -10.125 MW
102
1
16000
17
522
30
10727
18
For Air Combustion
Q = - 6.834 MW
102
1
10727
19
102
1
10727
20
15
1
16273
21
Temperature (C)
Pressure (bar)
Mass flow rate (kg/hr)

APPENDIX 5

BASE CASE	
Hydrogen Selling Price (€/MWh)	90
Investment Cost (M€)	200
Operating Cost (M€/a)	27
FREE CASH FLOW (Me/a):	

Year	**2015**	**2016**	**2017**	**2018**	**2019**	**2020**	**2021**	**2022**	**2023**	**2024**	**2025**	**2026**	**2027**	**2028**	**2029**	**2030**	**2031**	**2032**
+ hydrogen & heat sales (Me/a)	0,0	0,0	0,0	54,0	55,4	56,8	58,2	59,6	61,1	62,7	64,2	65,8	67,5	69,2	70,9	72,7	74,5	76,3
- operating cost (Me/a)	0,0	0,0	0,0	-29,1	-29,8	-30,5	-31,3	-32,1	-32,9	-33,7	-34,6	-35,4	-36,3	-37,2	-38,2	-39,1	-40,1	-41,1
- depriciation 15 a (Me)	0,0	0,0	0,0	-13,3	-13,3	-13,3	-13,3	-13,3	-13,3	-13,3	-13,3	-13,3	-13,3	-13,3	-13,3	-13,3	-13,3	-13,3
EBIT (Me)	**0,0**	**0,0**	**0,0**	**11,6**	**12,2**	**12,9**	**13,5**	**14,2**	**14,9**	**15,6**	**16,3**	**17,1**	**17,8**	**18,6**	**19,4**	**20,2**	**21,1**	**21,9**
(sign ebit)	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
taxes of EBIT (Me)	0,0	0,0	0,0	-2,3	-2,4	-2,6	-2,7	-2,8	-3,0	-3,1	-3,3	-3,4	-3,6	-3,7	-3,9	-4,0	-4,2	-4,4
NOPLAT (Me)	0,0	0,0	0,0	9,3	9,8	10,3	10,8	11,4	11,9	12,5	13,1	13,7	14,3	14,9	15,5	16,2	16,9	17,5
+depriciation (Me)	0,0	0,0	0,0	13,3	13,3	13,3	13,3	13,3	13,3	13,3	13,3	13,3	13,3	13,3	13,3	13,3	13,3	13,3
-capital costs (Me)	-61,5	-126,1	-21,5	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
+ residual value (Me)	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
Free Cashflow (Me)	-61,5	-126,1	-21,5	22,6	23,1	23,6	24,2	24,7	25,3	25,8	26,4	27,0	27,6	28,2	28,9	29,5	30,2	30,9

IRR (%)	7 %
NPV (MEUR)	22,9